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CONTENTS.

(A)

VOL. 199.

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The Committee appointed by the *Royal Society* to direct the publication of the *Philosophical Transactions* take this opportunity to acquaint the public that it fully appears, as well from the Council-books and Journals of the Society as from repeated declarations which have been made in several former *Transactions*, that the printing of them was always, from time to time, the single act of the respective Secretaries till the Forty-seventh Volume; the Society, as a Body, never interesting themselves any further in their publication than by occasionally recommending the revival of them to some of their Secretaries, when, from the particular circumstances of their affairs, the *Transactions* had happened for any length of time to be intermitted. And this seems principally to have been done with a view to satisfy the public that their usual meetings were then continued, for the improvement of knowledge and benefit of mankind: the great ends of their first institution by the Royal Charters, and which they have ever since steadily pursued.

But the Society being of late years greatly enlarged, and their communications more numerous, it was thought advisable that a Committee of their members should be appointed to reconsider the papers read before them, and select out of them such as they should judge most proper for publication in the future *Transactions;* which was accordingly done upon the 26th of March, 1752. And the grounds of their choice are, and will continue to be, the importance and singularity of the subjects, or the advantageous manner of treating them; without pretending to answer for the certainty of the facts, or propriety of the reasonings contained in the several papers so published, which must still rest on the credit or judgment of their respective authors.

It is likewise necessary on this occasion to remark, that it is an established rule of the Society, to which they will always adhere, never to give their opinion, as a Body, upon any subject, either of Nature or Art, that comes before them. And therefore the thanks, which are frequently proposed from the Chair, to be given to the authors of such papers as are read at their accustomed meetings, or to the persons through whose hands they received them, are to be considered in no other light than as a matter of civility, in return for the respect shown to the Society by those communications. The like also is to be said with regard to the several projects, inventions, and curiosities of various kinds, which are often exhibited to the Society; the authors whereof, or those who exhibit them, frequently take the liberty to report, and even to certify in the public newspapers, that they have met with the highest applause and approbation. And therefore it is hoped that no regard will hereafter be paid to such reports and public notices; which in some instances have been too lightly credited, to the dishonour of the Society.

INDEX SLIP.

Jeans, J. H.—The Stability of a Spherical Nebula.
Phil. Trans., A, vol. 199, 1902, pp. 1–53.

Meteoritic Hypothesis of Planetary Evolution.
Jeans, J. H. Phil. Trans., A, vol. 199, 1902, pp. 1–53.

Nebular Hypothesis.
Jeans, J. H. Phil. Trans., A, vol. 199, 1902, pp. 1–53.

Planetary Systems—Evolution of.
Jeans, J. H. Phil. Trans., A, vol. 199, 1902, pp. 1–53.

Rotating Mass of Gas—Stability and Equilibrium of.
Jeans, J. H. Phil. Trans., A, vol. 199, 1902, pp. 1–53.

PHILOSOPHICAL TRANSACTIONS.

I. *The Stability of a Spherical Nebula.*

By J. H. JEANS, *B.A., Fellow of Trinity College, and Isaac Newton Student in the University of Cambridge.*

Communicated by Professor G. H. DARWIN, *F.R.S.*

Received June 15,—Read June 20, 1901. Revised February 28, 1902.

INTRODUCTION.

§ 1. THE object of the present paper can be best explained by referring to a sentence which occurs in a paper by Professor G. H. DARWIN.[*] This is as follows :—

" The principal question involved in the nebular hypothesis seems to be the stability of a rotating mass of gas ; but, unfortunately, this has remained up to now an untouched field of mathematical research. We can only judge of probable results from the investigations which have been made concerning the stability of a rotating mass of liquid."

In so far as the two cases are parallel, the argument by analogy will, of course, be valid enough, but the compressibility of a gas makes possible in the gaseous nebula a whole series of vibrations which have no counterpart in a liquid, and no inference as to the stability of these motions can be drawn from an examination of the behaviour of a liquid. Thus, although there will be unstable vibrations in a rotating mass of gas similar to those which are known to exist in a rotating liquid, it does not at all follow that a rotating gas will become unstable, in the first place, through vibrations which have a counterpart in a rotating liquid : it is at any rate conceivable that the vibrations through which the gas first becomes unstable are vibrations in which the compressibility of the gas plays so prominent a part, that no vibration of the kind can occur in a liquid. If this is so, the conditions of the formation of planetary systems will be widely different in the two cases.

With a view to answering the questions suggested by this argument, the present paper attempts to examine in a direct manner the stability of a mass of gravitating gas, and it will be found that, on the whole, the results are not such as could have been predicted by analogy from the results in the case of a gravitating liquid. The

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[*] " On the Mechanical Conditions of a Swarm of Meteorites, and on Theories of Cosmogony," 'Phil. Trans.,' A, vol. 180, p. 1 (1888).

main point of difference between the two cases can be seen, almost without mathematical analysis, as follows :—

§ 2. Speaking somewhat loosely, the stability or instability may be measured by the resultant of several factors. In the case of an incompressible liquid we may say that gravitation tends to stability, and rotation to instability; the liquid becomes unstable as soon as the second factor preponderates over the first. The gravitational tendency to stability arises in this case from the surface inequalities caused by the displacement: matter is moved from a place of higher potential to a place of lower potential, and in this way the gravitational potential energy is increased. As soon as we pass to the consideration of a compressible gas the case is entirely different.

Suppose, to take the simplest case, that we are dealing with a single shell of gravitating gas, bounded by spheres of radii r and $r + dr$, and initially in equilibrium under its own gravitation, at a uniform density ρ_0.

Suppose, now, that this gas is caused to undergo a tangential compression or dilatation, such that the density is changed from

$$\rho_0 \text{ to } \rho_0 + \Sigma \rho_n \mathrm{S}_n,$$

where ρ_n is a small quantity, and S_n is a spherical surface harmonic of order n.

It will readily be verified that there is a decrease in the gravitational energy of amount

$$4\pi r^3 (dr)^2 \Sigma \frac{\rho_n^2}{(2n+1)} \iint \mathrm{S}_n^2 \sin\theta \, d\theta \, d\phi.$$

As this is essentially a positive quantity, we see that any tangential displacement of a single shell will decrease the gravitational energy.

This example is sufficient to show that when the gas is compressible, the tendency of gravitation may be towards instability. The gravitation of the surface inequalities will as before tend towards stability, but when we are dealing with a gaseous nebula, it is impossible to suppose that a discontinuity of density can occur such as would be necessary if this tendency were to come into operation. Rotation as before will tend to instability, and the factor which makes for stability will be the elasticity of the gas.

We can now see that there is nothing inherently impossible, or even improbable, in the supposition that for a gaseous nebula the symmetrical configuration may become unstable even in the absence of rotation. The question which we shall primarily attempt to answer is, whether or not this is, in point of fact, a possible occurrence, and if so, under what circumstances it will take place. To investigate this problem, it will be sufficient to consider the vibrations of a non-rotating nebula about a configuration of spherical symmetry.

§ 3. Unfortunately, the stability of a gaseous nebula of finite size is not a subject which lends itself well to mathematical treatment. The principal difficulty lies in finding a system which shall satisfy the ordinarily assumed gas equations, and shall at the same time give an adequate representation of the primitive nebula of astronomy.

If we begin by supposing a nebula to consist of a gas which satisfies at every point the ordinarily assumed gas equations, and to be free from the influence of all external forces, then the only configuration of equilibrium is one which extends to an infinite distance, and is such that the nebula contains an infinite mass of gas. The only alternative is to suppose the gas to be totally devoid of thermal conductivity, and in this case there is an equilibrium configuration which is of finite size and involves only a finite mass of gas. But the assumption that a gas may be treated as non-conducting finds no justification in nature. When we are dealing, as in the present case, with changes extending through the course of thousands of years, we cannot suppose the gas to be such a bad conductor of heat, that any configuration, other than one of thermal equilibrium, may be regarded as permanent.

Professor DARWIN has pointed out that a nebula which consists of a swarm of meteorites may, under certain limitations, be treated as a gas of which the meteorites are the "molecules."* In this quasi-gas the mean time of describing a free path must be measured in days, rather than (as in the case of an actual gas) in units of 10^{-9} second. The process of equalisation of temperature will therefore be much slower than in the case of an actual gas, and it is possible that the conduction of heat may be so slow that it would be legitimate to regard adiabatic equilibrium as permanent.†

Except for this the mathematical conditions are identical, whether we assume the gaseous or meteoritic hypothesis. The present paper deals primarily with a nebula in which the equilibrium is conductive, but it will be found possible from the results arrived at, to obtain some insight into the behaviour of a nebula in which the equilibrium is partially or wholly convective.

§ 4. Whether we suppose the thermal equilibrium of the gas to be conductive or adiabatic, we are still met by the difficulty that the gas equations break down over the outermost part of the nebula, through the density not being sufficiently great to warrant the statistical methods of the kinetic theory. This difficulty could be avoided by supposing that the nebula is of finite size, and that equilibrium is maintained by a constant pressure applied to the outer surface of the nebula. If this pressure is so great that the density of gas at the outer surface of the nebula is sufficiently large to justify us in supposing that the gas equations are satisfied everywhere inside this surface, then the difficulty in question will have been removed. On the other hand, this pressure can only be produced in nature by the impact of matter, this matter

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* G. H. DARWIN, *loc. cit., ante.*

† *Ibid.*, p. 64.

consisting either of molecules or meteorites, so that we are now called upon to take account of the gravitational forces exerted upon the nebula by this matter. This whole question is, however, deferred until a later stage; for the present we turn to the purely mathematical problem of finding the vibrations of a mass of gas which is in equilibrium in a spherical configuration. We shall consider two distinct cases. In the first, equilibrium is maintained by a constant pressure applied to the outer surface of the nebula, this surface being of radius R_1. In the second, the nebula extends to infinity, and it is assumed that the ordinary gas equations are satisfied without limitation. We suppose for the present that the gas is in thermal equilibrium throughout. It is not, however, supposed that the gas is all at the same temperature; to make the question more general, and to give a closer resemblance to the state of things which may be supposed to exist in nature, it will be supposed that the gas is collected round a solid spherical core of radius R_0, and the temperature will be supposed to fall off as we recede from this core to the surface, the equation of conduction of heat being satisfied at every point. We shall also suppose that the gas is acted upon by an external system of forces, this system being, like the nebula, spherically symmetrical. The reason for these generalisations will be seen later; it will at any time be possible to pass to less general cases.

THE CRITERION OF STABILITY.

The Principal Vibrations of a Spherical Nebula.

§ 5. We shall take the point about which the nebula is symmetrical as origin. It will be convenient to use rectangular co-ordinates x, y, z, in conjunction with polar co-ordinates r, θ, ϕ. We shall imagine the nebula to undergo a small continuous displacement; let the components of this be ξ, η, ζ, when referred to rectangular co-ordinates, and u, rv, $rw \sin\theta$ when referred to polars. Thus the point initially at

$$x, y, z \quad \text{or} \quad r, \theta, \phi$$

is found after displacement at

$$x + \xi, \; y + \eta, \; z + \zeta \quad \text{or} \quad r + u, \; \theta + v, \; \phi + w.$$

The cubical dilatation of this displacement will be denoted by Δ, so that

$$\Delta = \frac{\partial \xi}{\partial x} + \frac{\partial \eta}{\partial y} + \frac{\partial \xi}{\partial z}$$

$$= \frac{1}{r^2} \frac{\partial}{\partial r}(r^2 u) + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta}(v \sin\theta) + \frac{\partial w}{\partial \phi}.$$

In general we shall denote the *density* by ρ, *pressure* by ϖ, *temperature* by T, *total potential* by V, *coefficient of conduction of heat* by κ, and the *gas constant* by λ, the last of these being given by the equation

$$\varpi = \lambda T \rho \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

In the equilibrium configuration each of the quantities just defined is a function of r only.

If c is any one of these quantities, we shall denote the

Value of c in the equilibrium configuration, evaluated at x, y, z, by c_0.
,, ,, displaced ,, ,, ,, ,, $c_0 + c'$.
,, ,, ,, ,, ,, at $x+\xi$, $y+\eta$, $z+\zeta$ by c_0+c_1.

The quantities c_0, c', c_1 are, of course, not independent. Since $c_0 + c_1$ is the same function of $x + \xi$, $y + \eta$, $z + \zeta$, as is $c_0 + c'$ of x, y, z, we have, as far as the first order of small quantities,

$$c_0 + c_1 = c_0 + c' + \xi \frac{\partial c_0}{\partial x} + \eta \frac{\partial c_0}{\partial y} + \zeta \frac{\partial c_0}{\partial z},$$

or, since c_0 is a function of r only,

$$c_1 = c' + u \frac{dc_0}{dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

§ 6. From the equation of continuity we have at once

$$\rho_1 = -\rho_0 \Delta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

Since λ remains the same throughout the motion of any given element of the gas,

$$\lambda_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Hence, from equation (1),

$$\varpi_0 + \varpi_1 = \lambda_0 (T_0 + T_1)(\rho_0 + \rho_1),$$

giving as the value of ϖ_1

$$\varpi_1 = \lambda_0 (T_1 \rho_0 + T_0 \rho_1) = \lambda_0 \rho_0 (T_1 - \Delta T_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

So long as we confine our attention to a single element of the gas, the coefficient of conduction of heat is proportional to the square root of the temperature, and is independent of the density.* We therefore have, as far as the first order of small quantities,

$$\frac{\kappa_1}{\kappa_0} = \frac{T_1}{2T_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6).$$

Lastly V′, regarded as the difference between $V_0 + V'$ and V_0, is seen to be the potential of a volume-distribution of matter of density ρ', to which must be added :

(i.) The potential of a surface-distribution over the sphere $r = R_0$, the surface density being

$$-\left[u(\rho_0 - \sigma_0)\right]_{r=R_0},$$

where σ_0 is the mean density of the core, and

(ii.) The potential of a surface-distribution over the sphere $r = R_1$, the surface density being

$$\left[u(\rho_0 - \sigma_1)\right]_{r=R_1},$$

where σ_1 is the density of the medium (if any) outside the nebula.

§ 7. We are now in a position to handle the equations of motion, and of conduction of heat. For the element which, in the undisturbed state, is at x, y, z, the equations of motion are three of the type

$$\frac{\partial^2 \xi}{\partial t^2} = \frac{\partial}{\partial x}(V_0 + V') - \frac{1}{(\rho_0 + \rho')}\frac{\partial}{\partial x}(\varpi_0 + \varpi') \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7).$$

Transforming to polar co-ordinates, these equations are equivalent to

$$\frac{\partial^2 u}{\partial t^2} = \frac{\partial}{\partial r}(V_0 + V') - \frac{1}{(\rho_0 + \rho')}\frac{\partial}{\partial r}(\varpi_0 + \varpi') \quad . \quad . \quad . \quad . \quad . \quad . \qquad (8).$$

$$r\frac{\partial^2 v}{\partial t^2} = \frac{1}{r}\frac{\partial V'}{\partial \theta} - \frac{1}{\rho_0 r}\frac{\partial \varpi'}{\partial \theta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (9).$$

$$r\sin\theta\frac{\partial^2 w}{\partial t^2} = \frac{1}{r\sin\theta}\frac{\partial V'}{\partial \phi} - \frac{1}{\rho_0 r\sin\theta}\frac{\partial \varpi'}{\partial \phi} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (10).$$

As an equation of equilibrium, we have

$$\frac{\partial V_0}{\partial r} - \frac{1}{\rho_0}\frac{\partial \varpi_0}{\partial r} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (11),$$

and with the help of this, equation (8) reduces to

$$\frac{\partial^2 u}{\partial t^2} = \frac{\partial V'}{\partial r} - \frac{1}{\rho_0}\frac{\partial \varpi'}{\partial r} + \frac{\rho'}{\rho_0^2}\frac{\partial \varpi_0}{\partial r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12),$$

as far as the first order of small quantities.

---

* BOLTZMANN, 'Vorlesungen über Gastheorie,' vol. 1, § 13.

Let us write

$$\chi = \mathrm{V}' - \varpi'/\rho_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13),$$

so that

$$\frac{\partial \chi}{\partial r} = \frac{\partial \mathrm{V}'}{\partial r} - \frac{1}{\rho_0}\frac{\partial \varpi'}{\partial r} + \frac{\varpi'}{\rho_0^2}\frac{\partial \rho_0}{\partial r},$$

then equation (12) becomes

$$\frac{\partial^2 u}{\partial t^2} = \frac{\partial \chi}{\partial r} + \frac{1}{\rho_0^2}\left(\rho'\frac{\partial \varpi_0}{\partial r} - \varpi'\frac{\partial \rho_0}{\partial r}\right),$$

and, by the use of equation (2), this is seen to be equivalent to

$$\frac{\partial^2 u}{\partial t^2} = \frac{\partial \chi}{\partial r} + \frac{1}{\rho_0^2}\left(\rho_1\frac{\partial \varpi_0}{\partial r} - \varpi_1\frac{\partial \rho_0}{\partial r}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14).$$

Equations (9) and (10) now take the simple forms,

$$\frac{\partial^2 v}{\partial t^2} = \frac{1}{r^2}\frac{\partial \chi}{\partial \theta} \qquad \frac{\partial^2 w}{\partial t^2} = \frac{1}{r^2 \sin^2\theta}\frac{\partial \chi}{\partial \phi}.$$

From these last two equations, we obtain at once

$$\frac{\partial^2}{\partial t^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial \theta}(v\sin\theta) + \frac{\partial w}{\partial \phi}\right\} = \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\,\frac{\partial \chi}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2 \chi}{\partial \phi^2},$$

or, what is the same thing,

$$\frac{\partial^2}{\partial t^2}\left\{\Delta - \frac{1}{r^2}\frac{\partial}{\partial r}(r^2 u)\right\} = \nabla^2\chi - \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \chi}{\partial r}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (15).$$

§ 8. The equation of conduction of heat is, as far as the first order of small quantities,

$$-\,\mathrm{M}\,\frac{\partial \rho_1}{\partial t} + \mathrm{C}_v\frac{\partial \mathrm{T}_1}{\partial t} = \frac{1}{\rho}\left\{\frac{\partial}{\partial x}\left(\kappa\frac{\partial \mathrm{T}}{\partial x}\right) + \frac{\partial}{\partial y}\left(\kappa\frac{\partial \mathrm{T}}{\partial y}\right) + \frac{\partial}{\partial z}\left(\kappa\frac{\partial \mathrm{T}}{\partial z}\right)\right\}. \quad . \quad . \quad (16),$$

in which ρ, κ, T stand for $\rho_0 + \rho'$, $\kappa_0 + \kappa'$, $\tau_0 + \tau'$ respectively. The notation is that of KIRCHHOFF; the equation may either be written down from first principles, or regarded as a simplified form of KIRCHHOFF's general equation.*

Since there is thermal equilibrium in the undisturbed configuration,

$$\frac{\partial}{\partial x}\left(\kappa_0\frac{\partial \mathrm{T}_0}{\partial x}\right) + \frac{\partial}{\partial y}\left(\kappa_0\frac{\partial \mathrm{T}_0}{\partial y}\right) + \frac{\partial}{\partial z}\left(\kappa_0\frac{\partial \mathrm{T}_0}{\partial z}\right) = 0. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17).$$

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* KIRCHHOFF, 'Vorlesungen über die Theorie der Wärme, p. 118.

Hence equation (16) reduces to the form

$$-\mathrm{M}\frac{\partial\rho_1}{\partial t}+\mathrm{C}_v\frac{\partial\mathrm{T}_1}{\partial t}=\frac{1}{\rho_0}\left\{\frac{\partial}{\partial x}\left(\kappa_0\frac{\partial\mathrm{T}'}{\partial x}\right)+\frac{\partial}{\partial y}\left(\kappa_0\frac{\partial\mathrm{T}'}{\partial y}\right)+\frac{\partial}{\partial z}\left(\kappa_0\frac{\partial\mathrm{T}'}{\partial z}\right)\right.$$
$$\left.+\frac{\partial}{\partial x}\left(\kappa'\frac{\partial\mathrm{T}_0}{\partial x}\right)+\frac{\partial}{\partial y}\left(\kappa'\frac{\partial\mathrm{T}_0}{\partial y}\right)+\frac{\partial}{\partial z}\left(\kappa'\frac{\partial\mathrm{T}_0}{\partial z}\right)\right\}\quad . \quad (18).$$

Since κ_0, T_0 are functions of r only, the bracket on the right-hand side of this last equation again reduces to

$$\frac{\partial\kappa_0}{\partial r}\frac{\partial\mathrm{T}'}{\partial r}+\kappa_0\nabla^2\mathrm{T}'+\frac{\partial\kappa'}{\partial r}\frac{\partial\mathrm{T}_0}{\partial r}+\kappa'\nabla^2\mathrm{T}_0\,.\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19),$$

and, cleared of accented symbols by the use of equation (2), this takes the form

$$\frac{\partial\kappa_0}{\partial r}\frac{\partial\mathrm{T}_1}{\partial r}+\kappa_0\nabla^2\mathrm{T}_1+\frac{\partial\kappa_1}{\partial r}\frac{\partial\mathrm{T}_0}{\partial r}+\kappa_1\nabla^2\mathrm{T}_0$$
$$-u\left\{\frac{\partial}{\partial r}\left(\frac{\partial\kappa_0}{\partial r}\frac{\partial\mathrm{T}_0}{\partial r}\right)+\kappa_0\nabla^2\left(\frac{\partial\mathrm{T}_0}{\partial r}\right)+\frac{\partial\kappa_0}{\partial r}\nabla^2\mathrm{T}_0\right\}$$
$$-2\frac{\partial u}{\partial r}\left\{\frac{\partial\kappa_0}{\partial r}\frac{\partial\mathrm{T}_0}{\partial r}+\kappa_0\frac{\partial^2\mathrm{T}_0}{\partial r^2}\right\}-\kappa_0\frac{\partial\mathrm{T}_0}{\partial r}\nabla^2 u.\quad . \quad . \quad . \quad . \quad (20).$$

Now equation (17) can be written in the form

$$\frac{\partial\kappa_0}{\partial r}\frac{\partial\mathrm{T}_0}{\partial r}+\kappa_0\nabla^2\mathrm{T}_0=0.\quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21),$$

whence, by differentiation with respect to r,

$$\frac{\partial}{\partial r}\left(\frac{\partial\kappa_0}{\partial r}\frac{\partial\mathrm{T}_0}{\partial r}\right)+\kappa_0\frac{\partial}{\partial r}\nabla^2\mathrm{T}_0+\frac{\partial\kappa_0}{\partial r}\nabla^2\mathrm{T}_0=0.\quad . \quad . \quad . \quad . \quad . \quad . \quad (22).$$

With the help of equation (22), the bracket in the second line of (20) reduces to

$$\frac{2\kappa_0}{r^2}\frac{\partial\mathrm{T}_0}{\partial r},$$

while, with the help of (21), that in the third line becomes

$$-\frac{2\kappa_0}{r}\frac{\partial\mathrm{T}_0}{\partial r}.$$

Again, if we substitute for κ_1 the value found for it in equation (6), the two last terms in the first line of (20) can be transformed as follows:

$$\frac{\partial\kappa_1}{\partial r}\frac{\partial\mathrm{T}_0}{\partial r}+\kappa_1\nabla^2\mathrm{T}_0=\kappa_0\frac{\partial}{\partial r}\left(\frac{\mathrm{T}_1}{2\mathrm{T}_0}\right)\frac{\partial\mathrm{T}_0}{\partial r}+\frac{\mathrm{T}_1}{2\mathrm{T}_0}\left\{\frac{\partial\kappa_0}{\partial r}\frac{\partial\mathrm{T}_0}{\partial r}+\kappa_0\nabla^2\mathrm{T}_0\right\},$$

and the last bracket vanishes by equation (21).

Collecting results, and substituting for ρ_1 from equation (3), we find that equation (18) takes the form

$$\mathrm{M}\rho_0 \frac{\partial \Delta}{\partial t} + \mathrm{C}_v \frac{\partial \mathrm{T}_1}{\partial t} = \frac{1}{\rho} \left\{ \frac{\partial \kappa_0}{\partial r} \frac{\partial \mathrm{T}_1}{\partial r} + \kappa_0 \nabla^2 \mathrm{T}_1 + \kappa_0 \frac{\partial}{\partial r} \left(\frac{\mathrm{T}_1}{2\mathrm{T}_0} \right) \frac{\partial \mathrm{T}_0}{\partial r} \right.$$
$$\left. - \kappa_0 \frac{\partial \mathrm{T}_0}{\partial r} \left(\frac{2u}{r^2} - \frac{4}{r} \frac{\partial u}{\partial r} + \nabla^2 u \right) \right\} \quad . \quad . \quad . \quad (23).^*$$

§ 9. In addition to the volume-equations which have just been found, there are certain boundary conditions which must be satisfied. These are as follows:

(i.) The pressure must remain constant at the outer surface, so that we must have

$$[\varpi_1]_{r=\mathrm{R}_1} = 0.$$

(ii.) The temperature must remain unaltered at $r = \mathrm{R}_0$, or else the flow of temperature across the surface $r = \mathrm{R}_0$ must remain *nil*. These two suppositions require respectively

$$[\mathrm{T}_1]_{r=\mathrm{R}_0} = 0, \quad \text{or} \quad \left[\frac{d\mathrm{T}_1}{dr} \right]_{r=\mathrm{R}_0} = 0.$$

(iii.) A similar temperature condition must be satisfied at $r = \mathrm{R}_1$.

(iv.) The kinematical and dynamical boundary conditions at the surface $r = \mathrm{R}_0$ must be satisfied. These express that the normal velocities shall be continuous at this surface, and that the motion of the rigid core shall be such as would be caused by the forces acting upon it from the gas.

§ 10. Equations (14), (15) and (23) give the rates of change in u, Δ and T_1 in terms of these quantities. Hence these equations enable us theoretically to trace the changes in u, Δ and T_1, starting from any arbitrary values of u, Δ, T_1, du/dt and $d\Delta/dt$, which are such as to satisfy the boundary conditions.

Imagine initial values of u, Δ, T_1, du/dt and $d\Delta/dt$, in which the latitude and longitude enter only through the factor S_n, where S_n is any spherical harmonic of order n. Then it can be shown that the solution through all time (so long as the squares of the displacement may be neglected) is such that the latitude and longitude enter only through the factor S_n. For, assuming a solution of this form, the value of V' found in § 6 will contain S_n as a factor, as will also ρ_1, ϖ_1, ϖ' (equations 3, 5, 2) and χ (equation 13). The same is true of $\nabla^2\chi$, $\nabla^2\mathrm{T}_1$ and $\nabla^2 u$, since

$$\nabla^2 [f(r)\,\mathrm{S}_n] = \left\{ \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{df(r)}{dr} \right) - \frac{n(n+1) f(r)}{r^2} \right\} \mathrm{S}_n,$$

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[*] Sections 5–8 were re-written in November, 1901. I take this opportunity of expressing my thanks to the referee for the care and trouble which he has bestowed upon my paper. To him I am indebted for several improvements in these four sections, in particular for the present form of equation (23), and also for the removal of a serious inaccuracy from my original equations.

where $f(r)$ is any function of r. It therefore appears that every term in equations (14), (15) and (23) will contain S_n as a factor. Dividing out by this factor, we are left with equations which do not involve θ and ϕ, and this verifies our statement.

§ 11. It therefore follows that there are principal vibrations* in which u, Δ and T_1 are of the form

$$u = AS_n e^{ipt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24),$$

$$\Delta = BS_n e^{ipt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (25),$$

$$T_1 = CS_n e^{ipt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26),$$

in which A, B, C are functions of r only. The relations between A, B, C and p must be found from the equations (14), (15), (23), and the boundary conditions.

The value of ρ' for the vibration just specified is

$$\rho' = \rho_1 - u\frac{d\rho_0}{dr} = -\left(\Delta\rho_0 + u\frac{d\rho_0}{dr}\right) = -\left(A\frac{d\rho_0}{dr} + B\rho_0\right)S_n e^{ipt}.$$

We shall in future drop all zero suffixes, there being no longer any danger of confusion. Calculating V′ after the manner explained in § 6, we find (*cf.* THOMSON and TAIT, 'Nat. Phil.,' § 542),

$$V' = VS_n e^{ipt},$$

where

$$V = \frac{4\pi}{(2n+1)r^{n+1}}\left\{-\int_{R_0}^{r}\left(A\frac{d\rho}{dr} + B\rho\right)r^{n+2}\,dr - \left[A(\rho-\sigma_0)r^{n+2}\right]_{r=R_0}\right\}$$
$$+ \frac{4\pi r^n}{(2n+1)}\left\{-\int_{r}^{R_1}\left(A\frac{d\rho}{dr} + B\rho\right)\frac{dr}{r^{n-1}} + \left[\frac{A(\rho-\sigma_1)}{r^{n-1}}\right]_{r=R_1}\right\} \quad . \quad . \quad . \quad (27).$$

We have further, by equations (2) and (5),

$$\varpi' = \varpi_1 - u\frac{d\varpi}{dr} = \lambda\rho(C - BT)S_n e^{ipt} - A\frac{d\varpi}{dr}S_n e^{ipt},$$

and hence we obtain (equation 13)

$$\chi = FS_n e^{ipt},$$

where

$$F = V - \lambda(C - BT) + \frac{A}{\rho}\frac{d\varpi}{dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28).$$

Substituting the assumed solutions for u, Δ and T_1, and the corresponding values for χ, ρ_1, ϖ_1, in equations (14), (15) and (23), and dividing throughout by the factor $S_n e^{ipt}$, we find the relations

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* In order to avoid circumlocution, we shall find it convenient to use the terms "principal co-ordinate" and "principal vibration," although we are ignorant as to whether the nebula is stable or unstable. It will ultimately be found that we only apply our results to nebulæ which are either stable or in the limiting state of neutral equilibrium.

$$-p^2\mathrm{A} = \frac{d\mathrm{F}}{dr} - \frac{\mathrm{B}}{\rho}\frac{d\varpi}{dr} - \frac{\lambda}{\rho}\frac{d\rho}{dr}(\mathrm{C} - \mathrm{BT}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (29),$$

$$-p^2\left(\mathrm{B} - \frac{1}{r^2}\frac{d}{dr}(r^2\mathrm{A})\right) = -\frac{n(n+1)}{r^2}\mathrm{F} \quad . \quad . \quad . \quad . \quad . \quad . \quad (30),$$

$$ip\rho(\mathrm{M}\rho\mathrm{B}+\mathrm{C}_v\mathrm{C}) = \frac{d\kappa}{dr}\frac{d\mathrm{C}}{dr} + \frac{\kappa}{r^2}\left\{\frac{d}{dr}\left(r^2\frac{d\mathrm{C}}{dr}\right) - n(n+1)\mathrm{C}\right\} + \kappa\frac{d}{dr}\left(\frac{\mathrm{C}}{2\mathrm{T}}\right)\frac{d\mathrm{T}}{dr}$$
$$-\kappa\frac{d\mathrm{T}}{dr}\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\mathrm{A}}{dr}\right) - \frac{4}{r}\frac{d\mathrm{A}}{dr} - \frac{n(n+1)-2}{r^2}\mathrm{A}\right\} \quad . \quad (31).$$

The boundary-equations found in § 9 reduce to the following :—

(i) $[\mathrm{C} - \mathrm{BT}]_{r=\mathrm{R}_1} = 0$ . . . . (32),

(ii) $\mathrm{C}_{r=\mathrm{R}_0} = 0$ or $\left[\frac{d\mathrm{C}}{dr}\right]_{r=\mathrm{R}_0} = 0$ . . . . (33),

(iii) Equations similar to (33) at $r = \mathrm{R}_1$ . . . . (34),

(iv) $(\mathrm{A})_{r=\mathrm{R}_0} = 0$, when n is different from unity, or a more complex equation in the case of $n = 1$ . . . . (35).

§ 12. From the manner in which the analysis has been conducted, it will be clear that every principal vibration must either be one of the class just investigated, or else a vibration such that u, Δ, and T vanish everywhere.

For the latter class of vibration there are no forces of restitution. Thus the frequency of vibration is zero, and the motion consists of the flow of the gas in closed circuits, this flow being entirely tangential, and the gas behaving like an incompressible fluid. Obviously these steady currents are of no importance in connection with the question of stability or instability.

Discussion of the Frequency Equation.

§ 13. Returning to the class of vibrations in which u, Δ, and T do not all vanish, we have seen that the frequency equation is found by the elimination of F, A, B, and C from equations (28) to (35). Now p only enters into three of these equations; namely (31), in which it enters through the factor ip, and (29) and (30), in which it enters through the factor $-p^2$ or $(ip)^2$. Regarding ip, A, B, C, and F as unknowns, it will be seen that the coefficients which occur in equations (28) to (35) are all real. The four volume equations enable us to determine A, B, C, and F except for certain constants of integration, and the values of these quantities will be wholly real if ip is real. The boundary-equations enable us to determine the constants of integration and also provide an equation for ip. Every term in these equations will be real if ip is real. Hence the frequency equation can be written in the form

$$f(ip) = 0,$$

where $f(x)$ is a function of x in which all the coefficients are real, these coefficients being functions of n and of the quantities which determine the equilibrium configuration of the nebula.

It follows that the complex roots of ip will occur in pairs of the form

$$ip = \gamma \pm i\,\delta,$$

where γ and δ are both real. There may also be roots for which ip is purely real, so that $\delta = 0$, and γ exists alone.

The vibration corresponding to any root is stable or unstable according as γ is negative or positive.

If the equilibrium configuration of the nebula changes in any continuous manner, so as always to remain an equilibrium configuration, the values of ip will also change in a continuous manner, and for physical reasons these values can never become infinite. Hence, if the configuration of the nebula changes from one of stability to one of instability, it must do so by passing through a configuration in which there is a vibration for which $\gamma = 0$.

§ 14. For the present we shall not discuss the actual stability or instability of any configuration, but shall examine under what circumstances a transition from stability to instability can occur.

We therefore proceed to search for configurations in which there are vibrations such that $\gamma = 0$. Now for such a vibration we have either a root of the frequency equation $p = 0$, or else a pair of roots of the form $ip = \pm\, i\,\delta$.

In the latter case the corresponding vibration is one in which a dissipation of energy does not occur. A necessary condition for such a vibration is that no conduction of heat shall take place. Hence both sides of the equation of conduction of heat (equation 31) must vanish. Excluding adiabatic motion (represented by the vanishing of the factor $M\rho B + C_v C$), this condition compels us to take

$$p = 0$$

together with

$$\frac{d\kappa}{dr}\frac{dC}{dr} + \frac{\kappa}{r^2}\left\{\frac{d}{dr}\left(r^2\frac{dC}{dr}\right) - n\,(n+1)\,C\right\} + \kappa\frac{d}{dr}\left(\frac{C}{2T}\right)\frac{dT}{dr}$$

$$- \kappa\frac{dT}{dr}\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dA}{dr}\right) - \frac{4}{r}\frac{dA}{dr} - \frac{n\,(n+1)-2}{r^2}A\right\} = 0 \quad . \quad . \quad (36).$$

Thus vibrations for which $\gamma = 0$, if they exist, must satisfy equations (32) to (36), and also equations (29) and (30), in which p is put equal to zero, and equation (28).

The case of $n = 0$ will be considered later (§ 28). Excluding this for the present, we find that putting $p = 0$ in (30) leads to

$$\mathrm{F} = 0 \quad \ldots\ldots\ldots\ldots \quad (37).$$

Equation (29) now reduces to

$$\mathrm{B}\frac{d\varpi}{dr} + \lambda\frac{d\rho}{dr}(\mathrm{C} - \mathrm{BT}) = 0 \quad \ldots\ldots\ldots \quad (38),$$

or, replacing ϖ by its value $\lambda\mathrm{T}\rho$,

$$\mathrm{B}\rho\frac{d}{dr}(\lambda\mathrm{T}) + \lambda\frac{d\rho}{dr}\mathrm{C} = 0 \quad \ldots\ldots\ldots \quad (39).$$

Equation (28) becomes

$$\mathrm{V} = \lambda(\mathrm{C} - \mathrm{BT}) - \frac{\mathrm{A}}{\rho}\frac{d\varpi}{dr} = 0 \quad \ldots\ldots\ldots \quad (40),$$

and the elimination of $\mathrm{C} - \mathrm{BT}$ from this equation and (38) leads to the equation

$$\frac{d\rho}{dr}\mathrm{V} = -\left(\mathrm{A}\frac{d\rho}{dr} + \mathrm{B}\rho\right)\frac{1}{\rho}\frac{d\varpi}{dr} \quad \ldots\ldots\ldots \quad (41).$$

Substituting for V from equation (27), this becomes

$$\frac{4\pi}{(2n+1)r^{n+1}}\left\{\int_{\mathrm{R}_0}^{r}\left(\mathrm{A}\frac{d\rho}{dr} + \mathrm{B}\rho\right)r^{n+2}\,dr + \left[\mathrm{A}(\rho - \sigma_0)r^{n+2}\right]_{r=\mathrm{R}_0}\right\}$$
$$+ \frac{4\pi r^n}{(2n+1)}\left\{\int_{r}^{\mathrm{R}_1}\left(\mathrm{A}\frac{d\rho}{dr} + \mathrm{B}\rho\right)\frac{dr}{r^{n-1}} - \left[\frac{\mathrm{A}(\rho - \sigma_1)}{r^{n-1}}\right]_{r=\mathrm{R}_1}\right\}$$
$$= \left(\mathrm{A}\frac{d\rho}{dr} + \mathrm{B}\rho\right)\frac{1}{\rho}\frac{d\varpi}{dr}\Big/\frac{d\rho}{dr} \quad \ldots\ldots\ldots\ldots \quad (42).$$

§ 15. With a view to transforming this equation, let us consider the equation

$$\frac{4\pi}{(2n+1)r^{n+1}}\left\{\int_{\mathrm{R}_0}^{r}\mathrm{J}r^{n+2}\,dr + \mathrm{K}_0\right\} + \frac{4\pi r^n}{(2n+1)}\left\{\int_{r}^{\mathrm{R}_1}\frac{\mathrm{J}}{r^{n-1}}\,dr + \mathrm{K}_1\right\} = \mathrm{L} \quad (43).$$

in which J and L are any functions of r, and K_0, K_1 are constants. If we multiply by r^{n+1}, and differentiate with respect to r, we obtain, after some simplification,

$$4\pi r^{2n}\left\{\int_{r}^{\mathrm{R}_1}\frac{\mathrm{J}}{r^{n-1}}\,dr + \mathrm{K}_1\right\} = \frac{d}{dr}(\mathrm{L}r^{n+1}) \quad \ldots\ldots \quad (44),$$

while by multiplying (43) by r^{-n} and differentiating, we obtain in a similar way

$$-\frac{4\pi}{r^{2n+2}}\left\{\int_{\mathrm{R}_0}^{r}\mathrm{J}r^{n+2}\,dr + \mathrm{K}_0\right\} = \frac{d}{dr}(\mathrm{L}r^{-n}) \quad \ldots\ldots \quad (45).$$

Divide (44) by r^{2n} and differentiate with respect to r, then

$$-\frac{4\pi J}{r^{n-1}} = \frac{d}{dr}\left\{\frac{1}{r^{2n}}\frac{d}{dr}(Lr^{n+1})\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46),$$

or, writing ξ for Lr, and simplifying

$$\frac{d^2\xi}{dr^2} - \frac{n(n+1)}{r^2}\xi = -4\pi r J \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (47),$$

and this same equation could have been deduced from (45) instead of (44).

Equation (47) is more general than (43) since the two constants K_0, K_1 have disappeared. In fact equation (47), being a differential equation of the second order, will contain two arbitrary constants in its solution, and these correspond to the two missing constants K_0 and K_1. We can, however, determine K_0, K_1 in terms of these two arbitrary constants, and if these constants are chosen so as to give the right values for K_0, K_1, the solution of (47) will be equivalent to the original equation (43).

To determine K_0, K_1, put $r = R_1$ in (44) and we obtain

$$4\pi K_1 = \left[\frac{1}{r^{2n}}\frac{d}{dr}(\xi r^n)\right]_{r=R_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48),$$

and similarly from (45)

$$4\pi K_0 = -\left[r^{2n+2}\frac{d}{dr}(\xi r^{-(n+1)})\right]_{r=R_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49).$$

Hence we see that equation (43) is exactly equivalent to the three equations (47), (48), and (49).

§ 16. Comparing (42) with (43), it appears that (42) is exactly equivalent to the following equations :—

$$\xi = \left(A\frac{d\rho}{dr} + B\rho\right)\frac{r}{\rho}\frac{d\varpi}{dr}\bigg/\frac{d\rho}{dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (50).$$

$$\frac{d^2\xi}{dr^2} - \frac{n(n+1)}{r^2}\xi = -4\pi r\left(A\frac{d\rho}{dr} + B\rho\right) \quad . \quad . \quad . \quad . \quad . \quad (51).$$

$$4\pi K_1 \equiv \left[\frac{1}{r^{2n}}\frac{d}{dr}(\xi r^n)\right]_{r=R_1} = -\left[\frac{A(\rho - \sigma_1)}{r^{n-1}}\right]_{r=R_1} \quad . \quad . \quad . \quad . \quad (52).$$

$$4\pi K_0 \equiv -\left[r^{2n+2}\frac{d}{dr}(\xi r^{-(n+1)})\right]_{r=R_0} = \left[A(\rho - \sigma_0)\, r^{n+2}\right]_{r=R_0} \quad . \quad . \quad . \quad (53).$$

The right-hand member of (51) is equal to

$$-4\pi\xi\frac{d\rho}{dr}\bigg/\frac{1}{\rho}\frac{d\varpi}{dr},$$

so that if we introduce a new quantity u, defined by

$$u = 2\pi\rho r^2 \frac{d\rho}{dr} \Big/ \frac{d\varpi}{dr} \quad \dots\dots\dots\dots (54),$$

equation (51) may be written in the form

$$r^2 \frac{d^2\xi}{dr^2} = \{n(n+1) - 2u\}\,\xi. \quad \dots\dots\dots\dots (55).$$

The solution of this will be of the form

$$\xi = \mathrm{E}_1\phi_1(r) + \mathrm{E}_2\phi_2(r) \quad \dots\dots\dots\dots (56),$$

in which E_1, E_2 are constants of integration. We have, from the definition of ξ,

$$\mathrm{A}\frac{d\rho}{dr} + \mathrm{B}\rho = \frac{\xi u}{2\pi r^3} = \frac{u}{2\pi r^3}\{\mathrm{E}_1\phi_1(r) + \mathrm{E}_2\phi_2(r)\} \quad \dots\dots (57),$$

and the elimination of B from this equation and (39) gives

$$\lambda\frac{d\rho}{dr}\,\mathrm{C} = \frac{d}{dr}(\lambda\mathrm{T})\left\{\mathrm{A}\frac{d\rho}{dr} - \frac{u}{2\pi r^3}\{\mathrm{E}_1\phi_1(r) + \mathrm{E}_2\phi_2(r)\}\right\} \quad \dots (58).$$

If we imagine this value for C substituted in equation (36), we shall have a differential equation of the second order for A. The solution of this will be of the form

$$\mathrm{A} = \mathrm{E}_1 f_1(r) + \mathrm{E}_2 f_2(r) + \mathrm{E}_3 f_3(r) + \mathrm{E}_4 f_4(r) \quad \dots\dots (59),$$

in which E_3 and E_4 are the new constants of integration. From this value of A we can deduce the values of B and C (equations (57) and (58)) without introducing any further constants of integration.

Turning to the boundary conditions, we now find that there are six boundary-equations to be satisfied (equations (32), (33), (34), (35), (52), (53)) and only three arbitrary constants at our disposal, namely, the ratios of the four E's. If we eliminate these E's we shall be left with three equations to determine the configuration of the nebula at which instability sets in, and these equations will in general be inconsistent.

§ 17. In order to put the right interpretation upon this result, it will be necessary to return to the general equations of free vibrations found in § 12.

If we eliminate F from equations (29) and (30), we obtain

$$p^2\left\{A + \frac{1}{n(n+1)}\frac{d}{dr}(r^2B) - \frac{d}{dr}(r^2A)\right\} = \frac{\lambda}{\rho}\frac{d\rho}{dr}C + \frac{d}{dr}(\lambda T)B \quad . \quad . \quad (60),$$

while equation (30) may, with the help of (28), be written in the form

$$V = \xi/r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (61),$$

in which ξ is now defined by

$$\frac{\xi}{r} = \lambda(C - BT) - \frac{A}{\rho}\frac{d\varpi}{dr} + \frac{p^2}{n(n+1)}\left\{r^2B - \frac{d}{dr}(r^2A)\right\} \quad . \quad . \quad . \quad (62).$$

Substituting for V from equation (27), and treating the equation so formed in the manner explained in § 15, we find, as the equivalent of equation (61),

(i.) A volume equation, analogous in form to (51), namely,

$$\frac{d^2\xi}{dr^2} - \frac{n(n+1)}{r^2}\xi = -4\pi r\left(A\frac{d\rho}{dr} + B\rho\right) \quad . \quad . \quad . \quad . \quad . \quad (63).$$

(ii.) Two boundary equations analogous in form to (52) and (53). . . (64), (65).

Thus the equations found in § 11 may be replaced by

(α) Three volume equations, namely, equations (60), (63), and (31).

(β) Six boundary equations, namely, equations (32), (33), (34), (35), (64), (65).

We may conduct the elimination of B and C from the three equations (α) in a symbolic manner as follows:—

Let D_n be a symbol which is used to denote any linear differential operator of order n, the differentiations being with respect to r. The symbol has reference solely to the order of the highest differential coefficient which occurs, and must in no case have reference to any particular differential operator. Thus we write D_n indiscriminately for every operator of the form

$$f_n(r)\frac{\partial^n}{\partial r^n} + f_{n-1}(r)\frac{\partial^{n-1}}{\partial r^{n-1}} + \ldots$$

The laws governing the manipulation of this symbol are as follows:

$$\begin{aligned}
&\text{(i.)} \quad -D_n\phi = D_n\phi. \\
&\text{(ii.)} \quad D_n\phi + D_m\phi = D_n\phi \ (n > m). \\
&\text{(iii.)} \quad D_n(D_m\phi) = D_{m+n}\phi.
\end{aligned}$$

It must be particularly noticed that in general

$$D_n\phi - D_n\phi = D_n\phi.$$

Corresponding, however, to any two specified operators of order n, say $(D_n)_1$ and $(D_n)_2$, it will always be possible to find two functions of r, say a and b, such that

$$a\,(D_n)_1\,\phi - b\,(D_n)_2\,\phi = D_{n-1}\phi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (66).$$

In terms of this operator, the three equations (α) (p. 16) may be written in the following forms:

$$p^2\,(D_2A + D_1B) + D_0B + D_0C = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (67),$$

$$D_2A + D_2B + D_2C + p^2\,(D_3A + D_2B) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (68),$$

$$ip\,(D_0B + D_0C) + D_2C + D_2A = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (69).$$

Now D_n is commutative with regard to functions of r, and is of course commutative with regard to p. This enables us to eliminate B and C from the above equations.

To make this clearer, consider a simple case, say the pair of equations

$$D_2A = D_nB \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (70).$$

$$D_1A = p^2D_mB \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (71).$$

If we operate on (71) with d/dr, we get an equation of the form

$$D_2A = p^2D_{m+1}B,$$

and from this and equation (70), we can, with the help of the property expressed in equation (66), deduce an equation of the form

$$D_1A = D_nB + p^2D_{m+1}B.$$

From this and equation (71) we can in a similar way obtain an equation of the form

$$D_0A = D_nB + p^2D_{m+1}B.$$

We may regard this as an equation giving A, and substitute for A in (71). In this way we obtain

$$D_{n+1}B + p^2D_{m+2}B = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (72),$$

and the elimination of A has been effected.

It will be clear that throughout this elimination we have followed a method which would have been successful in eliminating A if d/dr had been regarded as a mere multiplier. The result of the elimination is accordingly exactly the same as might have been obtained directly from the original equations (70) and (71), by regarding the D's as multipliers and eliminating according to the ordinary laws of algebra.

It will now be apparent that we can eliminate any two of the three unknowns, A, B, and C, from equations (67)–(69) by this method. The differential equation satisfied by the remaining unknown (say A) will be

$$\Delta \mathrm{A} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (73),$$

where, symbolically,

$$\Delta \equiv \begin{vmatrix} p^2\mathrm{D}_2, & p^2\mathrm{D}_1 + \mathrm{D}_0, & \mathrm{D}_0 \\ p^2\mathrm{D}_3 + \mathrm{D}_2, & p^2\mathrm{D}_2 + \mathrm{D}_2, & \mathrm{D}_2 \\ \mathrm{D}_2, & ip\mathrm{D}_0, & ip\mathrm{D}_0 + \mathrm{D}_2 \end{vmatrix} \quad . \quad . \quad . \quad . \quad (74).$$

We may expand this determinant according to the rules already laid down for the manipulation of the D's, and so obtain

$$\Delta = ip^5\mathrm{D}_4 + p^4\mathrm{D}_6 + ip^3\mathrm{D}_4 + p^2\mathrm{D}_6 + ip\mathrm{D}_2 + \mathrm{D}_4 \quad . \quad . \quad . \quad . \quad (75).$$

§ 18. We can now see the explanation of the difficulty which occurred in § 16. The occurrence of the term D_6 in Δ points to a differential equation of the sixth order, which is satisfied by any one of the quantities A, B, or C in the general case, in which p does not vanish. As soon, however, as p is put equal to zero, the expression for Δ reduces to D_4, and the differential equation is one of the fourth order only. It therefore appears that by putting $p = 0$ *before* solving the differential equations, the order of these equations is reduced automatically, and two solutions are entirely lost from sight.

These two last solutions, it is easy to see, are solutions which do not approximate to a definite limit, when p approximates to zero. The remaining four solutions will approximate to the same forms as would be obtained by putting $p = 0$ before solving the differential equations. Thus, instead of equation (59), we must write the complete limiting solution for A in the form

$$\underset{p=0}{\mathrm{L}^t} \mathrm{A} = \mathrm{E}_1 f_1(r) + \mathrm{E}_2 f_2(r) + \mathrm{E}_3 f_3(r) + \mathrm{E}_4 f_4(r) + \mathrm{E}_5 f_5(r, p) + \mathrm{E}_6 f_6(r, p)^* \; . \; (76).$$

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* I have not found it possible to investigate the form of these two last solutions in the general case, but it is easy to examine the nature of the solutions at infinity, when the nebula extends to infinity, and this enables us to form some idea as to the general nature of the solutions. Suppose that at infinity we have

$$\underset{r=\infty}{\mathrm{L}^t} \frac{1}{\lambda\rho}\frac{d\varpi}{dr}\frac{d\lambda}{dr} = \pm\, a^2 r^{-s},$$

in which a is real, then it can be shown that $\mathrm{A} = \phi(r, p)\,\mathrm{A}'$, &c., in which A', B', C', are functions of r only, and

$$\phi(r, p) = \mathrm{E}_5 \cos\left(2\sqrt{an(n+1)}\, r^{-s/2}/isp\right) + \mathrm{E}_6 \sin\left(2\sqrt{an(n+1)}\, r^{-s/2}/isp\right)$$

when the negative sign is taken in the above ambiguity, the circular functions being replaced by hyperbolic functions when the positive sign is taken. The value of ip is wholly real when squares of ip may be neglected (*cf.* § 13).

If we deduce the values of B and C from the solution (76), and substitute in the six boundary equations the values so obtained, we shall be left with six linear and homogeneous equations between the six E's. Eliminating the six E's, we have a single relation between n, the constants of the nebula and p. Now it will be seen that it will always be possible to pass to the limit $p = 0$ in this equation, since this amounts only to finding the *ratio* of the values of f_5 or f_6 at the two boundaries. The equation obtained in this manner will give us a knowledge of the configurations at which a change from stability to instability can take place.

§ 19. It therefore appears that it is not sufficient to consider vibrations of frequency $p = 0$ as represented by positions of "limiting equilibrium." The method of POINCARÉ[*] for determining points of transition from stability to instability is not sufficiently powerful for the present problem; indeed it appears that it is liable to break down whenever there are boundary-equations to be satisfied.[†]

It is of interest to notice that this complication is not (as might at first sight be suspected) a consequence of our having taken thermal conductivity into account. For we can put $C = 0$ and remove the equation of conduction of heat without causing any change in our argument, except that the right-hand member in equation (74) must be replaced by a determinant consisting only of the minor of the bottom right-hand member in the present determinant. The value of Δ is now

$$\Delta = p^2 D_4 + D_2,$$

and the number of boundary-equations is of course reduced from six to four. Thus an exactly similar situation presents itself, although we are now dealing with a strictly conservative system.

The consequences of this result are more wide-reaching than would appear from the present problem, inasmuch as all problems of finding adjacent configurations of equilibrium are affected. For instance, it appears that an equilibrium theory of tides is meaningless except in very special cases (*e.g.*, when the elements of the fluid in which the tide is raised are physically indistinguishable).

If we attempt to calculate by the ordinary methods the tide raised in a mass of compressible fluid by a small tide-generating potential, we reach a number of equations which are (except in special cases) contradictory. To take a simple case, suppose we have a planet of radius R_0 covered by an ocean of radius R_1, the whole being surrounded by an atmosphere which maintains a constant pressure ϖ at the surface of the ocean. Let the law of compressibility be $\varpi = c\rho$, where c varies from layer to layer of the ocean. Let the tide generating potential be $a_0 r^n S_n$. Then the equations of this paper will hold if we write $p = 0$, $C = 0$, ignore the equation of conduction of heat, replace λT everywhere by c, and include in

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[*] "Sur l'Equilibre d'une Masse fluide . . . ."—'Acta. Math.,' 7, p. 259.

[†] There is not, of course, a flaw in POINCARÉ'S analysis, but he works on the supposition that the potential-function is a holomorphic function of the principal co-ordinates, and this supposition excludes a case like the present one.

V a term $a_0 r^n$. Equation (39) gives (except in the special case of c = constant), B = 0. Equations (50) and (51) remain unaltered, and give a solution of the form

$$A = E_1 f_1(r) + E_2 f_2(r).$$

Now we must have A = 0 when $r = R_0$, and this determines the ratio E_1/E_2. Also equation (49) must be satisfied, and this leads to a second and different value for E_1/E_2.

A second example, of less interest but greater simplicity, will perhaps help to elucidate the matter. Imagine a non-gravitating medium in equilibrium under no forces inside a rigid boundary. Let the law connecting pressure and density for any particle be $\varpi = \kappa\rho$, where κ varies from particle to particle. In equilibrium ϖ has a constant value ϖ_0. Suppose now that we attempt to find an adjacent configuration which is one of equilibrium under a small disturbing potential V. The general equations of equilibrium are three of the form

$$\frac{dV}{dx} = \frac{1}{\rho}\frac{d\varpi}{dx}.$$

If the position of equilibrium only varies slightly from the initial position, $d\varpi/dx$ will be a small quantity of the first order, so that (to the first order of small quantities) ρ may be replaced by its equilibrium value ϖ_0/κ. We now have

$$\frac{d\varpi}{dx} = \frac{\varpi_0}{\kappa}\frac{dV}{dx},$$

and therefore, since ϖ is a single-valued function of position,

$$\int \frac{1}{\kappa}\frac{dV}{ds}\,ds = 0 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad \text{(i.)},$$

the integral being taken along any closed path. Since V and κ are absolutely at our disposal, this equation is, in general, self contradictory. What we have proved is that there will only be an "adjacent" configuration of equilibrium under a potential V if V is a single valued function of κ, a condition which will not in general be satisfied by arbitrary values of V and κ.

It is not difficult to see the physical interpretation of this last result. There were initially an infinite number of equilibrium positions, and therefore an infinite number of vibrations of frequency $p = 0$. To arrive at the configuration of equilibrium under the disturbing force we must imagine vibrations of frequency $p = 0$ to take place until equation (i.) is satisfied; the disturbed configuration will then differ only slightly from the configuration of equilibrium. For instance, if the disturbing field of force consists of a small vertical force g, the fluid must be supposed to arrange itself in horizontal layers of equal density, before we attempt to find the disturbed configuration.

The interpretation of the result obtained in the first instance is similar, but more difficult. Consider a linear series of equilibrium configurations, obtained by the variation of some parameter a, such that the spherical configuration of our example is given by $a = 0$. The other configurations are not symmetrical, the asymmetry being maintained, if necessary, by an external field of force. Every degree of freedom in the configuration $a = 0$ must have its counterpart in the configurations in which a is different from zero. In particular, the principal vibrations of § 12, in which (for the configuration $a = 0$) the dilatation, normal displacement, and temperature-increase all vanish, must have counterparts for all values of a. But when a is different from zero, the above three quantities cannot be supposed to all vanish. In general, therefore, these degrees of freedom provide solutions of the volume-equations, and these solutions contribute to the boundary-equations. In the special case of $a = 0$, these solutions do not affect the boundary-equations at all, so that to rectify the boundary-equations we must, so to speak, take an infinite amount of these solutions. In other words, the complete vibration of frequency $p = 0$ becomes identical with one of the vibrations of § 12, in which u, Δ, and T_1 all vanish.

An Isothermal Nebula.

§ 20. Let us now examine the form assumed by our equations in the simple case in which λ and T are the same at all points of the nebula. We find that, considering only the equations for the case of $p = 0$, equation (39) reduces to

$$C = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (77),$$

and, in virtue of this simplification, the equation of conduction of heat (36), and the two thermal boundary conditions (33 and 34) are satisfied identically. We are left with equation (55) to be satisfied throughout the gas, and equations (32), (35), (52), and (53) to be satisfied at the boundaries.

The solution of equation (55) is given in equation (56). Now we must satisfy equation (32) by taking $B = 0$ at $r = R_1$, and this, by equation (50), gives the value of A at $r = R_1$ in terms of E_1 and E_2. Hence equation (52) reduces to a homogeneous linear equation between E_1 and E_2.

When n is different from unity, we satisfy equation (35) by taking $A = 0$ at $r = R_0$, and this reduces equation (53) to a homogeneous linear equation between E_1 and E_2.

When $n = 1$, equation (35) reduces to a linear equation between $(A)_{r=R_0}$, E_1 and E_2. Equation (53) is a second equation of the same form, and the elimination of $(A)_{r=R_0}$ from these two equations leads to a homogeneous linear equation between E_1 and E_2.

Thus, in either case, we see that the whole system of equations reduces to a pair of homogeneous linear equations between E_1 and E_2. The elimination of these quantities leaves us with a single equation between n and the constants of the nebula.

We can, therefore, satisfy all the equations for a vibration of frequency $p = 0$ by imposing a single relation upon the constants of the nebula. The unknown solutions which are multiplied by E_5 and E_6 have not been taken into account at all, but since the condition that there shall be a vibration of frequency $p = 0$ must of necessity reduce to a single equation, it will be clear that if these solutions had been taken into account, we should have found it necessary to take $E_5 = E_6 = 0$.

Thus, in the case which we are now considering, a vibration of frequency $p = 0$ is equivalent to a configuration of limiting equilibrium. It is not hard to see that this results from the fact that the particles of which the nebula is composed are physically indistinguishable. This very fact, however, introduces a further complication into the question. It will be noticed that, although the value of ξ has been found at every point of the nebula, it is impossible to determine the separate values of A and B. On the other hand, the physical vibration must have a definite limiting form when $p = 0$. Now it is easy to see that a motion of the gas in which ξ vanishes at every point of the gas, and in which A and B vanish separately at the boundary, will, in every configuration of the gas, satisfy our equations with $p = 0$. Such a motion, in fact, simply leads to a configuration which is physically indistinguishable from the initial configuration, and in which the potential energy remains unaltered. The motion which we have found from our equations is the sum of a motion of this kind, and a true limiting vibration. It is impossible to separate the two motions, except by considering vibrations of frequency different from zero, but fortunately the question is not one of any importance.

§ 21. Let us now attempt to form the final equation in some cases of interest. The equations of an isothermal nebula at rest under its own gravitation have been discussed by Professor DARWIN.* Our function u (equation 54) is given, in the case in which the nebula is isothermal, by the equation

$$u = \frac{2\pi\rho r^2}{\lambda T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (78),$$

and it will be seen that this is the same as the u of Professor DARWIN'S paper. It appears that in general u cannot be expressed as a function of r in finite terms, but a table of numerical values of u is given.† The value of u approximates asymptotically to unity at infinity, so that at infinity ρ varies as r^{-2}. DARWIN'S nebula extends from $r = 0$ to $r = \infty$, but it is obvious that we may, without disturbing the equilibrium, replace that part of the nebula which extends from $r = 0$ to $r = R_0$ by a solid core of mass equal to that of the gas which it replaces. We may also remove that part of the nebula which extends from $r = R_1$ to $r = \infty$, if we suppose a pressure to act upon the surface $r = R_1$ of amount equal to the pressure of the gas at this surface. We may suppose the medium outside this surface to be of any kind we please, but as it has already been pointed out that the pressure can, in nature, only be maintained by the impact of matter, we shall suppose that this matter is of a density σ which is continuous with the density ρ of the nebula at the surface of separation. We may now write equation (52) in the simple form

$$\left[\frac{d}{dr}(\xi r^n)\right]_{r=R_1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (79).$$

We have, up to the present, supposed the nebula to be acted upon by a spherically symmetrical system of forces in addition to its own gravitation. Now it is essential to the plan of our investigation that we shall be able to make the configuration of the nebula vary in some continuous manner, and this compels us to retain this generalisation. We shall, however, suppose that when the nebula extends to infinity, u retains some definite limiting value u_∞, thus including the free nebula as a special case.

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* G. H. DARWIN, 'Phil. Trans.,' A, vol. 180, p. 1.

† *Loc. cit.*, p. 15.

§ 22. Let us, in the first place, consider the "series" of nebulæ such that u has a different constant value for each. This series includes a single free nebula, for it appears from DARWIN'S paper that there is a nebula such that $u = 1$ at every point. This nebula, it is true, has infinite density at the centre, but this objection disappears when the innermost shells of gas are replaced by a solid core, the mean density of the core being equal to three times the density of the gas at its surface, and therefore finite. Let us, in the first instance, simplify the problem by supposing that the core is held at rest in space. The boundary equations (35 and 53) which have to be satisfied at $r = \mathrm{R}_0$ now take the forms

$$(\mathrm{A})_{r=\mathrm{R}_0} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (80),$$

$$\left[\frac{d}{dr}(\xi r^{-(n+1)})\right]_{r=\mathrm{R}_0} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (81),$$

independently of the value of n. The value of u in equation (55) being now independent of r, we may write the solution (56) in the form

$$\xi = \mathrm{E}_1 r^{\mu} + \mathrm{E}_2 r^{\mu'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (82),$$

in which μ, μ' are the roots of the quadratic,

$$t(t-1) = n(n+1) - 2u \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (83).$$

We accordingly have

$$\mu + \mu' = 1 \,; \quad \mu - \mu' = 2\sqrt{(n+\tfrac{1}{2})^2 - 2u} \,; \quad \mu\mu' = -n(n+1) + 2u \quad . \quad (84).$$

Equation (79) now takes the form

$$\mathrm{E}_1 (\mu + n)\, \mathrm{R}_1^{\mu+n-1} + \mathrm{E}_2 (\mu' + n)\, \mathrm{R}_1^{\mu'+n-1} = 0 \quad . \quad . \quad . \quad . \quad (85),$$

while equation (81) becomes

$$\mathrm{E}_1 (\mu - n - 1)\, \mathrm{R}_0^{\mu-n-2} + \mathrm{E}_2 (\mu' - n - 1)\, \mathrm{R}_0^{\mu'-n-2} = 0 \quad . \quad . \quad . \quad (86).$$

The elimination of E_1 and E_2 from these equations gives

$$\left(\frac{\mathrm{R}_1}{\mathrm{R}_0}\right)^{\mu-\mu'} = \frac{(\mu' + n)(\mu - n - 1)}{(\mu + n)(\mu' - n - 1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (87).$$

The fraction on the right hand can be simplified by the help of equations (84); it is equal to

$$\frac{2(u - (n+\frac{1}{2})^2) + (\mu - \mu')(n + \frac{1}{2})}{2(u - (n+\frac{1}{2})^2) - (\mu - \mu')(n + \frac{1}{2})}.$$

Now the left-hand member of (87) may be replaced by

$$\frac{\cosh\{\frac{1}{2}(\mu - \mu')\log(\mathrm{R}_1/\mathrm{R}_0)\} + \sinh\{\frac{1}{2}(\mu - \mu')\log(\mathrm{R}_1/\mathrm{R}_0)\}}{\cosh\{\frac{1}{2}(\mu - \mu')\log(\mathrm{R}_1/\mathrm{R}_0)\} - \sinh\{\frac{1}{2}(\mu - \mu')\log(\mathrm{R}_1/\mathrm{R}_0)\}}$$

so that the equation itself reduces to

$$\tanh \{\tfrac{1}{2}(\mu - \mu') \log (R_1/R_0)\} = \frac{\tfrac{1}{2}(\mu - \mu')(n + \tfrac{1}{2})}{u - (n + \tfrac{1}{2})^2} \quad . \quad . \quad . \quad . \quad (88).$$

This equation expresses the relation which must exist between R_1/R_0 and $\mu - \mu'$ (or, what is the same thing, between R_1/R_0 and u), in order that $p = 0$ may be a solution of the frequency equation.

§ 23. We shall be able to interpret this equation most easily by adopting a graphical treatment. If we write

$$x = \tfrac{1}{4}(\mu - \mu')^2, \quad y_1 = -\frac{2(n + \tfrac{1}{2})}{x + (n + \tfrac{1}{2})^2}, \quad y_2 = \frac{1}{\sqrt{x}} \tanh \{\sqrt{x} \log (R_1/R_0)\},$$

then the equation can be written in the form

$$y_1 = y_2.$$

It will be noticed that y_2 remains real when x is negative, an equivalent expression for y_2 being

$$y_2 = \frac{1}{\sqrt{-x}} \tan \{\sqrt{-x} \log (R_1/R_0)\}.$$

The roots of equation (87) are now represented by the intersections of the graphs which are obtained by plotting out y_1 and y_2 as functions of x. These two graphs are given in figs. 1 and 2 respectively, the graphs being drawn separately for the sake of clearness. The graph for y_1 is, of course, the same for all values of R_1/R_0; that for y_2 can be varied so as to suit any value of R_1/R_0 by supposing it subjected

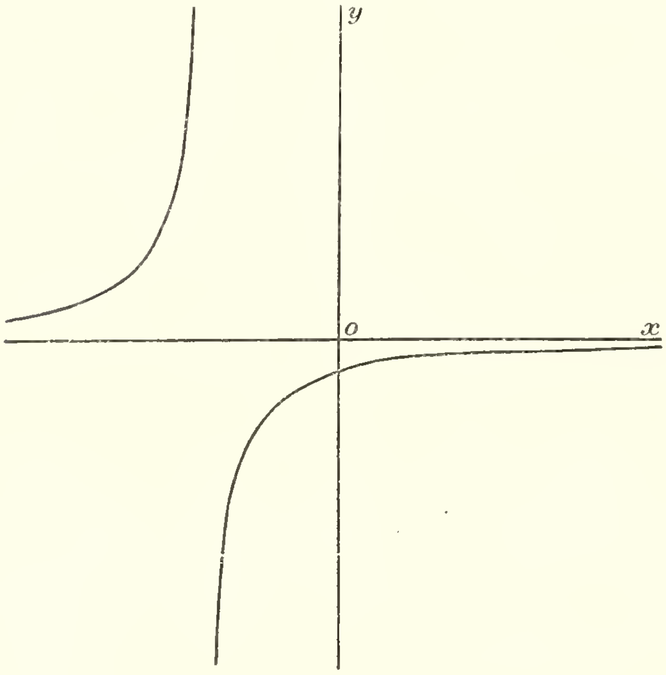

Fig. 1.

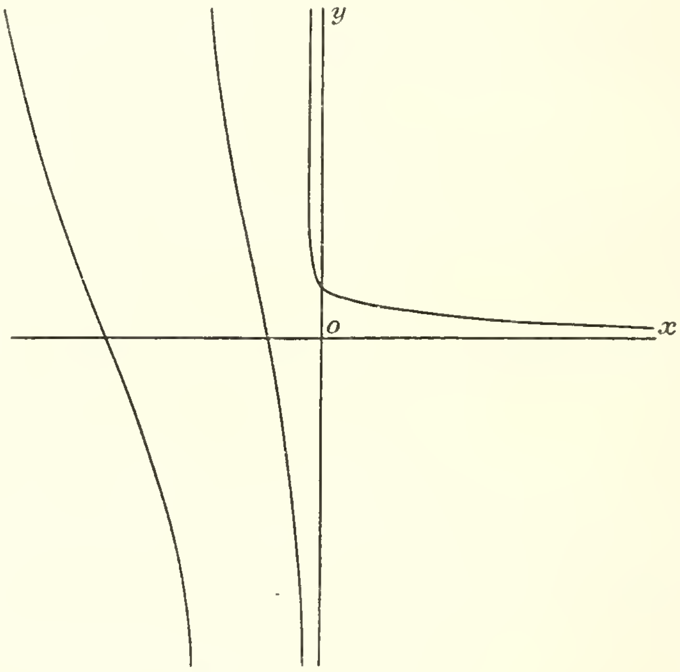

Fig. 2.

to an appropriate uniform extension parallel to the axis of y, and contraction parallel to the axis of x_1 or *vice versa.* Similarly, different values of $(n + \frac{1}{2})$ can be represented by contraction and extension of the first graph.

If we imagine these two graphs superposed, we see that there cannot, under any circumstances, be an intersection in the region in which x is positive, *i.e.* (equation (84)), for a value of u less than $\frac{1}{2}(n + \frac{1}{2})^2$. The lowest value of u for which an intersection can possibly occur is $u = 1$, and this occurs only when $R_1/R_0 = \infty$. As R_1/R_0 decreases from infinity downwards, the lowest value of u for which an intersection occurs will continually increase. Whatever the value of R_1/R_0 may be, there are always an infinite number of intersections in the region in which $u > \frac{1}{2}(n + \frac{1}{2})^2$.

The values of u found in this way determine the "points of bifurcation" on the linear series obtained by causing u to vary continuously. Thus we have seen that as u continually increases the first point of bifurcation of order n is reached when u has a value which is always greater than $\frac{1}{2}(n + \frac{1}{2})^2$. When R_1/R_0 is very large, the first point of bifurcation is of order $n = 1$, and its position is given by

$$u = 1\tfrac{1}{8} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (89).$$

§ 24. Let us, in future, confine our attention to the case in which R_1/R_0 is very large. If we gradually remove the restriction that u is to be independent of r, the various vibrations of frequency $p = 0$ will vary in a continuous manner. Equation (55) remains unaltered in form, and, at infinity, it assumes the definite limiting form

$$r^2 \frac{d^2\xi}{dr^2} = \{n(n + 1) - 2u_\infty\}\xi \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (90),$$

where u_∞ is the limit (supposed definite) of u at infinity. It therefore appears that at infinity the solution for ξ approximates asymptotically to that given by equation (82), if μ, μ' are now taken to be the roots of

$$t(t - 1) = n(n + 1) - 2u_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (91).$$

Equation (85) accordingly remains unaltered. Equation (81) takes a form which is no longer represented by equation (86), but which will impose some definite ratio upon E_1 and E_2. It is therefore clear that when R_1 is very great, equation (85) can only be satisfied, at any rate so long as μ and μ' are real, by taking $\mu - \mu'$ very small. Thus a point of bifurcation will again be given by $\mu - \mu' = 0$, our previous investigation sufficing to show that this gives a genuine solution to our problem, and does not correspond to an irrelevant factor introduced in the transformation of our equations. This point of bifurcation is moreover the first one reached as u increases, since it is at the point at which μ, μ' change from being real to being complex.

We conclude that, independently of the values of u at points inside the nebula, the smallest value of u_∞ for which a vibration of zero frequency and of order n is possible is given by

$$u_\infty = \tfrac{1}{2}(n + \tfrac{1}{2})^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (92),$$

or, for all orders, is given by

$$u_\infty = 1\tfrac{1}{8} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (93),$$

the limiting vibration being of order $n = 1$.

It ought to be noticed that for this limiting vibration equation (82) fails to represent the solution owing to μ and μ' becoming identical. The true solutions for real, zero, and imaginary values of $\mu - \mu'$ may be put respectively in the forms

$$\xi = \mathrm{C}_1\sqrt{r}\sinh\{\tfrac{1}{2}(\mu - \mu')\log \epsilon\mathrm{R}\},$$

$$\xi = \mathrm{C}_1\sqrt{r}\log \epsilon\mathrm{R},$$

$$\xi = \mathrm{C}_1\sqrt{r}\sin\left\{\frac{i}{2}(\mu - \mu')\log \epsilon\mathrm{R}\right\},$$

in which C_1 and ϵ are constants of integration.

At infinity ρ vanishes to the order of $1/r^2$, so that $d\rho/dr = -2\rho/r$. The value of ξ for very great values of r is therefore (equation (50))

$$\xi = \lambda\mathrm{T}(-2\mathrm{A} + \mathrm{B}r).$$

At the outer boundary a surface-equation (32) directs us to take $\mathrm{B} = 0$. Following this out, we find that at infinity A is of the same order as ξ, and therefore becomes infinite to the order of $\sqrt{r}$. Suppose, on the other hand, that we start by taking $\mathrm{A} = 0$, so that $\mathrm{B} = \xi/\lambda\mathrm{T}r$. The value of B now vanishes at infinity to the order of $1/\sqrt{r}$, and the surface-equation (32) is satisfied by a motion which vanishes at infinity. It would therefore appear to be easier to satisfy the boundary conditions when r is actually infinite than when r is merely very great. This result opens up a somewhat difficult question, which will be considered in the next section.

Before passing on, we may consider in what way the results which have already been obtained will be modified, if we suppose the core of the nebula to be free to move in space, instead of being held fast. For the free nebula $u_\infty = 1$, so that our results show that a free nebula will be stable if the core is supposed fixed. The same must therefore obviously be true when the core is free to move, since a motion in which nebula and core move as a single rigid body will not influence the potential energy. When the nebula is not free, fixing the core may be regarded as imposing a constraint which does no work; freedom of the core therefore tends towards instability. It will be proved in § 28, that a nebula is stable for values of u_∞ which are less than the critical value, and unstable for values greater than this value. Assuming this for the moment, we see that a nebula in which the core is free to move must necessarily be unstable if u_∞ has a value greater than $1\frac{1}{8}$.

If then, we start with a free nebula and imagine u_∞ to gradually increase from $u_\infty = 1$ upwards, the core being free, it follows that the nebula will first become unstable when u_∞ reaches some value such that

$$1\tfrac{1}{8} > u_\infty > 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (94).$$

§ 25. The nebula extending to infinity, let us attempt to find the displacement which will be caused by a small disturbing potential v_n given by

$$v_n = \frac{4\pi}{2n+1}\left\{\frac{a_0}{r^{n+1}} + a_1 r^n\right\} S_n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (95).$$

It is clear that the displacement required will be given by our equations if we include in V (equation (27)) the terms

$$\frac{4\pi}{2n+1}\left\{\frac{a_0}{r^{n+1}} + a_1 r^n\right\}.$$

The equation replacing (42) may be transformed in the manner of § 15, and the resulting equations will be those of § 16, except that we must replace (52) by

$$\left[\frac{1}{r^{2n}}\frac{d}{dr}(\xi r^n)\right]_{r=\mathrm{R}_1} = a_1 - \left[\frac{\mathrm{A}(\rho - \sigma_1)}{r^{n-1}}\right]_{r=\mathrm{R}_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad (96),$$

and (53) by a similar equation.

If a displacement can be found to satisfy these modified equations, the external disturbing potential which will be required to hold the system in this displaced position will be given by equation (94). Now the condition that this displaced position shall be one of limiting equilibrium is that this disturbing potential must vanish. To be more precise, v_n must be such that the force derived from it vanishes at every point of the nebula. We must therefore have

$$a_1 r^n = 0$$

at all points of the nebula, including $r = \mathrm{R}_1$. Now (95) may be regarded as an equation giving a_1 in terms of R_1. Taking $\rho = \sigma_1$, as before, we find from (95)

$$a_1 r^n = \left(\frac{r}{\mathrm{R}_1}\right)^n \left[\frac{1}{\mathrm{R}_1{}^n}\frac{d}{dr}(\xi r^n)\right]_{r=\mathrm{R}_1},$$

and this vanishes at all points, including $r = R_1$, in the case in which R_1 is put equal to infinity, if

$$\underset{r=\infty}{\mathrm{Lt}} \frac{\xi}{r} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (97).$$

The condition that a_0/r^{n+1} shall vanish at every point would lead to a similar equation to be satisfied at the origin, if there were no core. If, however, we retain the core, it leads to the same equation as was found in § 22 (equation (81), when the core is held at rest). Thus, our present method of finding a position of limiting equilibrium has led to a result different from that obtained by the search for a vibration of zero frequency, in that equation (97) replaces equation (79).

The value of ξ at infinity is given by equation (82); hence we have

$$\underset{r=\infty}{\mathrm{Lt}} \frac{\xi}{r} = [E_1 r^{\mu-1} + E_2 r^{\mu'-1}]_{r=\infty} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (98).$$

As before, the equation to be satisfied at $r = R_0$ determines the ratio of E_1 to E_2: equation (97) is therefore satisfied if the real parts of μ and μ' are each less than unity. Now μ, μ' are the roots of equation (91), hence this condition is satisfied provided

$$n(n+1) < 2u_\infty \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (99).$$

§ 26. Let the kinetic and potential energies of a small displacement be given, in terms of the principal co-ordinates, by

$$2T = a_1\dot{x}_1^2 + a_2\dot{x}_2^2 + \ldots$$
$$2V = b_1 x_1^2 + b_2 x_2^2 + \ldots$$

so that the equations of motion are

$$a_1\ddot{x}_1 - b_1 x = 0$$

&c., and p^2 is given by

$$a_1 p^2 = b_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (100).$$

The method of §§ 20–24 amounted to finding vibrations such that $p^2 = 0$, and therefore, by equation (100), solutions of

$$b_1 = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (101).$$

In § 25, on the other hand, we started with the supposition that the nebula extended to infinity, so that all the quantities a and b are liable to become infinite. The equation giving vibrations of frequency $p = 0$ is no longer equation (101), but is

$$\underset{R_1=\infty}{\mathrm{Lt}} \frac{b_1}{a_1} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (102),$$

and this is obviously more general than equation (101).

It will be noticed that the method of §§ 20–24 is the method which is mathematically appropriate to the case of a nebula enclosed in a surface maintained at constant pressure, while the method of § 25 is that appropriate to an infinite nebula. In the former case, a vibration of frequency $p = 0$ may represent a real change from stability to instability; in the latter case such a vibration leads to an adjacent configuration of equilibrium, and is, in this sense, a point of bifurcation, but does not denote a change in the sign of p^2.

The General Case of a Nebula extending to Infinity.

§ 27. The method to be followed has been explained in § 18. The general differential equation is of the sixth order. Four solutions have definite limiting forms when $p = 0$; the remaining two take singular forms. The former have been examined in § 16; the latter are represented mathematically (p. 18) by functions which do not approach a definite limit as p approaches a zero value, and physically (p. 11) by systems of steady currents.

There are six constants of integration, $E_1, E_2, E_3, E_4, E_5, E_6$, of which the two last belong to the singular solutions. Let us suppose (as is always possible (p. 19)) that the ratios of these six constants are determined from five of the boundary-equations, that which is not used being the equation satisfied by ξ at the outer boundary. This remaining boundary-equation now takes the form (*cf.* equation (56))

$$E_1\psi_1(R_1) + E_2\psi_2(R_1) + E_5\psi_5(R_1) + E_6\psi_6(R_1) = 0 \quad . \quad . \quad . \quad (103),$$

in which the four E's are definite quantities. The four ψ's must have definite limiting values (zero and infinity being included as possible values) when $R_1 = \infty$. Thus in equation (103) some terms must preponderate over the others. When the nebula is isothermal, these terms are the first two. Hence, when the nebula is not isothermal, it follows from the principle of continuity, that the same two terms must still preponderate, at any rate for some finite domain including the isothermal nebula. Otherwise it would be possible to change the stability or instability of a nebula by an infinitesimal change in the physical constitution of the nebula. Hence throughout this domain, equation (103) must reduce to its first two terms, *i.e.*, must become formally the same as in the case of the isothermal nebula. But the solution for ξ (and therefore the functions ψ_1, ψ_2), remain formally the same in the general case as in this particular case, and therefore the stability-criterion derived from equation (103) remains formally the same.

It follows that whether the nebula is isothermal or not (provided always that the configuration lies within a certain domain of equilibrium configurations) the critical configurations are given by the two equations (92) and (99).

Exchange of Stabilities.

§ 28. We have now completed an investigation of the configurations at which a transition from stability to instability can occur, as regards the spherical form, for vibrations of orders different from zero. It is unnecessary to discuss vibrations of order $n = 0$, for the following reason.

Our problem is to determine the changes in the configuration of a nebula which will take place as the nebula cools, starting from a spherical configuration, supposed stable. We are not concerned with the succession of spherical configurations, but only with an investigation of the conditions under which a spherical configuration becomes a physical impossibility. Now a point of bifurcation of order $n = 0$ does not indicate a departure from the spherical configuration. It indicates a choice of two paths, one stable and the other unstable, and the configurations on both paths will remain spherically symmetrical.

We have therefore determined already the circumstances under which a transition from a symmetrical to an unsymmetrical configuration can occur. It remains to show that there is, in effect, an exchange of stabilities at a point of bifurcation, and to examine on which side of the point of bifurcation the spherical configuration is stable.

We are going to prove that the spherical configuration is stable for all values of u less than u_0, the lowest value of u at which a point of bifurcation of order different from zero can occur. Our method will be as follows: Any two equilibrium configurations can be connected by a continuous linear series of equilibrium configurations, and u will vary continuously as we move along this series. If one of the two terminal configurations is stable, and if the linear series can be chosen so that u does not at any point of it pass through a value for which a vibration of frequency $p = 0$ is possible, then we know that the other terminal configuration is also stable.

The value of γ, the gravitation constant, has been taken equal to unity. If this constant is restored, the value of u becomes (equation (54))

$$u = 2\pi\gamma\rho r^2 \frac{d\rho}{dr} \bigg/ \frac{d\varpi}{dr} \cdot$$

Since $\varpi = \lambda \mathrm{T} \rho$, we have

$$\frac{d\varpi}{dr} = \rho \frac{d}{dr} (\lambda \mathrm{T}) + \lambda \mathrm{T} \frac{d\rho}{dr} \cdot$$

For an infinite nebula, the first term on the right-hand of this equation will vanish at infinity in comparison with the second. Hence we have as the value of u_∞

$$u_\infty = \underset{r=\infty}{\mathrm{L}^t_{\,t}} \frac{2\pi\gamma\rho r^2}{\lambda \mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (104).$$

If we write $\gamma = 0$ we pass to the case of a non-gravitating nebula, and we see that $u_x = 0$ provided the ratio of ρr^2 to λT remains finite at infinity. Now we can keep the value of ρ and λT the same at every point by subjecting the nebula to an appropriate external field of force, and this field of force will be exactly the same as the gravitational field which was annihilated upon putting $\gamma = 0$. It is spherically symmetrical, and its potential vanishes at infinity to the order of $1/r$, so that it comes within the scope of our previous analysis. For values of γ intermediate between the natural value ($\gamma = 1$) and the value $\gamma = 0$ we can obtain the same result by taking a field of force equal to $1 - \gamma$ times the foregoing. As we increase γ from 0 to 1 we obtain a linear series, in which the configuration of the nebula is unaltered, the nebula being gradually endowed with the power of gravitation.

For the general configuration of this series, consider the work done in a specified displacement, which is proportional to S_n at every point. The potential (gravitational + that of external field) after displacement will be of the form

$$a + b\gamma S_n.$$

where a and b are functions of r and independent of γ. The total work done against this field during the displacement is therefore of the form

$$B\gamma,$$

where B is independent of γ and depends solely upon the particular displacement selected. The work done against the elastic forces is of course independent of γ, and depends solely upon the displacement selected. This work is essentially positive. The total work is therefore of the form

$$A + B\gamma,$$

where A is positive and B may (§ 2) be negative. Since γ is proportional to u_∞ this may be written

$$A + B'u_x \quad \ldots\ldots\ldots\ldots \quad (105).$$

Suppose this function calculated for all possible displacements. Then we shall find that for values greater than some definite value of u_∞ it is possible for the work done to become negative. For values of u_∞ less than this critical value, the work will be positive for all displacements. Hence from the form of expression (105) it follows that the passage of u_∞ through a critical value denotes a real change from stability to instability, and that the stable configurations are given by the smaller values of u_x.

Recapitulation and Discussion of Results.

§ 29. We have seen that the vibrations of any spherical nebula may be classified into vibrations of orders $n = 0, 1, 2$, &c., a vibration of any order n being such that the displacement and change in temperature at any point are each proportional to some spherical surface harmonic S_n of order n. The frequency of vibration is independent of the particular spherical harmonic chosen, depending only upon the order n.

The vibrations of order $n = 0$ have been seen to be of no importance; the stability of the vibrations of orders different from zero has been discussed, in the limiting case in which the nebula extends to infinity, with the following results:—

Starting from any stable configuration of spherical symmetry, the vibrations of any order n, different from zero, all remain stable until the function u_∞, defined by equation (104), passes through a certain critical value. In any case this critical value is first attained for a vibration of order $n = 1$.

For a nebula which actually extends to infinity, the critical value is $u_x = 1$. When this value is reached we come to a second series of equilibrium configurations, the form of which will be investigated later. If this value is passed, the configuration remaining spherical, there will not be vibrations in which the time enters through a real exponential factor, because the critical vibrations remain of frequency $p = 0$, the inertia of the nebula being infinite.

If the radius R_1 of the nebula is regarded as very great but not infinite, this statement is not true, since the inertia cannot now become infinite. In this case the first new series of equilibrium configurations is again reached when $(u)_{r=R_1}$ attains a certain critical value, and the critical vibration is again of order $n = 1$. The critical value of $(u)_{r=R_1}$ has not been calculated, but when R_1 becomes infinite, it has a limiting value which has been shown to lie between 1 and $1\frac{1}{8}$.

Taking $\gamma = 1$, we have as the value of u_x,

$$u_x = \underset{r=\infty}{\mathrm{L}t} \frac{2\pi\rho r^2}{\lambda T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (106).$$

The question of stability turns entirely upon the value of this function, which may appropriately be termed the "stability-function."

We now see that the whole question of stability depends upon the ratio of the density to the elasticity at infinity. This result is not hard to understand. In the first place, since the nebula extends to infinity, we may, so to speak, measure it upon any linear scale we like. If we measure it on a sufficiently great scale, the nebula still remains of infinite extent, but the variations in temperature or structure which occur near the centre can be made to appear as small as we wish, and the solid core can be made to appear as insignificant as we wish. Thus by measuring any nebula upon a sufficiently great scale we can make it appear indistinguishable from an isothermal nebula, and the critical vibration for which $p = 0$ does not disappear from sight, since in the limit this vibration (measured by ξ/r) remains finite at infinity. Further, as Professor DARWIN points out, we can make it appear like a nebula in which u maintains a constant value throughout.* Passing on, we notice that the stability function now depends solely upon the ratio of the density to the elasticity. The different elements of the nebula are attracted towards one another by their mutual gravitation, and are kept apart by the elasticity of the gas. For certain values of the ratio of these two systems of forces, it will be possible to find displacements in which the work done by one system exactly balances that done against the other, and these are the critical vibrations.

The stability function u_∞ is a function only of the quantities determining the equilibrium configuration of the nebula, and its value may therefore be found from the equations of equilibrium. We proceed to examine the value.

EVALUATION OF THE STABILITY FUNCTION.

General Case of a Nebula at Rest.

§ 30. We have already quoted Professor DARWIN'S result that $u_\infty = 1$ for an isothermal nebula at rest, and the considerations put forward in the last section will probably suggest that the result in the more general case will be found to be independent of variations in temperature at finite distances, provided only that the temperature has a definite limit at infinity. We shall, however, examine the question *ab initio*, using a slight modification of DARWIN'S method, and making the problem more general by retaining a spherically symmetrical system of external forces.

We shall denote the potential of this system of forces by V′, and use V to denote the gravitational potential of the nebula itself. The total potential is now V + V′, so that the equation of equilibrium, equation (11), takes the form

$$\frac{1}{\rho}\frac{d}{dr}(\lambda \mathrm{T}\rho) - \frac{d}{dr}(\mathrm{V} + \mathrm{V}') = 0,$$

and if M is the mass of the solid core, this can be written

$$\frac{r^2}{\rho}\frac{d}{dr}(\lambda \mathrm{T}\rho) + 4\pi\int_{\mathrm{R}_0}^{r} \rho r^2\, dr + \mathrm{M} - r^2\frac{d\mathrm{V}'}{dr} = 0 \quad . \quad . \quad . \quad . \quad (107).$$

Differentiating with respect to r,

$$\frac{d}{dr}\left(\frac{r^2}{\rho}\frac{d}{dr}(\lambda \mathrm{T}\rho)\right) + 4\pi\rho r^2 - \frac{d}{dr}\left(r^2\frac{d\mathrm{V}'}{dr}\right) = 0.$$

Write

$$\lambda \mathrm{T}\rho = e^y,$$

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* G. H. DARWIN (*l.c. ante*, p. 16), "If we view the nebula from a very great distance, . . . the solution of the problem becomes $y = \log 2x^2$." Now $u = -\frac{1}{2}x^2\, d^2y/dx^2$, so that this solution is equivalent to $u = 1$. This justifies our statement, and shows at the same time that for any nebula at rest and in equilibrium u_∞ has the critical value $u_\infty = 1$, provided it is acted upon by no forces except its own gravitation.

and

$$x = \int_r^\infty \frac{dr}{\lambda \mathrm{T} r^2},$$

so that

$$\frac{d}{dr} = \frac{1}{\lambda \mathrm{T} r^2} \frac{d}{dx},$$

then the above equation may be written

$$\frac{d^2y}{dx^2} + 4\pi e^y r^4 - r^2 \frac{d}{dr}\left(r^2 \frac{d\mathrm{V}'}{dr}\right) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (108).$$

At infinity we are supposing $\lambda\mathrm{T}$ to have a definite and finite limit, so that the limiting value of x is $1/\lambda\mathrm{T}r$. Let us further suppose that $\frac{d}{dr}\left(r^2 \frac{d\mathrm{V}'}{dr}\right)$ has a definite limit given by

$$\frac{d}{dr}\left(r^2 \frac{d\mathrm{V}'}{dr}\right) = \mathrm{V}'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (109),$$

and that squares of V'' may be neglected. Then the limiting form of (108) at infinity is

$$\frac{d^2y}{dx^2} + \frac{4\pi e^y}{(\lambda \mathrm{T} x)^4} - \frac{\mathrm{V}''}{(\lambda \mathrm{T} r)^2} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (110).$$

Write

$$y = \eta + \log \frac{\lambda^4 \mathrm{T}^4 x^2}{2\pi},$$

then

$$\frac{d^2y}{dx^2} = \frac{d^2\eta}{dx^2} - \frac{2}{x^2} + 4 \frac{d^2}{dx^2} \log (\lambda \mathrm{T}),$$

and

$$\frac{4\pi e^y}{(\lambda \mathrm{T} x)^4} = \frac{2e^\eta}{x^2}.$$

Equation (110) is now transformed into

$$\frac{d^2\eta}{dx^2} + \frac{2}{x^2}(e^\eta - 1) + 4 \frac{d^2}{dx^2} \log (\lambda \mathrm{T}) - \frac{\mathrm{V}''}{(\lambda \mathrm{T} x)^2} = 0 \quad . \quad . \quad . \quad . \quad (111).$$

In the special case in which $\frac{d^2}{dx^2} \log (\lambda\mathrm{T})$ vanishes, this may be written

$$\frac{d^2\eta}{dx^2} + \frac{2}{x^2}\left(\eta + \tfrac{1}{2}\eta^2 + \tfrac{1}{6}\eta^3 + \ldots - \frac{\mathrm{V}''}{2\lambda^2\mathrm{T}^2}\right) = 0,$$

and at infinity (*i.e.*, for very small values of x), the solution is

$$\eta = \frac{\mathrm{V}''}{2\lambda^2\mathrm{T}^2} + \sqrt{\frac{x}{\mathrm{A}}} \cos\left(\tfrac{1}{2}\sqrt{7} \log \frac{x}{\mathrm{B}}\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad (112)$$

where A, B are the two constants of integration.

In the more general case in which $\frac{d^2}{dx^2}\log(\lambda\mathrm{T})$ cannot be supposed to vanish, it is clear that this term will vanish at infinity in comparison with the other terms in (111), if η has the limiting value given by (112), and therefore that (112) is the limit, at infinity, of the solution of (108).

Of the two arbitrary constants, A and B, the former corresponds to the indeterminateness of the linear scale upon which the nebula is measured, the second to the indeterminateness of the conditions at the inner surface of the nebula. If there is no core, there is only one value of A/B which will give a finite density of matter at the centre of the nebula. Further information as to equilibrium configurations can be found in Professor DARWIN's paper, or in a paper by A. RITTER.*

For our purpose it is sufficient to know that the second term in η vanishes with x for all values of A and B. Hence at infinity

$$y = \frac{\mathrm{V}''}{2\lambda^2\mathrm{T}^2} + \log\frac{\lambda^4\mathrm{T}^4x^2}{2\pi},$$

$$\rho = \frac{e^y}{\lambda\mathrm{T}} = \frac{\lambda^3\mathrm{T}^3x^2}{2\pi}\,e^{\mathrm{V}''/2\lambda^2\mathrm{T}^2} = \frac{\lambda\mathrm{T}}{2\pi r^2}\,e^{\mathrm{V}''/2\lambda^2\mathrm{T}^2},$$

and hence (equation (107))

$$u_\infty = \frac{2\pi\rho r^2}{\lambda\mathrm{T}}\,e^{\mathrm{V}''/2\lambda^2\mathrm{T}^2} = 1 + \frac{\mathrm{V}''}{2\lambda^2\mathrm{T}^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (113).$$

Putting $\mathrm{V}'' = 0$, we arrive at the anticipated result that the stability function has a unit value, for every nebula which extends to infinity in such a way that $\lambda\mathrm{T}$ has a finite limit at infinity.

A Slowly Rotating Nebula.

§ 31. The case which is of the greatest physical interest, is that in which the nebula is not at rest but is rotating in a position of relative equilibrium

Here the arrangement is no longer in spherical shells, so that the foregoing analysis breaks down. If, however, we suppose the rotation ω to be so small that ω^4 may be neglected, it will be easy to modify the foregoing analysis, so as to take account of rotation.

We shall still suppose the nebula to extend to infinity, so that we must not suppose the rotation to be the same at all distances, for in this case a finite value of ω would imply an infinite velocity of those parts of the nebula which are at infinity. Let us

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* 'Wied. Ann.,' vol. 16, p. 166.

suppose that at infinity the linear velocity approximates to a finite limit, so that we may write

$$\omega = \Omega / r$$

for all values of r greater than a certain amount.*

So long as we are only concerned with configurations of equilibrium and vibrations of frequency $p = 0$, the rotation may be allowed for by the introduction of a force of amount $\omega^2 r \sin \theta$ per unit mass, acting perpendicular to the axis of rotation ; or, what comes to the same thing, by the introduction of a potential

$$\tfrac{2}{3}(1 - P_2) \int^r \omega^2 r \, dr,$$

or

$$(1 - P_2) V'$$

where, for all values of r greater than a certain value,

$$V' = \tfrac{2}{3} \Omega^2 \log r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (114).$$

Let us examine separately the two effects arising from the two terms of this potential, beginning with the term $-P_2 V'$. There will in this case be a correction to be applied to all equations, and this correction will consist of the addition of a small term containing $\omega^2 P_2$. Let us suppose that all symbols which have so far denoted functions of r, denote in future the mean value of the corresponding quantities averaged over a sphere of radius r. For instance, ρ is no longer the density at distance r from the centre, but is the mean density over the sphere of radius r. The density at any point will be of the form $\rho + \omega^2 P_2 \rho_2$, where ρ_2 is a function of r. We may in every case equate the coefficients of different harmonics, and by equating the coefficients of terms which do not contain the terms $\omega^2 P_2$, we shall obtain the same equations as were obtained in the case of $\omega = 0$, except that the meaning of every term is altered.

The equations derived from the parts which do not contain ω will suffice, as before, to determine p, so that the values of p are of the same form as before, except that the quantities involved have a slightly different meaning. Hence the stability criterion is still given by the value of the stability function u_∞ ; while equation (107)

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* This particular law is chosen for examination because it leads most quickly to the required result. The case in which ω vanishes at infinity more rapidly than $1/r$ is covered by taking $\Omega = 0$. Here, however, the angular momentum vanishes in comparison with the mass, and it is not surprising to find that a rotation of this kind does not affect the question of stabitity. The case in which ω vanishes less rapidly than $1/r$ is physically impossible, since it gives an infinite linear velocity at infinity, but may be theoretically included in the case of $\Omega = \infty$.

Any special assumption about the value of ω at infinity must, however, disappear when we turn to the case of a finite nebula (§ 26), in which Ω may be appropriately supposed to correspond to the surface velocity ωR_1.

remains true, if the new meaning is given to the symbols in each case. We conclude that the question of stability is not affected by the potential $-\mathrm{P}_2\mathrm{V}'$.

The remaining potential term is the spherically symmetrical term V'. The total potential may now be taken to be $\mathrm{V}+\mathrm{V}'$, and this potential, besides being spherically symmetrical, satisfies the condition which was postulated in the determination of the criterion of stability; namely, that its radial differential coefficient shall vanish at infinity to the order of $1/r$. The value of the derived function V'' (equation (109)) is

$$\mathrm{V}'' = \underset{r=\infty}{\mathrm{L}t}\, \frac{d}{dr}\left(r^2 \frac{d\mathrm{V}'}{dr}\right) = \tfrac{2}{3}\Omega^2, \text{ by equation (114).}$$

Hence the stability function is given by (*cf.* equation (113))

$$u_\infty = 1 + \frac{\Omega^2}{3\lambda^2\mathrm{T}^2}.$$

We have therefore found that when an infinite nebula is rotating, with such angular velocities that the linear velocities at infinity have the limiting value Ω, the value of u_∞ is greater than unity no matter how small Ω may be. This result has only been obtained on the supposition that ω^4 may be neglected. We have obtained no information as to what happens when ω^4 is taken into account, *i.e.*, when the square of the "ellipticity" of the nebula is taken into account.

Influence of Viscosity.

§ 32. No account has so far been taken of the viscosity of the gas. The terms arising from viscosity which may be supposed to occur in the true equations of motion, will contain the coefficient of viscosity (μ), and will in each case depend on velocities and not on displacements. Hence viscosity enters the equations of motion through the factor μip. The vibrations for which $p = 0$ are accordingly unaffected by viscosity, and since it is upon the existence of such vibrations that the whole question of stability turns, it is clear that the results already obtained must remain true even in the presence of viscosity.

It can be shown that equations (24) to (26) specify a principal vibration, whether the gas is viscous or not. The result is stated without proof, as the proof is rather lengthy, and has no bearing upon the main question under discussion.

A Nebula in Process of Cooling.

§ 33. In the mathematical investigation we have been concerned with vibrations about a position of absolute equilibrium. In nature, no such position of absolute equilibrium will occur; the condition of the nebula will be incessantly changing.

Let us suppose the temperature of the nebula to be continually cooling, owing either to radiation of heat from its surface or to a process of quasi-evaporation such as is described in Professor DARWIN's paper (§ 13 or p. 66). Since the gas (or quasi-gas) is not a perfect conductor, the nebula will not at any time be in perfect thermal equilibrium. The changes in density of all parts, and in the temperature of the inner parts of the nebula will, so to speak, lag behind their equilibrium values as determined by the changes in the temperature of the outer part of the nebula. It is, therefore, clear that so long as the nebula is cooling, the ratio of the density to elasticity in the outermost layers of gas will be greater than that calculated upon the assumption of perfect equilibrium. This "lag" accordingly decreases the value of the stability-function, and so supplies a factor which tends to instability.

SUMMARY AND DISCUSSION OF RESULTS.

§ 34. Let us now examine to what extent we have found solutions of the two problems propounded in § 4.

Firstly, as regards the stability of a spherical nebula of very great size, of which the outer surface is maintained at constant pressure. We have found that the stability-function for such a nebula (in the limiting case in which the outer radius is infinite) has a unit value when the nebula is in equilibrium and at rest. This value is increased by allowing for the "lag" in temperature caused by the cooling of the nebula. It is also increased by a rotation of the nebula, at any rate so long as this rotation is small. The nebula will become unstable as soon as the stability-function becomes greater than a certain value, which has not been calculated, but is known to be between 1 and $1\frac{1}{8}$. The investigation of § 23 leads us to expect that the critical value of the stability-function will increase as R_1 decreases, although this has only been strictly proved for a single case.

It is therefore possible that, even when the nebula is non-rotating, the temperature-lag may be sufficient to make the nebula unstable. If we disregard the temperature-lag, it seems probable that a small rotation will suffice to bring about instability. This latter question, however, deserves more detailed examination.

§ 35. Let us suppose that the nebula starts from rest in a configuration of absolute equilibrium, and that the rotation is gradually increased. In this way we obtain a linear series of configurations of relative equilibrium. When the rotation is small, the configuration, instead of being strictly spherical is slightly spheroidal. The series we are considering is therefore the analogue of the series of MACLAURIN spheroids of an incompressible fluid. So long as the rotation remains small, we may separate the two terms of the rotation-potential in the manner explained in § 31. We may, in fact, suppose our analysis still to apply as if the configuration remained spherical, and the only effect of the rotation is to increase the value of the stability-function. For larger values of ω^2, all our results are subject to a correction of the order of ω^4. For small values of ω^2, the value of ω^2 will be proportional as we have seen (§ 31) to $u_\infty - 1$, so that this correction may be supposed to be proportional to $(u_\infty - 1)^2$. The first points of bifurcation of orders 1, 2 occur (in the spherical configuration) at $u_\infty - 1 = \theta$, $2\frac{1}{8}$ respectively, where θ is known to be less than $\frac{1}{8}$. Now it would seem to be fairly safe to neglect θ^2, but even if we waive this point, it will be admitted that the correction of the order of $(u_\infty - 1)^2$ cannot be so great as to change the order in which these two points of bifurcation will occur.

We therefore see that a rotating nebula will become unstable for a comparatively small value of ω^2, the critical vibration being of order $n = 1$. The new linear series is one in which (except for the spheroidal deformation caused by the rotation) the surfaces of equal density remain spheres, which are no longer concentric. The linear series of order $n = 2$ will accordingly be unstable: this is the analogue to the series of Jacobian ellipsoids in the incompressible fluid.

§ 36. The case of a nebula which actually extends to infinity is much simpler. Here the value of u_∞ is again unity, and this value is increased, as before, either by temperature-lag or rotation. Every point at which u_∞ is greater than unity is in one sense a point of bifurcation, since starting from this point there is a series of unsymmetrical equilibrium configurations. Strictly speaking, these points do not indicate an exchange of stabilities, for the critical vibrations remain of frequency $p = 0$ even after passing the point. They possess, however, the property that a critical vibration, if once started, will continue increasing, since the forces of restitution (of whichever sign) vanish in comparison with the momentum of the vibration.

§ 37. Let us now try and examine which of these two hypotheses is best capable of representing the "primitive nebula" of astronomy. Imagine a sphere S drawn in the nebula, the radius being a, and the pressure at this surface π. The matter inside S is to form a spherical nebula of finite extent, bounded by a sphere over which the pressure is π, and this matter is to be of a density sufficient to warrant us in assuming the gas-equations at every point. The surface S will be continually traversed by matter, but this will be of no consequence if the losses and gains balance in every respect. The matter outside S must supply the pressure π, and will also, as was explained in the introduction (§ 3), influence the matter inside S by its motion.

Imagine the matter inside S to be executing a small vibration, and consider two extreme hypotheses as to the behaviour of the matter outside S.

Suppose, in the first place, that the matter outside S is such that it and the matter inside S together form a perfect spherical nebula at rest. Then the motion of the matter outside S is given by the equations of vibration of such a nebula, and the influence of this matter upon that inside S is exactly that required in order to enable the matter inside S to execute the vibrations given by the equations of an infinite nebula.

Suppose, next, that the matter outside S consists mainly of molecules or of masses of matter which are describing hyperbolic or parabolic orbits, or which come from infinity and after rebounding from the nebula return to infinity. Suppose, further, that the interval during which such a mass is appreciably under the influence of the matter inside S is so small that it is not appreciably affected by the motion of the latter. In this case the matter outside S may be regarded as arranged at random, independently of the vibrations of the matter inside S; it will not, as under our first supposition, take up the motion of the matter inside S to any appreciable extent. Hence the matter outside S will exert no force upon that inside S except the constant pressure π, and the vibrations of the matter inside S will be those of a spherical nebula of finite size, bounded by a surface at constant pressure π.

These two extreme hypotheses lead, as we can now see, to the two conceptions of a nebula put forward in § 4. In nature the truth will lie somewhere between these two hypotheses, and it is by no means easy to decide which of the two gives the better representation of an actual nebula. We shall, however, be within the limits of safety if we assert of an actual nebula only those propositions which are true of both our ideal nebulæ.

§ 38. We may accordingly sum up as follows :—

(i.) A nebula at rest and in absolute equilibrium in a spherical configuration will always be stable.

(ii.) Such a nebula may become unstable as soon as the temperature-lag is taken into account.

(iii.) There will be a linear series of configurations of relative equilibrium of a rotating nebula, starting from a non-rotating spherical nebula (supposed stable), and such that the configuration is symmetrical about the axis of rotation. This linear series corresponds to the series of Maclaurin spheroids.

(iv.) The first point of bifurcation on this series occurs for a comparatively small value of the angular rotation.

(v.) The second series through this point is one in which the configurations possess only two planes of symmetry. Initially the configuration is such that the equations to the surfaces of equal density contain only terms in the first harmonic in addition to those required by the angular rotation.

(vi.) There is a linear series which corresponds to the series of Jacobian ellipsoids, each configuration possessing three planes of symmetry. The point of bifurcation at which this series meets the series mentioned in (iii.) is a point at which the angular rotation is much larger than that at the point of bifurcation mentioned in (iv.).

(vii.) This latter linear series appears to be always unstable.

The Unsymmetrical Configurations of a Nebula.

The Second Series of Equilibrium Configurations.

§ 39. Let us now try to examine the second series of equilibrium configurations, which, as we have seen, is a series of stable configurations replacing the series of Jacobian ellipsoids. In this way we shall be able to gather some evidence with a view to forming a judgment whether the behaviour of the nebula after leaving the symmetrical configuration is such as is required by the nebular hypothesis.

Let us suppose, in the first instance, that the symmetrical configuration from which this series starts is one in which there is no rotation, so that the configuration is one of perfect spherical symmetry. If the nebula is one in which cooling takes place very slowly, the configuration of the nebula will always be very approximately an equilibrium configuration. This configuration will be one of the spherically symmetrical series until the first point of bifurcation is reached; after this the configuration will change so as to move along the other series, which passes through this point.

Now we have already found the manner in which the configuration first diverges from spherical symmetry; in other words, we have a knowledge of the unsymmetrical series in the immediate neighbourhood of the point of bifurcation. If then, we can, by some method of continued approximation, obtain a more extended knowledge of this series of configurations, we shall be able to trace the motion of a nebula which is cooling with infinite slowness, and in this way form some idea of the motion to be expected in the more general case.

Let us assume, as a general form for the "series" now under discussion,

$$\rho = \rho_0 + \rho_1 \mathrm{P}_1 + \rho_2 \mathrm{P}_2 + \rho_3 \mathrm{P}_3 + \dots \quad . \quad . \quad . \quad . \quad . \quad . \quad (115),$$

where P_s is the zonal harmonic of order s, and ρ_0, ρ_1, ρ_2 are functions of r and of some parameter a. This parameter determines the position of any particular configuration in the series. We shall suppose that at the point of bifurcation $a = 0$, and we then know that when a is very small the limiting form of ρ is

$$\rho = \rho_0 + \rho_1 \mathrm{P}_1.$$

In the notation which has been in use throughout the paper, we find that corresponding to the density distribution given by equation (72) the gravitational potential at the point r, θ is

$$\mathrm{V} = \theta_0 + \theta_1 \mathrm{P}_1 + \theta_2 \mathrm{P}_2 + \theta_3 \mathrm{P}_3 + \dots \quad . \quad . \quad . \quad . \quad . \quad . \quad (116),$$

where

$$\theta_s = \frac{4\pi}{2s+1} \left\{ \frac{1}{r^{n+1}} \int_{\mathrm{R}_0}^{r} \rho_s r^{n+2}\, dr + r^n \int_{r}^{\mathrm{R}_1} \frac{\rho_s\, dr}{r^{n-1}} \right\} \quad . \quad . \quad . \quad . \quad . \quad (117).$$

The functions $\rho_1, \rho_2 \ldots$ are to be determined from the condition that V and ρ shall satisfy the three equations of equilibrium, which are of the form

$$\frac{1}{\rho}\frac{d\varpi}{dx} = \frac{dV}{dx}.$$

An Isothermal Nebula.

§ 40. Let us suppose, for the sake of simplicity, that the nebula is at uniform temperature, and extends from $r = 0$ to $r = \infty$. We have already seen (equation (77)) that the critical vibration for a nebula initially isothermal, is one in which the nebula remains isothermal. Hence it follows that if a nebula changes its configuration through coming to a point of bifurcation, when moving on a series of isothermal and spherical configurations, then the new series will also be one in which the equilibrium is isothermal.

We may now write $\varpi = \kappa\rho$, where κ is a constant, and the three equations of equilibrium become equivalent to the single equation,

$$\kappa \log \rho = V + c,$$

or

$$\rho = e^{\frac{V+c}{\kappa}} \quad \ldots \ldots \ldots \ldots \quad (118).$$

Now the series in question is, as we have seen, approximately represented, near to the point of bifurcation, by taking only two terms of (115), and consequently only two terms of (116). In this case equation (118) becomes:

$$\rho_0 + \rho_1 P_1 = e^{\frac{\theta_0 + c}{\kappa}} \left\{1 + \frac{\theta_1}{\kappa} P_1 + \tfrac{1}{2}\left(\frac{\theta_1}{\kappa} P_1\right)^2 + \ldots\right\} \quad \ldots \quad (119).$$

Equating coefficients, we find that ρ_0 is given by the equation

$$\rho_0 = e^{\frac{\theta_0+c}{\kappa}},$$

the same equation as in the case of perfect spherical symmetry. Also ρ_1 is given by the equation

$$\rho_1 = \frac{\rho_0}{\kappa}\theta_1.$$

It will be easily verified that this equation is exactly equivalent to our former equation (38). The equation contains an arbitrary multiplier in its solution. This may be taken to be a, the parameter of the series, so that we may write

$$\rho_1 = a\sigma_1,$$

where σ_1 is a completely determined function of r. Thus, as far as a, the solution is seen to be

$$\rho = \rho_0 + a\sigma_1 P_1.$$

We shall now show that, as far as a^2, the solution is

$$\rho = \rho_0 + a^2\sigma_{02} + a\sigma_1 P_1 + a^2\sigma_2 P_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (120).$$

The substitution of this in equation (118) leads to

$$\rho_0 + a^2\sigma_{02} + a\sigma_1 P_1 + a^2\sigma_2 P_2$$
$$= e^{\frac{\theta_0+c}{\kappa}}\left\{1 + \frac{a\phi_1}{\kappa}P_1 + \tfrac{1}{2}\left(\frac{a\phi_1}{\kappa}P_1\right)^2 + \ldots + \frac{a^2\phi_2}{\kappa}P_2 + \ldots + \frac{a^2\phi_{02}}{\kappa} + \ldots\right\},$$

where ϕ_1 stands in the same relation to σ_1 as does θ_1 to ρ_1. The right-hand member of this equation is equal to

$$e^{\frac{\theta_0+c}{\kappa}}\left\{1 + \tfrac{1}{6}\frac{a^2\phi_1{}^2}{\kappa^2} + \frac{a^2\phi_{02}}{\kappa} + \frac{a\phi_1}{\kappa}P_1 + \left(\frac{a^2\phi_2}{\kappa} + \tfrac{1}{3}\frac{a^2\phi_1{}^2}{\kappa^2}\right)P_2 + \ldots\right\},$$

in which the unwritten terms are of degree at least equal to 3 in a.

Neglecting a^3 the equation is satisfied if

$$\rho_0 = e^{\frac{\theta_0+c}{\kappa}}, \quad \sigma_{02} = \rho_0\left\{\tfrac{1}{6}\frac{\phi_1{}^2}{\kappa^2} + \frac{\phi_{02}}{\kappa}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (121),$$

$$\sigma_1 = \frac{\rho_0\phi_1}{\kappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (122),$$

$$\sigma_2 = \frac{\rho_0\phi_2}{\kappa} + \tfrac{1}{3}\frac{\rho_0\phi_1{}^2}{\kappa^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (123).$$

These equations determine σ_{02} and σ_2 uniquely.

It is obvious that this method is capable of indefinite extension, and that the general form of configuration in the series will be given by

$$\rho = \rho_0 + a^2\sigma_{02} + a^4\sigma_{04} + \ldots + (a\sigma_1 + a^3\sigma_{13} + a^5\sigma_{15} + \ldots)P_1$$
$$+ (a^2\sigma_2 + a^4\sigma_{24} + \ldots)P_2 + (a^3\sigma_3 + a^5\sigma_{35} + \ldots)P_3 + \&c. \quad . \quad (124).$$

§ 41. Let us examine in greater detail the solution as far as a^2, this being given by equation (115). The important question, as will be seen later, is the determination of the sign of σ_2. We therefore pass at once to the consideration of equation (123). Written out in full, this becomes

$$\sigma_2 = \frac{4\pi\rho_0}{5\kappa}\left\{\frac{1}{r^3}\int_0^r \sigma_2' r'^4\,dr' + r^2\int_0^r \frac{\sigma_2'}{r'}\,dr'\right\} + \tfrac{1}{3}\frac{\rho_0\phi_1{}^2}{\kappa^2}.$$

This equation may be transformed in the same way as equation (39). If we write

$$y = \frac{\kappa r}{\rho_0}\left(\sigma_2 - \tfrac{1}{3}\frac{\rho_0 \phi_1^2}{\kappa^2}\right),$$

we find that the above equation is equivalent to (*cf.* equations (47), (48), (49), (54), (56))

$$\frac{d^2 y}{dr^2} - \frac{6y}{r^2} = -4\pi\sigma_2 r = -\frac{4\pi\rho_0}{\kappa}\left\{y - \frac{r\phi_1^2}{3\kappa}\right\} \quad . \quad . \quad . \quad . \quad . \quad (125),$$

together with the two equations

$$\left[\frac{1}{r^2}\frac{d}{dr}(yr^2)\right]_{r=\infty} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (126),$$

$$\left[r^3 \frac{d}{dr}(yr^{-3})\right]_{r=0} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (127).$$

Writing

$$u = \frac{2\pi\rho_0 r^2}{\kappa},$$

equation (119) becomes

$$\frac{d^2 y}{dr^2} - \frac{y}{r^2}(6 - 2u) = -\frac{r\rho_0\phi_1^2}{3\kappa^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (128).$$

Referring to the table of values for u, which will be found on p. 15 of Professor DARWIN's paper, it appears that u increases from a zero value at the origin up to a maximum value of about 1·66; it then decreases to a minimum of about ·8, and after this increases to 1, its value at infinity. Thus the factor $6 - 2u$ has a range of values from 6 to about $2\frac{2}{3}$.

Now the solution of

$$\frac{d^2 y}{dr^2} - \frac{y}{r^2} n(n+1) = -\frac{r\rho_0\phi_1^2}{3\kappa^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (129)$$

is easily found to be

$$y = \frac{4\pi r}{2n+1}\left\{\frac{1}{r^{n+1}}\int_0^r \frac{\rho_0\phi_1^2}{3\kappa^2} r'^{n+2}\, dr' + r^n \int_r^\infty \frac{\rho_0\phi_1^2}{3\kappa^2 r'^{n-1}}\, dr'\right\} + C_1 r^{-n} + C_2 r^{n+1} \quad . \quad (130),$$

in which C_1 and C_2 are constants of integration, which may at once be put equal to zero, if n is positive, and if y is to satisfy conditions (126) and (127).

Comparing (128) with (129), we see that if u had a constant value u_0 at every point of the nebula, the value of y would be given by equation (130), in which C_1, C_2 would be put equal to zero, and n would be the positive root of

$$n(n+1) = 6 - 2u_0,$$

provided only that $6 - 2u_0$ were positive.

For the range of values for u_0 from $u_0 = 0$ to $u_0 = 1{\cdot}66$, the value of n would have a range of values from 2 to 1·2. Thus the form of solution is materially the same for all of these values of u_0. It will be seen without difficulty that the solution of (128), in which u has not a constant value, but varies over the range from 0 to 1·66 as r varies, will be such that the graph expressing y as a function of r will present the same features as are common to the graphs given by equation (130) for ranges of n from 2 to 1·2.

Now the value of y given by equation (130) is positive for all values of r, hence we infer that the solution of (128) is such that y is positive for all values of r. We therefore have, for all values of r,

$$\sigma_2 = \tfrac{1}{3}\frac{\rho_0\phi_1^2}{\kappa^2} + \text{a positive quantity},$$

so that σ_2 is positive for all values of r.

§ 42. We therefore see that the initial motion, in which u and Δ are each proportional to the first harmonic, will first break down owing to the introduction of terms involving the second harmonic. The sign of these terms is such that there is, in all the shells of which the nebula is composed, a diminution of density in the equatorial regions, and a condensation at both poles, which must be added to that given by the terms involving the first harmonic.

The nature of this motion will become clearer upon a reference to fig. 3. This figure consists of the four curves*

$$r = a_0 \qquad r = a_0 + a_1 \mathrm{P}_1$$

$$r = a_0 + a_{11}\mathrm{P}_1 + a_2\mathrm{P}_2 \qquad r = a_0 + a'_{11}\mathrm{P}_1 + a'_2\mathrm{P}_2,$$

and these may be supposed to represent curves of equal density in the three stages. It is easy to see that of the pear-shaped surfaces of equal density, the equations of which contain the two first harmonics, some will be turned in one direction, and some in the other. For if they were all turned in the same direction the centre of gravity could no longer remain at the centre of co-ordinates. Thus, if the narrow ends of these pear-shaped figures point in one direction at infinity, we must, as we go inwards, come to a place at which they have the transition shape, namely, ellipsoids of revolution, and after this they will point in the opposite direction.

It appears, therefore, that the initial motion is such as to suggest the ultimate division of the nebula into two parts, this division being effected by the outer layers condensing about one radius of the nebula, so as to leave room for the ejection of a

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* The particular values for which the curves are drawn are in the ratio $a_0 = 11$, $a_1 = 2$, $a_{11} = 5$, $a_2 = 2$, $a'_{11} = 7$, $a'_2 = 4$. Thus the equation of the last curves are in polar co-ordinates,

$$r = \frac{a_0}{11}(10 + 5\cos\theta + 3\cos^2\theta), \qquad r = \frac{a_0}{11}(9 + 7\cos\theta + 6\cos^2\theta).$$

central nucleus in the direction of the opposite radius. Whether or not actual separation takes place would probably depend on the amount of the angular velocity.

It is of interest to compare the result just arrived at, with the corresponding result found by POINCARÉ for the motion when an ellipsoid of JACOBI first becomes unstable.* This is described as follows :—

"La plus grande portion de la matière semble se rapprocher de la forme sphérique, tandis que la plus petite portion de cette même matière sort de l'ellipsoïde par l'extremité du grand axe, comme si elle voulait se séparer de la masse principale."

Thus, although the initial motions are, since they start from different configurations, necessarily different, yet it would seem as if the final result was very much the same in the two cases. In either case we have a diminution of matter in the equatorial regions, suggesting the ultimate division of the mass into two, and in each case these two masses are of unequal size, a result which could hardly have been foreseen without analysis.

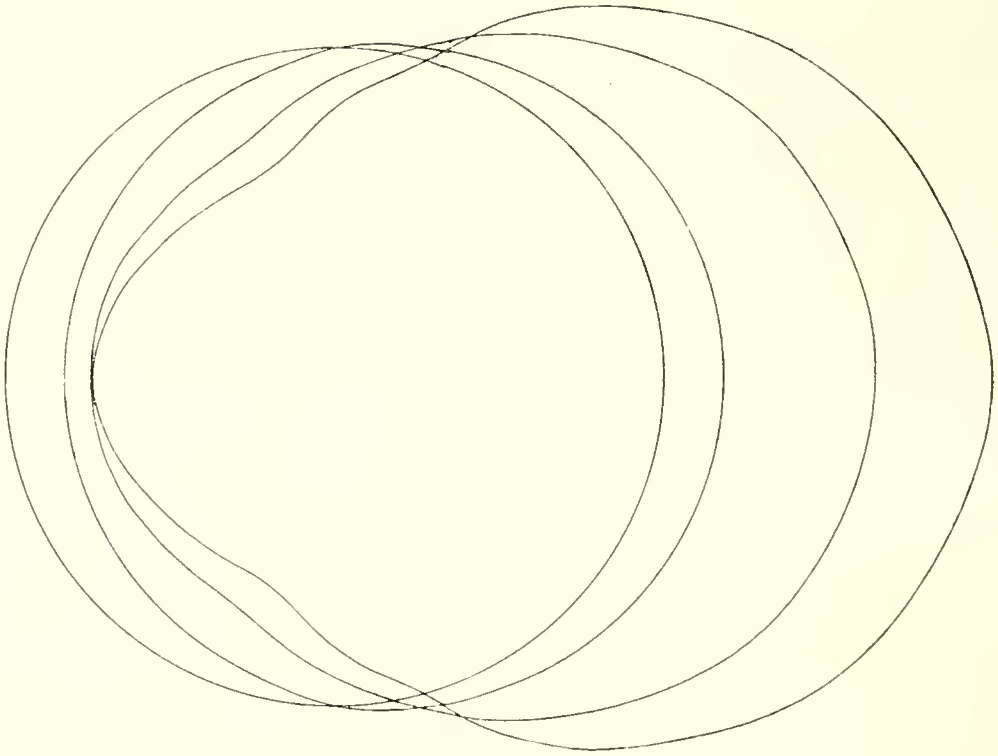

Fig. 3.

§ 43. If the rate of cooling of a nebula is appreciable, the motion will not be along a "series" of equilibrium configurations. The value of p, the frequency which is nearest to instability, will be changing at a finite rate, and may run to some distance beyond the zero value, before the deviation of the nebula from the spherical shape is sufficient to invalidate the analysis of our paper. In this case we can imagine the first unstable vibration, that for which $p = 0$, being overtaken by other unstable vibrations of greater and greater frequency, the corresponding velocity of divergence

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* 'Acta Mathematica,' vol. 7, p. 347.

from spherical symmetry becoming continually greater. It is therefore quite conceivable that the motion may become adiabatic at an early stage, and it is possible that it may be better imagined as a collapse or explosion, rather than as a gradual slipping from a spherical state of equilibrium into and through a series of unsymmetrical states of equilibrium.

But an examination of the physical character of the motion will show that in this extreme case, as also in any intermediate case, the motion must be, in its essentials, the same as that which has been found for the other extreme case, namely, that of infinitely slow cooling and perfect thermal equilibrium. In the spherical state, the outermost layers of gas may be regarded as stretched out in opposition to their gravitational attractions, being maintained in this state by the elasticity of the gas. The balance between these two agencies (which is, speaking loosely, measured by the stability function, u_∞) must be supposed to be continually changing, and instability always results from the same cause, namely, that the elasticity of these outer layers becomes inadequate to resist the gravitational tendency to collapse. In every case the outer layers concentrate about a single radius of the nebula, the axis of harmonics ($\theta = 0$ in equation (72)) and so increase the pressure along this radius, while decreasing that along the opposite radius ($\theta = \pi$). This pressure acting upon the inner layers of gas and the core sets them in motion, and in this way we have the tendency to separation into two nebulæ.

A Nebula in "Isothermal-adiabatic" Equilibrium.

§ 44. A nebula which consists of an isothermal nucleus with a layer in convective equilibrium above it, is said to be in "isothermal-adiabatic" equilibrium. At the surface at which the law changes from the adiabatic to the isothermal, the quantities ϖ, T and ρ must all be continuous.

The isothermal part is capable of executing a vibration of frequency $p = 0$ while remaining in isothermal equilibrium throughout, provided the forces acting upon it from the adiabatic part are the same as would act if the adiabatic part were replaced by an isothermal part in such a way that the whole made up an infinite isothermal nebula. If the nebula is rotating, the amplitude of vibration of the infinite nebula will vanish at infinity proportionally to some inverse power of r, this power increasing with the rotation. For sufficiently large rotations, the vibrations may be regarded as inappreciable except over the original isothermal nucleus, so that the vibration is approximately unaltered when the outer layers are again replaced by layers in convective equilibrium.

We see, therefore, that an "isothermal-adiabatic" nebula may become unstable, for sufficiently large rotations, through a vibration of order $n = 1$. No attempt is made to obtain any numerical results. We can, however, follow up the subsequent motion in the same way as in the case of an isothermal nebula.

Over the part of the nebula which is in adiabatic equilibrium, the relation between density and pressure is

$$\varpi = c\rho^{\gamma},$$

where c is a constant, so that the equations of equilibrium become

$$c\gamma\rho^{\gamma-2}\frac{d\rho}{dx} = \frac{dV}{dx}, \text{ \&c.},$$

and are therefore equivalent to the single equation

$$\frac{c\gamma}{\gamma-1}\rho^{\gamma-1} = V - V_0,$$

where V_0 is the potential of the outer boundary of the nebula. This takes the form

$$V - V_0 = \frac{c\gamma\rho_0{}^{\gamma-1}}{\gamma-1}\left\{1 + (\gamma-1)\frac{\rho_1}{\rho_0}P_1 + \frac{(\gamma-1)(\gamma-2)}{2}\left(\frac{\rho_1}{\rho_0}P_1\right)^2 + \ldots\right.$$
$$\left. + (\gamma-1)\frac{\rho_2}{\rho_0}P_2 + \ldots\right\},$$

or,

$$\theta_0 - V_0 + \theta_1 P_1 + \theta_2 P_2 + \ldots = \frac{c\gamma\rho_0{}^{\gamma-1}}{\gamma-1}\left\{1 + \frac{(\gamma-1)(\gamma-2)}{6}\left(\frac{\rho_1}{\rho_0}\right)^2\right.$$
$$\left. + (\gamma-1)\frac{\rho_1}{\rho_0}P_1 + \left((\gamma-1)\frac{\rho_2}{\rho_0} + \frac{(\gamma-1)(\gamma-2)}{3}\left(\frac{\rho_1}{\rho_0}\right)^2\right)P_2 + \ldots\right\}.$$

It is obvious that equation (124) again gives the general form of solution, and that, as far as a^2, the equations are (*cf.* equations 121, 123)

$$\theta_0 - V_0 = \frac{c\gamma\rho_0}{\gamma-1} \quad \ldots \ldots \quad (131),$$

$$\phi_1 = c\gamma\rho_0{}^{\gamma-1}\left(\frac{\sigma_1}{\rho_0}\right) \quad \ldots \ldots \quad (132),$$

$$\phi_2 = c\gamma\rho_0{}^{\gamma-1}\left\{\frac{\sigma_2}{\rho_0} + \tfrac{1}{3}(\gamma-2)\left(\frac{\sigma_1}{\rho_0}\right)^2\right\} \quad \ldots \ldots \quad (133),$$

$$\phi_{02} = \frac{c\gamma(\gamma-2)}{6}\rho_0{}^{\gamma-1}\left(\frac{\sigma_1}{\rho_0}\right)^2 \quad \ldots \ldots \quad (134).$$

Writing κ for $c\gamma\rho_0{}^{\gamma-1}$, we see that equations (132) and (133) may be written

$$\sigma_1 = \frac{\rho_0\phi_1}{\kappa} \quad \ldots \ldots \quad (135).$$

$$\sigma_2 = \frac{\rho_0\phi_2}{\kappa} + \tfrac{1}{3}(2-\gamma)\frac{\sigma^2}{\rho_0\kappa} \quad \ldots \ldots \quad (136).$$

These are equations similar to (122) and (123); the last term in (136) is different from the last term in (123), but both terms agree in being invariably positive. Hence it appears that the question of the sign of σ_2 turns, as in § 37, upon the sign of the factor $(6 - 2u)$. We can no longer actually evaluate this factor, as in § 37, but it seems to be safe to infer from analogy that it will be positive at every point, and this in turn shows that σ_2 must be positive at every point. Hence it appears probable that the motion will be that described in § 38.

Rotating Nebula.

§ 45. The equations of an unsymmetrical series starting from a symmetrical configuration in which there is a finite amount of rotation would be extremely complicated, and no attempt to handle them is made in this paper. The correction for a small rotation will clearly consist merely of an increase in the terms containing the second harmonic, so that the general shape of the curves will be similar to that of the last two curves of fig. 3.

Little difficulty will be experienced in imagining the shape of curves appropriate to larger rotations.

PROBLEMS OF COSMIC EVOLUTION.

Infinite Space filled with Matter.

§ 46. A limiting solution of the equations of equilibrium (corresponding to $A = \infty$, $B = \infty$ in equation (114)) gives a nebula in which the density is constant everywhere. This solution may be supposed to represent infinite space filled with matter distributed at random. If space has no boundary there is presumably no need to satisfy a boundary-equation at infinity, so that ρ may have any value; if, however, this equation must be satisfied the only solution is $\rho = 0$.

Let us consider the former case. Space is filled with a medium of mean density ρ and of mean temperature T. Since the space under consideration is infinite, we may measure linear distances on any scale we please, and, by taking this scale sufficiently great, we can cause all irregularities in density and temperature to disappear. We may, therefore, suppose at once that the density and temperature have the constant values ρ and T.

The equations of motion for small displacements referred to rectangular axes are, in the old notation (*cf.* § 6), since V_0 and ϖ_0 are constants,

$$\frac{d^2\xi}{dt^2} = \frac{dV'}{dx} - \frac{1}{\rho_0}\frac{d\varpi'}{dx}, \text{ \&c.,} \qquad \ldots \ldots \ldots \qquad (137),$$

or, operating with d/dx, d/dy, d/dz, and adding

$$\frac{d^2\Delta}{dt^2} = \nabla^2 V' - \frac{1}{\rho_0} \nabla^2 \varpi' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (138).$$

Since V′ is the gravitational potential of a distribution of density $-\Delta\rho$ (*cf.* § 6), we have

$$\nabla^2 V' = 4\pi\Delta\rho, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (139),$$

while if we suppose, for the sake of simplicity, that the motion is adiabatic, so that the ratio of pressure to density changes at a constant rate κ, we have (*cf.* equation (3), p. 5)

$$\nabla^2 \varpi' = \kappa \nabla^2 \rho' = -\kappa\rho_0 \nabla^2 \Delta.$$

Hence equation (138) becomes

$$\frac{d^2\Delta}{dt^2} - 4\pi\rho\Delta - \kappa\nabla^2\Delta = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (140).$$

The simplest solution of this is of the form

$$\Delta = \frac{1}{r} e^{i(pt \pm qr)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (141),$$

where

$$q^2 = \frac{p^2 + 4\pi\rho}{\kappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (142),$$

and the general solution can be built up by superposition of such solutions.

Now solution (141) gives $\Delta = 0$ at infinity, provided q is real, and therefore provided $p^2 + 4\pi\rho$ is positive, a condition which admits of p being imaginary. There is therefore a possible motion, which consists of a concentration of matter about some point, the amount of this concentration vanishing at infinity, and the amount at any point increasing, in the initial stages, exponentially with the time.

We conclude, therefore, that a uniform distribution in space will be unstable, independently of the mean temperature or density of this distribution.*

The Evolution of Nebulæ.

§ 47. We can also see that a distribution of matter which is symmetrical about a single point will be equally unstable. For, if this distribution of matter were perfectly

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* An interesting field of speculation is opened by regarding the stars themselves as molecules of a quasi-gas. If space were Euclidean and unbounded, there would be no objection to this procedure, and we should be led to the conclusion that the matter of the universe must become more and more concentrated in the course of time. If space is non-Euclidean, this concentration might reach a limit as soon as the coarsegrainedness of the structure attained a value so great that the distance between individual units became comparable with the radii of curvature of space. In any case, it may reach a limit as soon as an appreciable fraction of the space in question becomes occupied by matter.

homogeneous, the whole mass of matter would form a spherical nebula of literally infinite extent, and would therefore be in neutral equilibrium. The introduction of even the smallest irregularities into this structure is equivalent to the application ot an external field of force. This, as has already been seen, will destroy the spherical symmetry, and it can easily be seen that the motion from spherical symmetry is such as to lead to a concentration of matter about points of maximum density.

It appears, therefore, that the configuration which will naturally be assumed by an infinite mass of matter in the gaseous or meteoritic state consists of a number of nebulæ (*i.e.*, clusters round points of maximum density). We may either suppose the outer regions of these nebulæ to overlap, each nebula satisfying the gas-equations by being of infinite extent, or we may suppose the nebulæ to be distinct and of finite size, the interstices being filled by meteorites or other matter, which by continual bombardment upon the surfaces of the nebulæ supply the pressure which is required at these surfaces by the equations of equilibrium.

§ 48. What, we may inquire, will determine the linear scale upon which these nebulæ are formed? Three quantities only can be concerned: γ the gravitational constant, ρ the mean density, and λT the mean elasticity. Now these quantities can combine in only one way so as to form a length, namely, through the expression

$$\sqrt{\frac{\lambda T}{\gamma\rho}},$$

of which the dimensions will be readily verified to be unity in length, and zero in mass and time. We conclude, then, that the distance between adjacent nebulæ will be comparable with the above expression.

Now the value of γ is 65×10^{-9}, and if we assume the primitive temperature to be comparable with 1000° (absolute) we may take $\lambda T = 10^9$ (corresponding accurately to an absolute temperature of 350° for air, 2800° for hydrogen). If we take the sun's diameter as a temporary unit of length, the earth's orbit is (roughly) of diameter 200. If we suppose the fixed stars to be at an average parallactic distance of $0{\cdot}5''$ apart, measured with respect to the earth's orbit, we find for their mean distance apart, about 4×10^7 sun's radii. The density of the sun being, in C.G.S. units, roughly equal to unity, we may, to the best of our knowledge, suppose the mean density of the primitive distribution of matter to be about $(4 \times 10^7)^{-3}$, or say 10^{-23}. Substituting these values for γ, λT and ρ, we find as the scale of length a quantity of the order ot $10^{19\cdot 5}$ centims. The distance which corresponds to a parallax of $0{\cdot}5''$ would be about $10^{18\cdot 6}$ centims. It will therefore be seen that we are dealing with distances which are of the astronomical order of magnitude.

The Evolution of Planetary Systems.

§ 49. Let us now regard a single centre, together with the matter collected round it, as the spherical nebula which is the subject of discussion. On account of the way in which it has been formed, this nebula will, in general, be endowed with a certain amount of angular momentum. We have seen that a primitive nebula of this kind may be supposed, under certain conditions, to become unstable. We have also seen that the motion, when the nebula becomes unstable, is such as to strongly suggest the ejection of a satellite.

As a nebula cools the rotation increases, owing to the contraction of the nebula, and Ω also increases. Thus the quantity $\Omega^2/3\lambda^2 T^2$, which measures the rotational tendency to instability, has a double cause of increase; firstly owing to the increase in Ω, and secondly owing to the decrease in T. We can accordingly imagine the primitive nebula becoming unstable time after time, throwing off a satellite each time.

In the usually accepted form of the nebular hypothesis, the rotation is supposed to be the sole cause of instability, so that the system resulting from a single nebula ought theoretically to be entirely symmetrical about an axis. On the view of the present paper, there is no reason for expecting this symmetry. For large rotations of the primitive nebula, the configuration of the resultant planetary system will approximate to perfect symmetry, but for small rotations, a slight irregularity occurring at the critical moment, at a point out of the equatorial plane, may produce a satellite of which the orbit is far removed from the equatorial plane.

In conclusion, two particular cases of "irregularities" may be referred to. If the nebula is penetrated by a wandering meteorite, at a moment at which it is close to a state of instability, the presence of the meteorite will constitute an irregularity, and may easily result in the formation of a satellite. And if a quasi-tide is raised in the nebula by the presence of a distant mass, the same result may be produced. In the former case, the plane of the satellite would, if the rotation is sufficiently small, be largely determined by the path of the meteorite; in the second case, by the position (or path) of the attracting mass. It would not, in either case, depend much upon the axis of rotation of the nebula.

CONCLUSION.

§ 50. To sum up, it appears that the behaviour of a gaseous nebula differs in at least two important respects from that of an incompressible liquid. In the first place, it differs as regards the amount of rotation which is required to produce instability, and, in the second place, it differs as regards the disposition of the orbits of the planets which will be formed out of the primitive nebula. It will be noticed that no definite numerical results have been obtained; my aim has been to obtain qualitative rather than quantitative results, so as to show, if possible, that the results to be expected for a gaseous nebula are of so much more general a kind than those usually inferred from the analogy of a liquid mass, that no difficulty need be experienced in referring existent planetary systems to a nebular or meteoritic origin, on the ground that the configurations of these systems are not such as could have originated out of a rotating mass of liquid.

In conclusion, I wish to express my indebtedness to Professor DARWIN for much assistance which I have received from him throughout the course of my work.

INDEX SLIP.

Callendar, Hugh L.—Continuous Electrical Calorimetry.
Phil. Trans., A, vol. 199, 1902, pp. 55–148.

Calorimetry—Continuous Electrical Method.
Callendar, Hugh L. Phil. Trans., A, vol. 199, 1902, pp. 55–148.

Conductivity of Liquid—Electrical Method of Measurement.
Callendar, Hugh L. Phil. Trans., A, vol. 199, 1902, pp. 55–148.

Current—Absolute Measurement by Electrodynamometer.
Callendar, Hugh L. Phil. Trans., A, vol. 199, 1902, pp. 55–148.

Specific Heat of Water—Variation determined by Electrical Method.
Callendar, Hugh L. Phil. Trans., A, vol. 199, 1902, pp. 55–148.

Thermometry—Compensated Box for Electrical Thermometry.
Callendar, Hugh L. Phil. Trans., A, vol. 199, 1902, pp. 55–148.

II. *Continuous Electrical Calorimetry.*

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TABLE OF CONTENTS.

PART I.—INTRODUCTION.

PART II.—ELECTRICAL MEASUREMENTS.

A. *Potential.*

B. *Resistance.*

C. *Current.*

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(313.) 11.8.02

Part III.—Electrical Thermometry.

Part IV.—Calorimetry.

Part V.—Discussion of Results.

List of Illustrations.

PART I.—INTRODUCTION.

(1.) *General Account of the Origin and Progress of the Investigation.*

THE method of Continuous Electrical Calorimetry, described in the following paper, was originally devised as part of a Fellowship Dissertation on applications of the platinum thermometer, at Trinity College, Cambridge, in the year 1886, but, on account of unforeseen difficulties, the experiments did not at that time get beyond the preliminary stage. In the first rough apparatus, a steady flow of water, passing through a tube about 30 centims. long and 3 millims. in diameter, was heated by an electric current in a fine spiral of platinum wire of about 5 ohms resistance, nearly fitting the tube. The steady difference of temperature between the inflow and the outflow was measured by a pair of delicate mercury thermometers, which it was of course intended to replace in the final apparatus by a differential pair of platinum thermometers. The electrical energy supplied was measured by the potentiometer method in terms of a set of 5 Clark cells and a large German-silver resistance of 5 ohms in series with the platinum spiral. The potentiometer was specially made for the work, and consisted of a metre slide-wire, and ten resistances, each equal to the slide-wire, for extending the scale so as to secure sufficient accuracy of reading. This potentiometer was still in existence at the Cavendish Laboratory in 1893. The set of 5 Clark cells were tested by GLAZEBROOK and SKINNER ('Phil. Trans.,' A, 1892), and were still in good condition at a later date. The external heat-loss in these experiments was found to be much larger than had been anticipated, and so variable that the results were of little or no value. In order to remedy this defect, I designed the vacuum-jacket, which was suggested by some experiments of Sir WILLIAM CROOKES ('Roy. Soc. Proc.,' vol. 31, 1881, p. 239), which appeared to indicate that the rate of cooling of a mercury thermometer in a very good vacuum was ten to twenty times less than in air. I therefore regarded the vacuum-jacket as a most essential part of the experiment, and expected a great improvement to result from its use. Unfortunately I failed to make the jacket for want of sufficient skill in glass-work, and abandoned the experiment for the time, until my appointment as Professor of Physics at McGill College, Montreal, gave me greater facilities for carrying out the work. Eventually it proved that the effect of the vacuum-jacket in diminishing the external loss of heat was not nearly so great as I had been led to imagine, but it possessed several advantages as a heat insulator over such materials as cotton wool or flannel. The thermal capacity of a vacuum being negligible, the time required for attaining a steady state was much shortened. Moreover there was no risk of error from damp, which is the worst drawback of ordinary lagging.

I had not originally intended to employ the electrical method for determining the *variation* of the specific heat of water, but only for comparing the electrical and thermal units at ordinary temperatures. In the meantime the work of GRIFFITHS, with which I was intimately acquainted, had shown that the electrical units were probably in error, and appeared to indicate a smaller rate of variation of the specific heat than that given by ROWLAND. In reconsidering the problem, in 1893, I therefore determined to attempt the absolute measurement of the ohm and the Clark cell, in addition to the variation of the specific heat of water over as wide a range as possible. The method of steady-flow calorimetry appeared to be particularly adapted to the latter object, as it afforded much greater facility than that of GRIFFITHS or ROWLAND in varying the conditions of experiment over a wide range. For the absolute measurement of the ohm, I immediately obtained estimates for a Lorenz apparatus of Professor V. JONES' pattern, which was eventually ordered in October, 1894, and is briefly described in Section 6 of this paper. For the absolute measurement of the Clark cell in terms of the ohm, after spending some time in designing various forms of electrodynamometer, I decided to employ the British Association pattern, with certain modifications, which are explained below, Sections 10 to 16. At the same time I commenced a series of investigations into the defects of the form of Clark cell described in the Board of Trade Memorandum, in which I was assisted by Mr. H. T. BARNES. This work included an accurate determination of the variation of the E.M.F. with temperature and with strength of solution, in addition to measurements of the solubility of zinc sulphate and of the density of its solutions. It extended further than I had at first anticipated, and was not completed till the summer of 1896. The results were published in the 'Proceedings of the Royal Society,' vol. 62, pp. 117–152.

In the meantime I had been engaged, during the winter of 1895 and the summer of 1896, in testing various methods of temperature regulation, and in studying the theory of the flow of water in fine tubes under the conditions presented by the proposed method of calorimetry. This was a most important part of the work, as the determination of the variation of the specific heat over a large range of temperature exacted great accuracy of regulation, and close attention to details of design. The method of regulation and circulation finally adopted may appear very simple and obvious, but it was not reached without considerable expenditure of time and thought. The experiments on the flow of water heated by an electric current (Section 33) threw some light on the causes of failure of the rough preliminary experiments, and supplied the data necessary for the design of the glass-work of the calorimeter and vacuum-jacket, which was ordered of Messrs. MÜLLER, in Bonn, early in October, 1896.

At this stage of the investigation, finding that I should not have sufficient leisure during the work of the session to carry out the research single-handed, as I had at first intended, I secured the assistance of Mr. BARNES, who had already proved his ability in the making and testing of Clark cells. Our first experiments were made on mercury, which, being itself a conductor of electricity, presented fewer difficulties than water. The water apparatus was fitted up and tested shortly before the meeting of the British Association, in 1897, but it was at that time incomplete in certain important details, and only three sets of observations, at 5°, 25°, and 45°, were obtained. At the commencement of the next session I secured the services of Mr. Stovel, the most promising of the electrical students of the previous session, to assist Mr. Barnes in setting up the apparatus and taking the observations. I spent a good deal of my leisure at this time in the adaptation of the method to the determination of the specific heat of steam, but continued to give the closest personal supervision to the work on the specific heat of water, and made several tests of the apparatus in the vacations when I had more leisure. A great part of the work during this session consisted in perfecting the mechanical details of the apparatus, which is always a most important and laborious process in an investigation of this character. The last work in which I personally assisted before leaving Montreal was the drawing and annealing of the platinum-silver wire for the Mica Current-Standards referred to in Section 7. By this time the fundamental portions of the apparatus had been practically perfected, but the observations, though very numerous, did not extend beyond the range 0° to 55°, and they had for the most part been taken for the purpose of testing improvements which from time to time were introduced, and could not be regarded as parts of a regular series.

When I left Montreal about the end of May, 1898, it was arranged that Mr. Barnes should continue the experiments throughout the summer, and should follow me to England with the apparatus as soon as I could make preparations for carrying on the work in my new laboratory. Unfortunately this plan proved to be impracticable, which caused some delay in the work, as I was unable to render him any material assistance by correspondence at such a distance, owing to the impossibility of detecting sources of error in any particular case without seeing the apparatus or the observations. But by the end of the McGill College session in April 1899, he had succeeded so well in overcoming his difficulties, and the work appeared to be progressing so favourably, that it seemed inadvisable to disturb the apparatus. I therefore reluctantly consented to abandon any further share in the observations. It had originally been intended that I should write the paper describing the theory and results of the investigation; but as, in the end, Mr. Barnes was solely responsible for the final series of observations, it seemed more appropriate that he should write the account of that part of the work.

The primary object of my own contribution is to supplement his account of the final observations by a general discussion of the theory of the experiment, and a description of the difficulties encountered in the earlier stages. He was unable to speak with authority on these points, as a good deal of this work was done before he joined the investigation, and I had not thought it necessary to give him a detailed account of it, since it was originally intended that we should finish the work together. A similar partition of authorship has already been sanctioned in a similar case in the work of Reynolds and Moorby, and possesses undoubted advantages in presenting the results from two distinct and independent points of view. It was the more necessary in the present instance owing to the comparative independence of our several shares in the work, and to the impossibility of satisfactory collaboration at such a distance. I had hoped at one time that it might be possible by some rearrangement of the matter to weld the separately written portions into a continuous whole, but as the part written by Dr. BARNES had already been accepted by the Royal Society, and the Abstract had been already published, it appeared desirable that it should be printed without alteration as nearly as possible as it was received, subject only to a rearrangement of the Tables of Results, and the addition of one or two samples of the original observations.

The delay in publication has been partly due to the necessity of this rearrangement, and partly to the difficulty of obtaining satisfactory determinations of the resistance of the manganin standard ohm, on which the absolute values of the results depended. I have taken advantage of this delay to verify the calculations as far as possible, and to subject the whole work to as complete and careful a revision as the time at my disposal would allow. The final results do not materially differ from those previously published in the 'Report of the British Association, Dover,' 1899, and in the 'Physical Review.' There was, therefore, no need for haste so far as the numerical results of the work were concerned, but it was important in an investigation of this character that all the details of the apparatus, and the theoretical and practical difficulties of the work should be adequately explained and illustrated.

[*Added March 11th*, 1902.—Frequent references are made in the following pages to the paper by Dr. BARNES, *infra*, pp. 149–263, describing his experimental results. These references are generally indicated by the name (BARNES) in brackets, with the addition of the page, table, or section referred to.

It is hardly necessary that I should say anything here in praise of the conscientious accuracy with which Dr. BARNES has carried out his share of the work. In re-arranging the tabular summary of observations (BARNES, Table XVIII., p. 243), I have endeavoured to indicate clearly the order of accuracy attained, and it must be evident to anyone who studies the paper, that it would be difficult to make any improvement in this respect.]

PART II. ELECTRICAL MEASUREMENTS.—(A.) POTENTIAL.

(2.) *Advantages of the Potentiometer Method.*

The simplest method of observing the electrical energy expended in the calorimeter would be to measure the current C, and to assume the value of the resistance R to be that corresponding to the observed mean temperature of the calorimeter. The watts expended would then be given by the formula, $W = C^2R$. This method was adopted by the majority of the earlier experimentalists. An equally simple method, but more seldom practised, would be to observe the difference of potential E on the conductor, assuming the resistance as before. The advantage of assuming the resistance is that one reading only is required, but, as ROWLAND pointed out, the temperature of the resistance, when the heating current is passing through it, must be considerably higher than that of the calorimeter. This would introduce a serious error, unless it were possible to use a wire of some material like manganin, in which the variation of resistance with temperature could be neglected.

GRIFFITHS ('Phil. Trans.,' A, 1893) adopted the method of balancing the potential difference on the conductor against a number of Clark cells in series, and deduced the expenditure of energy in watts from the formula $W = E^2/R$, by assuming the value of the resistance. He tried manganin to avoid the error of super-heating, but found that it was not sufficiently constant. In the end he found himself compelled to use platinum for the conductor, but avoided the error due to super-heating by measuring the actual excess-temperature of the wire as nearly as possible under the conditions of the experiment.

SCHUSTER ('Phil. Trans.,' A, 1895) adopted the same method of balancing the P.D. on the conductor, but did not assume the value of the resistance. Instead of this, he measured the time integral of the current with a silver voltameter. This is a theoretically perfect and most appropriate method of procedure, but it introduces an additional measurement, and limits the accuracy to that attainable with the silver voltameter.

For our method of experiment there were several objections to the use of the silver voltameter, which put it practically out of the question. As is well known, when the current is first turned through the voltameter, the resistance changes considerably for some time. This makes it difficult to keep the P.D. on the conductor accurately balanced against the Clark cells unless the whole resistance in circuit is large. A change of this kind in the current at the moment of starting the experiment would be a fatal defect in the steady-flow method of calorimetry, as it would disturb all the temperature conditions, which must be perfectly steady and constant before observations are commenced. Moreover, it happened to be most convenient for our purpose to employ currents from 5 to 10 amperes, which would require very large voltameters, and could not be *continuously* regulated without constructing special rheostats. In any case regulation by hand would involve some discontinuity in the heat-flow, which it was desirable to avoid. We found it best not to make any attempt to control the current artificially, but to employ very large and constant storage cells, and to compensate the slow rate of running down of the current by the running down of the head of water, so that the temperature-difference might remain practically constant throughout the experiment.

Besides the above special objections to the use of the silver voltameter, there are the general objections : (1) that the voltameter method gives only the time-integral of the current, and does not permit the course of variation of the current to be accurately followed throughout an experiment; (2) that with Clark or cadmium cells of a suitable pattern it is possible to attain an order of accuracy in the *relative* values of the readings about ten times as good as that attainable with a silver voltameter. It was most important for our purpose to obtain accurate relative values, and whatever might be the doubt as to the absolute values of the E.M.F. of the cells, there could be none as to their constancy, which was easily tested over considerable periods of time.

It therefore appeared most satisfactory to measure the current by passing it through a suitable resistance, and observing the P.D. on the terminals with a potentiometer in the usual manner. The introduction of the potentiometer may appear at first sight to be an additional complication and source of error; but it really made the observations much simpler, and I satisfied myself by careful tests of the instrument that an accuracy of 1 in 100,000 was readily attainable so far as the potentiometer readings were concerned. Besides, it was unnecessary, with the potentiometer, to keep the P.D. on the conductor balanced against an *integral* number of cells, and it was, therefore, possible to adjust the electric current to give the same rise of temperature with different values of the flow of liquid. This most essential adjustment could not be so conveniently or quickly effected by varying the flow of liquid as by regulating the electric current with a low-resistance rheostat. It also proved in practice to be much more convenient to take all the electrical readings on a single instrument, instead of having the silver voltameter as well as the potential balance to attend to.

It will be seen that our method is independent of any assumption with regard to the electrochemical equivalent of silver, although the contrary is apparently assumed in discussing our result both by AMES ('Report to the Paris Congress of 1900 on the Mechanical Equivalent of Heat'), and by GRIFFITHS ('Thermal Measurement of Energy,' p. 93). The method of measurement is ultimately equivalent to that of GRIFFITHS, as it makes the result depend on the International Ohm, and the Clark cell. The measurement of the current by observing the P.D. on a known resistance, when combined with the observation of the P.D. on the heating conductor itself, is in effect equivalent to the measurement of the resistance of the heating conductor under the actual conditions of the experiment, in the most direct manner possible. The watts expended are derived from the formula E^2/R, so that an error in the absolute value assumed for the standard cell is twice as important as an error in the value of the ohm.

If x_0 is the balance-reading of the potentiometer when the standard cells are connected, and e the E.M.F. of the standard cells, and if x', x'' are the readings corresponding to the P.D. on the heating conductor and the standard resistance S respectively, the expression for the heat-supply in watts is evidently

$$EC = e^2 x' x''/x_0^2 S.$$

The accuracy of the reading x_0 for the cells, which enters by its square, is twice as important as that of x' or x'', but it was also more easy to obtain with certainty, since the cells were kept at a constant temperature, and the reading x_0 seldom changed by more than 1 in 50,000 in the course of an experiment. It will be seen that, for the determination of the variation of the specific heat, the most important point in the electrical measurements is the question of the accuracy of calibration of the potentiometer, which is described in the following sections. The absolute values of the units are less important, but I have added a brief account of experiments on the absolute value of the Clark cells, and of the tests of the standard resistances, as they possess an interest of their own, even apart from the question of the absolute value of the "mechanical equivalent."

(3.) *Description of the Potentiometer.*

The form of potentiometer selected as being most convenient for the purpose was the well-known Thomson-Varley Slide-Box, which is described and figured in many electrical works (*e.g.*, MUNRO and JAMIESON'S "Pocket-Book," p. 150). The annexed figure shows the arrangement of the connections, and will be useful for reference in explaining the details of the calibration.

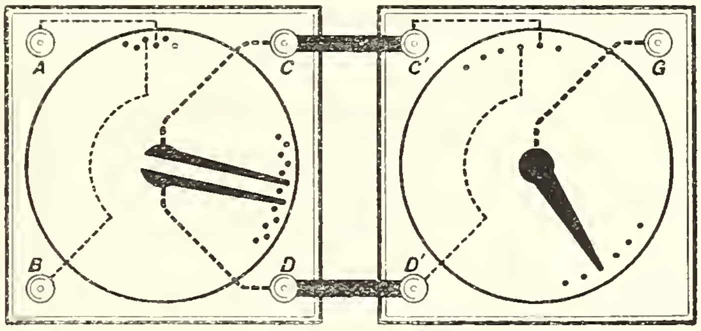

Fig. 1. Diagram of Thomson-Varley Slide-Box.

The main dial ABCD contains 101 coils, each of 1000 ohms resistance, connected in series, the ends of the series being connected to the terminals AB. The ends of each coil are connected to platinized studs, which are indicated by the black dots in the diagram. A pair of revolving contact springs, fixed to an ebonite handle, travel round the dial. These springs are severally connected to the terminals C and D, and the distance between them is adjusted so that they bridge over *two* of the 1000-ohm coils of the main dial.

The second, or "Vernier" dial, C′D′G, consists of a series of 100 coils of 20 ohms each, the ends of which are connected to C′ and D′, and are thus, by way of C and D and the double revolving contact of the main dial, in parallel with two of the 1000-ohm coils of the main dial. Since two coils of the main dial are always shunted in this manner by the vernier dial, the effective resistance between C and D is reduced to 1000 ohms, and the whole resistance of the potentiometer between the terminals A and B, to 100,000 ohms. The ends of each of the 20-ohm coils of the vernier dial are connected to platinized studs arranged in a circle, which make contact one at a time with a single revolving contact spring, connected to the galvanometer terminal G. This arrangement of main and vernier dials permits the sub-division of each hundredth part of the whole resistance into one hundred parts, so that the reading of the two dials gives the P.D. to be measured directly to one part in ten thousand of the P.D. on the terminals AB.

The advantages of this form of potentiometer, in addition to its high resistance, were (1) the great facility and rapidity of reading and manipulation, and (2) the symmetry of construction, which permitted a very high order of accuracy of calibration to be attained, and greatly facilitated the application of corrections, as compared with the usual type of instrument in which a bridge-wire is employed for the finer sub-divisions.

In the use of this instrument in our experiments the P.D. to be measured seldom exceeded 4 volts. The terminals AB were permanently connected to three Leclanché cells, which gave a very steady current through so high a resistance. The reading of the two Clark cells employed as a standard varied by a few parts in 10,000 only from week to week, and generally remained constant to 1 in 100,000 for the short interval of 15 minutes corresponding to any single experiment.

The galvanometer employed with this potentiometer had a resistance of 110,000 ohms. The astaticism of the needles was adjusted as carefully as possible, so that the effect of disturbance of earth-currents due to the electric railway might be negligible. The suspended system was fitted with a very perfect mirror and a damper to make it practically dead-beat. The sensitiveness was adjusted by control magnets to give a deflection of approximately 10 scale-divisions for one division of the vernier dial (1 in 10,000). The perfection and steadiness of the image was such as to permit reading to a small fraction of a scale-division. The first four figures of the reading were given by the setting of the dial contacts. It was easy to estimate the fifth figure at any moment by inspection of the galvanometer deflection. The temperature conditions were generally so steady in the course of an experiment, and the diminution of the electric current and the water-flow so gradual and regular, that it was possible, as a rule, to predict the reading of the P.D., either on the standard resistance or on the heating conductor, to 1 in 100,000 for at least five minutes ahead.

As there were no observational difficulties to contend with in the electrical readings, the relative order of accuracy of the results would be limited only by the constancy of the Clark cells and the current standards, and by the order of accuracy attainable in the calibration of the potentiometer and in the permanence of the relative values of the coils. The coils of the main dial, which were the most important, were all precisely similar, wound with the same wire and carefully protected from sudden or unequal changes of temperature. The ratio of the resistances of the two halves of the dial was frequently checked with consistent results, as a precaution to give warning of any accidental flaw. This precaution was by no means superfluous, for on one occasion in November, 1897, a fault, amounting very nearly to complete rupture of the wire, was discovered by Mr. King in this manner. It was however easily located and rectified without altering the relative values of the coils.

(4.) *Method of Testing.*

The method of testing the ratio of the two halves of the slide-box was as follows:—The slide-box was connected by the terminals AB in parallel with a 100,000-ohm box consisting of ten coils of 10,000 ohms each. The battery was connected as usual at A and B, one terminal of the galvanometer to G, and the other to the middle of the 100,000-ohm box. The slide-box contacts were set at 50,000 ohms. To take one particular experiment as an example, the deflection of the galvanometer observed on reversing the battery was 77 scale-divisions. When the contact was set at 50,010 ohms, the deflection was 215 scale-divisions in the same direction, showing a sensitiveness of 138 scale-divisions on reversal for a change of 1 in 5000 in the reading. The contact was then set back to 50,000, and the two halves of the box were interchanged with respect to the rest of the circuit by interchanging the connections at A and B. The deflection observed was increased from 77 to 181 scale-divisions in the same direction as before. The effect of interchanging the two halves is the same as if the slider were shifted through a resistance equal to their difference. Hence the difference of the two halves is to 10 ohms as 104 is to 138. The first half of the box is evidently the smaller, as the effect of interchanging is the same as that of increasing the reading. The correction to be applied to the reading, to reduce to mean ohms of the box, is half the difference of the two halves, and is negative, since the first half is the smaller. We have, therefore,

$$\text{Correction at reading } 50{,}000 \text{ ohms} = -10 \times 104/2 \times 138 = -3{\cdot}8 \text{ ohms.}$$

The galvanometer deflections in each case were observed several times and the mean taken. The details were also varied by using different resistances for the ratio arms in the comparison and different galvanometers. Observations were taken by different observers at various temperatures on several occasions, at intervals during five years. The greatest divergence of the results from the mean value is less than 1 part in 100,000 (·4 ohm in 50,000 ohms), which is strong evidence that the relative values of the corrections at any part of the box could be relied on at any time to a similar order of accuracy.

The following is a summary of the results of all the tests of which full details have been preserved, but several other tests were made from time to time as a precaution:—

TABLE I.—Verification of Correction at Middle Point of Slide-Box.

Date.	Observers.	Correction (ohms in 50,000).
February, 1894	CALLENDAR.	−3·8
December 20th, 1894	CALLENDAR.	−3·96
January 29th, 1895	KING.	−3·77
November 24th, 1896	THOMSON and STOVEL.	−4·2
February 2nd, 1897	BLAIR and MACDONALD.	−3·72
March 4th, 1897	PITCHER and EDWARDS.	−3·50
April 22nd, 1898	STOVEL.	−3·43
January 27th, 1899	BARNES.	−3·95

Some of the above observations were taken by fourth-year students in the course of their work, but in the majority of cases I personally verified the readings and results at the time of entry.

(5.) *Method of Calibration.*

In the calibration of the slide-box, the point of most importance was to determine the correction for each reading of the main dial, *i.e.*, at 100 equidistant points of the whole range. The vernier dial was so small in comparison that the errors of its individual coils were negligible in their effect on the whole reading, although it was necessary at each point to take account of the difference of resistance of the whole vernier dial and the pair of coils shunted by it in any position of the slider.

After several trials of various methods extending over nearly a month, I came to the conclusion that the most convenient and accurate method of performing the calibration was to determine the relative values of the coils of the main dial in pairs by comparison with the 2000 ohms of the vernier dial. The flexible copper cable connecting the terminals D and D′ was disconnected, and the terminals were connected to a galvanometer and to a pair of exactly similar resistances of 2000 ohms each forming the ratio arms P and Q of a Wheatstone bridge, the other two arms of which were the vernier dial S and any pair of consecutive coils R_n and R_{n+1} of the main dial. A battery of two storage cells, selected for constancy, was connected to the point between the ratio arms and to the terminals CC′. The deflection d_n of the galvanometer corresponding to any setting of the slider was proportional to the difference of the sum of the corresponding pair of coils R_n and R_{n+1} of the main dial from a unit SP/Q, which was approximately 2000 ohms, and remained constant throughout the comparisons. The value of this deflection was reduced to ohms by observing the change of galvanometer deflection s produced by a change of 1 ohm in one of the arms. This observation was repeated at intervals during the calibration.

The advantage of this particular arrangement was partly that of expedition and convenience, partly that of avoiding systematic errors due to changes of condition or temperature while the calibration was proceeding. The construction of the vernier dial, 100 coils of 20 ohms each, made it a good standard of comparison, as there was no risk of appreciable heating from the current employed, although it was necessarily kept on for more than an hour. Moreover, as it was constructed of similar wire and enclosed in a similar box to the main dial, it was probable that any change of the surrounding conditions of temperature would affect the two similarly. The heating effect of the current on P and Q would be sufficiently eliminated by their similarity of construction.

Readings taken in this manner, with the slider set in each position of the main dial, gave 100 equations of the following form :—

$$R_n + R_{n+1} = SP/Q + d_n/s \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

To determine the correction at each point of the main dial, and the relative values of the 101 resistances and the vernier dial, it was also necessary to determine the ratio of any two of the coils to each other, and the ratio of the two together to the vernier dial. This was effected by the method of interchanging, as already described for determining the ratio of the two halves of the slide-box.

The ratio of coils R_1 and R_2 to the vernier dial S was found to be

$$(R_1 + R_2)/S = 1\cdot000039.$$

The ratio of coils R_1 and R_2 to each other was found to be

$$R_1/R_2 = 1\cdot000400.$$

In the latter case the galvanometer contact was made by means of a copper wire to the stud between 1 and 2, the glass cover being removed for the purpose of this test.

The observation of the values of the deflections d for the 100 equations of the type (1), was repeated on two separate occasions. On the first occasion the 110,000-ohm galvanometer was employed, but it was found that when the galvanometer was adjusted to a suitable degree of sensitiveness for the experiment, its time period was too slow, and its zero not sufficiently constant to give the best results. It took upwards of an hour to obtain the first fifty observations. This series was not therefore continued throughout the box, but the observations were reduced to mean ohms of the box by reference to the value of the correction at the middle point of the box obtained from a separate observation. On the second occasion the 110,000-ohm galvanometer was replaced by one of 2000 ohms resistance, which was better suited for this particular experiment, though not so well adapted for observations in which the whole box was employed. The sensitiveness of this galvanometer was adjusted to give a deflection of 167 scale-divisions on reversal for a change of 1 ohm in 2000 with a time period of 5 seconds, and remained constant to less than one scale-division throughout the test of the whole box, which occupied only an hour and a half.

The observations and results of the two calibrations for the first half of the slide-box are compared in the following table. The first column contains the reading of the slider on the main dial. The second column the observed deflection of the galvanometer d in equation (1) reduced to ohms by dividing by s. Since $s = 167$ in the second series, one unit in the second decimal place of d/s corresponds to nearly 2 scale-divisions deflection observed. The observations were taken to half a scale-division, but owing to slight variations of sensitiveness and zero it was not considered worth while to work the values of d/s beyond the nearest hundredth of an ohm. The next column gives the error $d\mathrm{R}$ in ohms of each separate resistance of the main dial in terms of the mean of the whole, deduced from equations (1) by the aid of (2) and (3). The fourth column gives the correction dn in ohms to the reading at each point. This correction is equal to the sum of the errors of all the coils up to the point considered, subject only to a small correction, called the "vernier-correction," to allow for the fact that the next two coils are shunted by the vernier dial. The value of the vernier-correction is given by the following expression—

$$\text{Vernier-correction to reading } n = - n\,(\cdot 38 - 3d\mathrm{R}_{n+1} - 3d\mathrm{R}_{n+2})/400.$$

This correction is often negligible when n is small, but sometimes reaches ·5 or ·6 of an ohm near the higher readings. The next three columns in the table give the corresponding values of the same quantities d/s, $d\mathrm{R}$, and dn, deduced from the readings taken during the second calibration. Comparing the two sets it will be observed that the discrepancy very rarely exceeds half an ohm, which is only one part in 200,000 of the whole resistance.

Table II.—Calibration of 100,000-ohm Slide-Box. Corrections in ohms.

Reading, of main dial *n*.	Observations, Series I. November 24, 1894, at 15°·5 C.			Observations, Series II. December 20, 1894, at 20°·2 C.			Difference of Series I–II.
	d/*s*.	*d*R.	Correction.	*d*/*s*.	*d*R.	Correction.	
0	+1·04	–	0	+1·26	–	0	0
1	+0·52	+0·43	+0·43	+0·55	+0·45	+0·45	−0·02
2	+0·26	+0·05	+0·45	+0·20	+0·05	+0·49	−0·04
3	+0·64	−0·10	+0·36	+0·77	−0·26	+0·24	+0·12
4	+0·92	−0·34	+0·03	+1·11	−0·30	−0·07	+0·10
5	+0·40	+0·39	+0·40	+0·54	+0·31	+0·24	+0·16
6	+1·00	−0·06	+0·36	+1·21	+0·04	+0·30	+0·06
7	+1·42	−0·13	+0·26	+1·53	−0·25	+0·07	+0·19
8	+0·68	+0·54	+0·76	+0·74	+0·71	+0·74	+0·02
9	+0·40	+0·29	+1·03	+0·51	+0·06	+0·78	+0·25
10	+0·52	−0·20	+0·83	+0·62	−0·08	+0·71	+0·12
11	+0·50	+0·01	+0·84	+0·58	−0·17	+0·53	+0·31
12	+1·56	−0·08	+0·86	+1·70	+0·03	+0·66	+0·20
13	+1·50	−0·01	+0·85	+1·72	−0·21	+0·46	+0·39
14	+0·46	+0·98	+1·72	+0·51	+1·16	+1·50	+0·22
15	+0·44	−0·07	+1·65	+0·52	−0·19	+1·30	+0·35
16	+0·26	−0·06	+1·57	+0·37	−0·06	+1·22	+0·33
17	+0·32	−0·09	+1·48	+0·40	−0·18	+1·04	+0·44
18	+0·22	−0·24	+1·22	+0·31	−0·21	+0·82	+0·40
19	+0·04	−0·03	+1·16	+0·15	−0·15	+0·64	+0·52
20	+0·62	−0·34	+0·91	+0·84	−0·30	+0·44	+0·47
21	+0·90	−0·21	+0·74	+1·11	−0·30	+0·18	+0·56
22	+0·68	+0·24	+0·94	+0·94	+0·39	+0·54	+0·40
23	+0·32	+0·07	+0·95	+0·52	−0·04	+0·43	+0·52
24	+0·14	+0·02	+0·94	+0·26	+0·22	+0·60	+0·34
25	+0·16	−0·29	+0·65	+0·30	−0·46	+0·14	+0·56
26	+0·26	−0·16	+0·50	+0·45	−0·04	+0·13	+0·37
27	+0·30	−0·27	+0·24	+0·58	−0·42	−0·27	+0·51
28	−1·04	−0·06	−0·11	−0·84	+0·12	−0·45	+0·34
29	−0·96	−0·23	−0·34	−0·74	−0·29	−0·73	+0·39
30	+0·42	−1·40	−1·44	+0·71	−1·31	−1·72	+0·28
31	+0·30	−0·15	−1·62	+0·52	−0·19	−1·96	+0·34
32	+0·28	−0·02	−1·65	+0·35	+0·14	−1·86	+0·21
33	+0·16	−0·27	−1·95	+0·29	−0·38	−2·26	+0·31
34	+0·46	−0·04	−1·92	+0·67	−0·03	−2·20	+0·28
35	+0·36	−0·39	−2·34	+0·62	−0·43	−2·64	+0·30
36	+0·20	+0·26	−2·12	+0·41	+0·35	−2·35	+0·23
37	+0·12	−0·49	−2·63	+0·32	−0·49	−2·87	+0·24
38	+0·06	+0·10	−2·56	+0·27	+0·14	−2·75	+0·19
39	+0·80	−0·57	−2·92	+0·99	−0·58	−3·12	+0·20
40	+0·92	+0·04	−2·84	+1·07	+0·09	−3·00	+0·16
41	+0·82	+0·17	−2·70	+0·98	+0·14	−2·89	+0·19
42	+1·20	+0·16	−2·42	+1·38	+0·18	−2·58	+0·16
43	+0·54	+0·07	−2·56	+0·69	+0·05	−2·75	+0·19
44	+0·08	+0·54	−2·17	+0·24	+0·57	−2·33	+0·16
45	+0·16	−0·59	−2·74	+0·29	−0·64	−2·96	+0·22
46	+0·22	+0·08	−2·64	+0·41	+0·12	−2·80	+0·16
47	+0·64	−0·51	−3·01	+0·84	−0·59	−3·25	+0·24
48	+0·00	+0·14	−3·10	+0·13	+0·24	−3·26	+0·16
49	−0·20	−0·09	−3·37	−0·07	−0·15	−3·49	+0·12
50	−0·24	−0·50	−3·79	−0·06	−0·47	−3·96	+0·17

The following table gives the corrections found for the second half of the slide-box on the second occasion, December 20th, 1894.

TABLE III.—Calibration Corrections of Second half of Slide-Box.

Reading of main dial.	Correction in ohms.	Reading of main dial.	Correction in ohms.	Reading of main dial.	Correction in ohms.	Reading of main dial.	Correction in ohms.	Reading of main dial.	Correction in ohms.
50	−3·96	60	−4·58	70	−3·13	80	−1·33	90	−0·92
51	−4·42	61	−4·68	71	−3·32	81	−1·21	91	−0·96
52	−4·57	62	−4·07	72	−3·19	82	−1·11	92	−0·45
53	−5·09	63	−4·04	73	−3·03	83	−1·24	93	−0·70
54	−4·88	64	−3·69	74	−3·03	84	−1·38	94	−0·63
55	−5·15	65	−3·60	75	−2·47	85	−1·70	95	−0·82
56	−5·26	66	−3·62	76	−2·16	86	−1·83	96	−0·94
57	−5·31	67	−3·68	77	−1·92	87	−1·64	97	−0·22
58	−5·19	68	−3·45	78	−1·61	88	−1·71	98	−0·23
59	−5·23	69	−3·51	79	−1·64	89	−1·24	99	−0·06

In comparing the differences between the two calibrations given in the last column of Table II., it will be noticed that there is a cumulative divergence amounting to about half an ohm at the middle of the range. This is the kind of error to be expected in this method of calibration. It might be explained by the considerable difference in temperature of the box on the two occasions, but it is within the limits of error of the first series. The galvanometer was not sufficiently steady on that occasion, and the temperature rose nearly half a degree in the course of the observations. The observations serve, however, as a satisfactory verification of those of Series II.

It will be observed that the correction does not amount to so much as 1 part in 10,000 of the reading at any point of the slide-box, except quite near the beginning, a part which was never used in accurate comparisons. Also that the change of the correction in passing from one point to the next, never exceeds 1 part in 100,000 of the reading in the second half of the box, although the errors of two or three of the individual 1000-ohm coils exceeded 1 ohm. This is due to the levelling effect of the vernier.

It must be remembered that the corrections were never required beyond the nearest ohm, so that a difference of less than ·5 could be neglected.

It might be supposed that greater accuracy of calibration would have been attained by dividing up the box into subsidiary intervals of 10,000 ohms, and comparing each of these intervals with an auxiliary resistance, on the analogy of the method usually employed in the calibration of a mercury thermometer. I did not find, however, that any advantage was obtained by this procedure, and it is evident, on reflection, that the two cases are not precisely analogous. The advantage of employing longer columns in the case of a mercury thermometer is that the errors of estimation become of relatively less importance. It is practically possible to measure both the long and short columns to the same fraction of a degree, and an error of ·001° in a column of 20° is of much less relative importance than in a column of 2°. In the case of the resistance box, on the other hand, the relative accuracy of measurement is undoubtedly *greater* in the case of the smaller resistances. A 10,000-ohm coil cannot be measured with the same order of accuracy as one of 1000 ohms. This is partly due to difficulties of insulation in the winding of the coils themselves, and partly to the fact that wire finer than 2 or 3 millims. cannot be drawn and covered satisfactorily. As a consequence, high-resistance galvanometers are necessarily less efficient than low-resistance instruments of similar construction. The best high-resistance coils are constructed of a number of lower resistance coils in series, as in the Thomson-Varley slide-box, which permits a higher order of insulation than winding in a single coil.

(B.) Resistance.

(6.) *The Lorenz Apparatus.*

Although this apparatus was not actually applied to the direct determination of the resistances employed in this investigation, owing to delay in delivery, it was originally ordered with this object, and the preliminary experiments which were made by Professors Ayrton and Jones in testing the apparatus before it was sent out, are of so great value as bearing on the absolute value of the ohm that they cannot be passed over without mention. The null method of Lorenz, in which a resistance is directly determined in terms of the speed of rotation of a disc spinning in the field of a co-axial coil of known dimensions, is generally admitted to be the most accurate for the absolute measurement of resistance. The McGill College apparatus was constructed by Messrs. Nalder Bros. to my order, under the direct supervision of Professor Viriamu Jones, and embodied all the improvements introduced into the method by himself and by Lord Rayleigh. The most important new feature of the design was the winding of the coil on a heavy cylinder of marble, instead of metal as employed in Professor Jones' original apparatus. This material possesses the advantage of high insulating properties, great rigidity, and small thermal expansion. The employment of a marble cylinder made it possible to wind the coil with uncovered wire with the object of obtaining the most exact measurement of the dimensions, but on account of some difficulties of insulation, the original winding of bare wire was eventually replaced by one of silk-covered wire coated with paraffin and shellac varnish.

The results of the tests made by Professors Ayrton and Jones with this coil, at the laboratory of the Central Institution, during 1896 and 1897, have been published in the Reports of the British Association for 1897 and 1898, and in the 'Electrician.' They give a value for the Board of Trade standard ohm nearly 3 parts in 10,000 greater than 10^9 C.G.S. units. This divergence might be explained as due to imperfect insulation if the precautions taken had not been so great, but it more probably represents the order of accuracy at present attainable in the absolute measurement of resistance by this or any other method. It is hardly possible that it could be entirely accounted for by errors of measurement of the diameter of the coil and the disc, although a discrepancy of 1 in 10,000 was actually found between the calculated and measured diameters of the coil ('B.A. Rep.,' 1897, p. 217), which points to some uncertainty in this direction.

At the time when I first examined the coil of the Lorenz apparatus, some time after its arrival in Montreal, while it was being set up, it seemed to me that the wire had worked a little loose on the marble, owing to some effect of the drying of the insulating tape and varnish, or to straining of the soft insulated wire due to contraction on exposure to cold. This would necessarily occur owing to the great difference in the coefficients of expansion of the wire and the marble, and the very small limits of elasticity of the soft annealed wire. Professor V. JONES himself, with whom I discussed the question in September, 1897, shortly after the arrival of the apparatus in Montreal, considered that the diameter could not be satisfactorily measured with a silk-covered wire, and strongly recommended the re-winding of the coil with bare wire. Accordingly, I procured for this purpose a sample of highly elastic silicium-bronze wire of high conductivity. I satisfied myself that the limits of elasticity of this wire would be ample, if it were wound on under suitable tension at a suitable temperature, to keep it perfectly tight on the marble cylinder for any range of temperature to which it was likely to be exposed. The tightness of the wire in practice is most important, from the point of view of insulation as well as from that of accurate measurement of the diameter. If the diameter of the wire is nearly equal (as it must necessarily be) to the pitch of the screw thread, a very slight defect in tightness or straightness will produce a short circuit. It is quite a difficult matter to wind a perfect coil of 200 turns of this size, unless the wire is highly elastic and quite free from kinks.

Owing to the great importance of securing perfect insulation, I proposed to adopt the method which I had already put in practice in the case of the electro-dynamometer, namely, to wind the coil in a double screw thread with two separate wires, in order to have a check on the perfection of the insulation, which could be applied at any time after the coil had been wound, or at any moment during the actual experiments.

In consequence of the delay caused by the failure of insulation of the first coil, the apparatus did not arrive in Montreal until the beginning of September, 1897. Some time was occupied in the course of the winter in building a suitable pier, and setting up the apparatus. But when I was about to commence observations, I received news of my appointment to the Chair of Physics at University College, London, which made it necessary for me to abandon the work.

(7.) *Values of the Resistance Standards.*

The currents employed in this investigation were measured on the Thomson-Varley potentiometer by comparing the difference of potential on the terminals of a specially constructed resistance, called the Current-Standard, with that of a pair of hermetically sealed Clark cells. This current-standard consisted of a single 1-ohm coil, or of two 1-ohm coils in parallel, immersed in a well-stirred oil-bath. The resistance coils employed for this purpose in the earlier experiments were made of thick manganin wire of the best quality procured from Germany. The diameter of the wire was 1 millim., and the maximum current carried by each single wire was 2 amperes. The wire was not materially heated above the temperature of the oil, but, as no cooler was used in the earlier experiments, the temperature of the oil generally rose some 8 or 10° in the course of an hour. This was considered to be of no consequence with the manganin coils, as they had a temperature coefficient of only + ·000020 for rapid changes. On re-testing these coils after some months' work, it was found that their resistance had increased by two or three parts in 10,000, and that they continued to show small variations of this order. It was possible that these changes might have been due to the solder junctions, which would have explained certain anomalies observed in the earlier experimental results. It is equally likely, however, that they were caused by hysteresis in the wire as explained below.

Although the variations of the manganin coils did not exceed a few parts in 10,000, it was felt that they were quite inadmissible, as the potential readings were taken to 1 in 100,000. For this reason it was decided to make a pair of platinum-silver ohms wound on mica and annealed at a dull red heat *after winding.* These will be called the "Mica Current-Standards." They are fully described and illustrated by Dr. BARNES, p. 173. The method of construction was modelled on that of a platinum resistance thermometer, and had already been adopted for some years by the Instrument Company, Cambridge, for the manufacture of standard resistance coils. Standards constructed on this model possess great constancy, and their temperature can be determined with accuracy by immersion of the naked wire in an oil-bath. As compared with manganin coils, they have the disadvantage of a larger temperature coefficient, but the construction permits the determination of this coefficient with the greatest certainty, so that it is really no objection to their use for scientific purposes, for which constancy is the primary desideratum. The adoption of platinum-silver necessitated the addition to the oil-bath of a cooling coil of composition tubing, with a water circulation to keep the temperature steady.

For the determination of the variation of the specific heat of water, the absolute value of the current-standard was of no moment, but its constancy was of primary importance. It was also essential to be able to determine the temperature coefficient accurately, in order to reduce the observations at different temperatures in winter and summer to the same standard. This was determined under the actual conditions of observation with stirrer and cooler (BARNES, p. 174), by comparison with a manganin standard ohm, No. 4086, which was kept at a steady temperature. The value of the temperature coefficient of the mica current-standards is, therefore, independent of any assumption with regard to the temperature coefficients of the other standards employed. The low value ·000248 of the coefficient found is explained by the perfect annealing of the wire.

The absolute values of the mica current-standards were referred to the manganin standard No. 4086. The comparisons of this coil with the mica standards, which extended over two years, are given in Table IX. (BARNES), and do not show any relative changes of importance. The observations were taken on twelve different dates at temperatures varying from 15° to 21° C., the mean temperature of all the comparisons being 18°·36 C.

The temperature coefficient of the manganin standard No. 4086 was assumed to be ·000018 in the reduction of these observations. This value was determined by observing the change of resistance due to changes of temperature of the oil-bath in which the coil was immersed, the changes of temperature being effected at the rate of 10° C. in two or three hours. The results in Table IX. (BARNES) are reduced to a temperature of 20° C. If, however, we reduce the results to 18°·4 C., the mean temperature of the comparisons, we shall be independent of any assumption with regard to the temperature coefficients. We thus obtain the values :—

Mica current-standard, No. I. at 18°·27 = No. 4086 + ·00091 at 18°·4 C.
,, ,, ,, ,, II. ,, 18°·46 = ,, ,, − ·00035 ,, ,,
No. I. and No. II. in parallel at 18°·36 C. = Half No. 4086 + ·00014 . . (1).

The manganin standard No. 4086 had a Cambridge certificate No. 378 dated 1893, which stated its value to be ·99978 of a true ohm at 15·9° C. The preliminary results for the value of the calorie in terms of the electrical units, communicated to the British Association in September, 1899, were expressed in terms of this certificated value as correct. A comparison was subsequently made at McGill College of No. 4086 with a set of 10 platinum-silver standard ohms of the old pattern, the coils of which were embedded in paraffin wax. These 10 coils all possessed Cambridge certificates, and their relative values when tested agreed fairly with those obtained several years previously, showing no certain indication of change. The mean of the certificates of these 10 coils gives the value :—

Mean of 10 Pt-Ag standard ohms = ·99962 at 16°·5 C. . . . (2).

The details of the comparison of No. 4086 by Dr. BARNES* with 9 of these

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* The standard No. 3566 omitted by BARNES happens to be so near the mean of the 10 as to make no material difference in the result.

standards are given in Table VII. (Barnes). The mean of the results may be stated as follows :—

No. 4086 at 21°·74 C. = Mean of 10 Pt-Ag ohms — ·00054 at 21°·59 C. . (3).

The coils were also compared about the same time by Mr. Fraser at a lower temperature. The value of No. 4086 in terms of the mean deduced from this second comparison is :—

No. 4086 at 14°·8 C. = Mean of 10 Pt-Ag ohms + ·00153 at 13°·6 C. . (4).

The details of this comparison are given in Table VIII. (Barnes).

If the mean values of the 10 Pt-Ag ohms at 21°·6 and 13°·6 C., respectively, are deduced from the certificated value of the mean at 16°·5 C., adopting ·000254, the value taken by Barnes as the temperature coefficient, we obtain the following values for No. 4086 :—

No. 4086 at 21°·74 C. = 1·00037 ohms (from standards at 21°·6 C.) . (5).
„ „ „ 14°·8 C. = 1·00041 „ „ „ 13°·6 C.) . (6).

These results are evidently inconsistent with the value + ·000018 for the temperature coefficient of No. 4086. The individual observations, however, are too consistent to admit of the supposition of an error of the order of two parts in 10,000 in the mean of the comparisons. It seems more likely that the value ·000254 assumed for the temperature coefficient of the Pt-Ag standards is too small. In any case, if we take the mean of the two comparisons, we shall obtain a result which is nearly independent of the value assumed for the temperature coefficient. We thus obtain :—

No. 4086 at 18°·4 C. = 1·00039 ohms (Pt-Ag standards at 17°·6 C.) . (7).

It happens that the temperature 18°·4 C. is precisely that at which the value of No. 4086 is required for the comparisons with the mica current-standards.

(8.) *Comparisons at the National Physical Laboratory.*

It appeared practically certain from these comparisons that the value of No. 4086 had increased since the date of the original certificate by nearly ·00060 ohm. For further verification No. 4086 was sent over in a box from Montreal to Cambridge, and thence to Kew, to be compared with the original standards. Mr. Glazebrook very kindly undertook the comparison himself, with the following results :—

Value of No. 4086 from Observations at the National Physical Laboratory.

Date.	Temperature.	Value from 3715.	Temperature.	Value from "Flat."*
	°		°	
July 20	25·0	1·00067	24·9	1·00067
" 26	24·4	1·00072	24·4	1·00059
" 28	21·4	1·00063	21·3	1·00059
" 28	21·6	1·00062	—	—
" 30	18·9	1·00057	—	—
August 1	16·0	1·00045	—	—

These observations give a mean value of 1·00061 ohms at a temperature of 21°·96 C., and indicate a temperature coefficient of about ·000027 for changes taking place in a few days. This result is inconsistent with the value (5) 1·00037 at 21°·74 C. found by Barnes, unless we suppose the temperature-coefficient employed by Barnes for the Pt-Ag coils to be a little too small, or unless No. 4086 had *increased* in value on its journey from Canada. Mr. Glazebrook was not perfectly satisfied with these observations, as the temperature was too high and variable, and the difference to be measured on the Pt-Ir bridge-wire, as well as the temperature correction of the standards, was rather large. He therefore repeated the observations in December, at a lower temperature, under much steadier conditions, with the following results :—

Value of No. 4086 from National Physical Laboratory Standards.

Date.	Temperature.	Value from 3715.	Temperature.	Value from "Flat."
	°		°	
December 13, 1900 . .	12·1	1·00018	11·9	1·00020
" 18 and 19 .	13·2	1·00016	13·0	1·00018
" 20	11·3	1·00016	11·5	1·00015
" 21	12·1	1·00017	12·1	1·00015
" 28	10·3	1·00010	—	—

The results of these observations give a mean value of 1·00016 at a temperature of 12°·0 C. This appeared inconsistent with the July observations. It was also much lower than the value (6) 1·00041 at 14°·8 found by Fraser, unless we suppose either that the coefficient ·000254 applied by Barnes to the platinum-silver coils was too small, or that No. 4086 had *fallen* in value in the interval.

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* "Flat" is one of the original B.A. unit standard coils belonging to the British Association, the temperature coefficient of which is taken to be ·000277, as determined by Fleming in 1876. 1 ohm is assumed to be 1·01358 B.A. unit. No. 3715 is a more recent standard ohm.

In order to throw further light on the question, Mr. GLAZEBROOK undertook a determination of the temperature-coefficient of No. 4086 by heating it up to 20° C. and allowing it to cool slowly, the case being full of oil. Taking only the morning observations, which Mr. GLAZEBROOK considers the most reliable, we obtain the following mean results on the two days :—

TEMPERATURE-COEFFICIENT of No. 4086 at the National Physical Laboratory.

Date.	Mean temperature.	Mean value from 3715.
January 4, 1901 . .	17·2°	1·00024
,, 5 ,, . .	9·4	1·00005

These observations give a mean value of 1·00015 at 13°·3 C., which agrees very closely with the December comparisons, but is slightly lower, as though the diminution of resistance were still in progress. The value of the temperature-coefficient deduced is + ·000024, which is a very probable value for this kind of manganin for temperature changes of 10° in one day.

(9.) *Hysteresis in Manganin Coils.*

From my own experience of the behaviour of manganin, I am inclined to explain these discrepancies as follows :—The temperature-coefficient of a manganin coil frequently depends to some extent on the past history and on the rate of heating or cooling. It may exhibit a kind of lag or hysteresis, the resistance continuing to increase gradually for some time after a rise of temperature, so that the value of the coefficient found by short-period observations is often smaller than the value which applies to changes of long period. Taking the July and December observations at the National Physical Laboratory as being correct, we find a long-period temperature-coefficient for No. 4086 of +·000047, which is about twice as large as the short-period coefficients ·000027 and ·000024, deduced from the observations from day to day. It was for this reason that I discontinued the use of manganin for accurate work in platinum thermometry some years ago, preferring to use platinum-silver coils annealed at a red heat and compensated for temperature by means of platinum similarly annealed. The defect is of a kind that would escape notice except in very accurate work over long periods with coils exposed to considerable changes of temperature. It also appears to depend on the manner in which the wire has been annealed.

It is worthy of notice, as a confirmation of this view, that a small effect of this nature was observed by HARKER and CHAPPUIS in their platinum thermometry

('Phil. Trans.,' A, 1900, vol. 194, p. 59), though they do not appear to have appreciated its full significance. In order to reduce the temperature correction, they selected a resistance box with manganin coils made by Messrs. CROMPTON in preference to one with platinum-silver coils annealed at a red heat after the pattern made by the Cambridge Instrument Company. In attempting to determine the temperature-coefficient of their box by raising the temperature for a short period, they noticed that the resistances did not return at once to their original values on cooling. They also observed a considerable increase of resistance in all the coils, which was most rapid at the outset, and which they attributed to the effect of recovery from the soldering. We have seen that No. 4086 underwent a similar increase of resistance at the outset. Messrs. HARKER and CHAPPUIS do not seem to have observed the long-period effect of hysteresis, which is more insidious. The correction for this cannot be accurately applied, but it appears that it might explain some of their errors of observation.

In order to reconcile the observations of BARNES and FRASER with each other and with those of GLAZEBROOK, it is necessary to suppose that the value of the temperature coefficient ·000254 assumed by BARNES for the McGill Pt-Ag standard ohms is a little too small. According to my own experiments with these particular standards, in 1893 and 1894, made by heating the coils in a water-bath, the value should be ·000275. I tested only two of the coils, but it is clear from the agreement of the relative differences observed by BARNES and FRASER that the temperature coefficients of all the coils are nearly the same. The changes in the relative differences observed by them are in no case greater than can be explained by the uncertainty of temperature, as the coils were not immersed in a water-bath in their comparisons.

Adopting the value ·000275 for the temperature coefficient of the 10 Pt-Ag standard ohms, we find the following corrected results in place of (5) and (6),

BARNES, No. 4086 at 21°·74 C. = 1·00048 ohms . . . . (8).
FRASER ,, ,, ,, 14°·8 C. = 1·00035 ohms . . . . (9).

The difference between these two values gives a temperature coefficient for No. 4086 of ·000020, which agrees with their other results supposing that FRASER's observations were taken in the basement within a few days of those of BARNES. In comparing these results with those of GLAZEBROOK, it must be remembered that owing to the solidity of the construction and the perfection of the heating arrangements in the Physics Building at McGill College, the temperature of the Heat Laboratory very rarely fell below 15° in winter (except in a few corners near the windows), or rose above 22° in summer. No. 4086 was never exposed at Montreal to so great changes of temperature as it experienced in the temporary observing room at Kew. The results of the comparisons as regards the absolute values of the current-standards at McGill College are, therefore, deserving of greater weight than might be supposed at first sight.

Taking the mean of the observations of BARNES and FRASER as fairly applying to the mean temperature of the Heat Laboratory at the time, we obtain

No. 4086 at 18°·4 C. = 1·00042 ohms in terms of ten McGill standards . (10).

Taking the long-period coefficient ·000047 as appropriate for deducing the value of No. 4086 at the same temperature, from GLAZEBROOK's observations we find

No. 4086 at 18°·4 C. = 1·00046 ohms in terms of original B.A. standards (11).

This agreement is as close as could reasonably be expected, and we may conclude that the value of No. 4086 is known from the comparisons to at least 1 part in 20,000. Adopting the latter value for 4086, we obtain finally for the value of the mica current-standards,

Mica current-standards in parallel at 18°·36 C. = ·50037 ohm . . (12).

Assuming the temperature coefficient ·000248 for the mica current-standards, we find for the values at 5°, 10°, 15°, and 20°, respectively,

VALUES of Mica Current-standards in Parallel.

Temp. Cent.	5°	10°	15°	20°
Value	·49871	·49933	·49995	·50057

These values are in practical agreement with those obtained by BARNES from the McGill comparisons alone, but he does not make any attempt to explain the apparent discrepancies. They are probably correct in terms of the International Standard Ohm to 1 part in 20,000, but the uncertainty of the absolute value of the International Ohm itself may amount to 2 or 3 parts in 10,000. If the Board of Trade Ohm really exceeds the C.G.S. Ohm by nearly 3 parts in 10,000, according to the result of the measurements of Professors JONES and AYRTON with the McGill College apparatus, the electrical watts supplied in the calorimeter have been over-estimated to that extent, so that the absolute value of the equivalent of the calorie in terms of electrical energy as deduced from this investigation would require to be reduced by about 1 part in 4,000.

It should be observed that the absolute values of the current-standards are of comparatively little importance for the present investigation, as they do not at all affect the question of the variation of the specific heat. I have thought it worth while, however, to discuss the question somewhat fully for two reasons. In the first place, the comparisons illustrate a possible objection to the use of manganin coils for accurate work, which is not I think sufficiently appreciated. In the second place, it is possible that at some future time the absolute values of the electrical standards may be more accurately determined, in which case it is desirable that the apparent discrepancies in the comparisons of the standards employed in the present investigation should be clearly explained, in order that the correction may be suitably applied.

The above explanation of the discrepancies observed in the comparisons of the manganin standard No. 4086, was submitted to Mr. GLAZEBROOK for his approval in January, 1901. He considered, however, that the measurements in his possession at that time were not conclusive evidence of hysteresis, as four other manganin coils of German make, which had been tested at the same time, had shown similar though not identical variations. He was himself inclined to explain these irregularities by uncertainties of temperature or of temperature-coefficient of the Pt-Ag standards, especially at the higher temperature in the July observations. The large value of the coefficient ·000047 for the manganin coil, deduced from the July and December observations, might be explained by supposing that the value of the coefficient assumed for the Pt-Ag coils was too large. This, however, would not explain the smaller values of the coefficient for the manganin coil deduced from the observations from day to day, in which the same value of the Pt-Ag coefficient was assumed.

In order to settle the question, a further series of comparisons of No. 4086 was made in June and July, 1901, at the National Physical Laboratory, which completely confirmed the observations made in the previous July, showing that they were not merely accidental results due to erratic change of No. 4086 or to uncertainty in the temperature conditions prevailing at that time in the observing room.

As a further test of the possibility of hysteresis theory already advanced, a special comparison was made, in which No. 4086 was heated through a small range of temperature and allowed to cool slowly, being tested against a *manganin* standard kept at a steady temperature throughout the comparison. This test gave a very small coefficient, but the curve representing the observations gave unmistakable indications of hysteresis. It was confirmed by a second test, in which No. 4086 was cooled, and allowed to warm up slowly. The curve representing the observations in this case had the opposite curvature. The two curves combined gave a figure similar to one of the familiar cycles of magnetic hysteresis. These effects could not be explained as due to a real lag of temperature, since the rate of change of temperature was very slow, and the case was filled with oil in direct contact with the wire and also with the thin metal tube on which the wire was wound. With this direct evidence of the existence of hysteresis over short periods and small ranges of temperature, it becomes easier to admit the possibility of larger variations of long period, such as those indicated by the July and December comparisons with the platinum-silver standards.

My assistant, Mr. EUMORFOPOULOS, is now engaged in testing the conditions of existence of the long-period effect, by a differential method designed for the purpose.

(C.) CURRENT.

(10.) *The Electrodynamometer.*

For the absolute measurement of the E.M.F. of the Clark cells employed in this investigation in terms of the standard ohm, I proposed to employ an electrodynamometer of the pattern constructed by LATIMER CLARK for the Electrical Committee of the British Association. This instrument is described and figured in MAXWELL'S "Electricity and Magnetism," vol. 2, p. 339. The moment of the couple due to the current is measured by means of a bifilar suspension, the constant of which is determined by observations of the time of oscillation. It has been usual of recent years to prefer the current-weighing method, in which the force due to the current is directly balanced by weights, to methods depending on the observation of an angular deflection; but it appeared to me that the British Association apparatus, with certain modifications of detail, would escape most of the errors generally urged against the deflection method, and that it possessed important advantages in other respects.

The electro-dynamometer in the possession of McGill College, as originally constructed by Messrs. NALDER, was intended to be an exact duplicate of the apparatus in the Cavendish Laboratory at Cambridge. The coils of the Cambridge apparatus were wound under the supervision of MAXWELL, whose measurements of the large coils were assumed by LORD RAYLEIGH in his determination of the electrochemical equivalent of silver. As a preliminary step, the apparatus was set up and tested in October, 1894, with the assistance of Mr. R. O. KING, then a fourth-year student. The defects of the electrodynamometer, in its original form, were found to be so serious that it was necessary to re-wind the coils, and make other extensive alterations. This involved considerable delay, while the necessary materials were being obtained and preparations made; and the apparatus was not set up in its final form until the return of Mr. KING from Harvard in September, 1897.

The principal defects of the original apparatus were found to be as follows:—(1) The framework of the large coils, and the pulley arrangement for equalising the tensions of the bifilar suspension were not sufficiently rigid. It was not possible to obtain the desired order of accuracy in the observation of the times of oscillation, or in the deflections. (2) The most serious defect was the uncertainty of the insulation between adjacent layers of the windings of the coils. This could not be directly tested, but was inferred from a comparison of the mean radii of the coils determined by electrical methods with the values calculated from the measurements. The difference could only be attributed to defective insulation, as the number of turns and the measurements were verified by unwinding the coils. The error amounted to nearly 1 part in 500 for the large coils (324 turns each), and about

1 in 300 for the small coils (576 turns each). The insulation between the coils and the metal frame-work was in all cases perfect, as the channels were lined with paraffined paper. The wire itself proved to be very carefully wound, and the double silk covering throughout was uninjured. The defects could not be attributed to excessive damp, as the winter climate of Montreal is extremely dry, and the laboratory was most efficiently heated. Having regard to the perfect condition of the wire, it seemed unlikely that absolute security of insulation could be attained with silk-covered wire, however carefully wound.

Owing to the extreme importance of securing perfect insulation, and of being able to test the insulation at any time, the small pair of coils were immediately re-wound with a double winding of two wires side by side throughout, with paper between each layer. They were then boiled in paraffin wax, and the insulation has since proved to be practically perfect. At the same time it was decided to re-wind the large coils with a double-winding of copper tape, of the same width as the channel, insulated with paraffined paper or silk between the layers. But as there was some delay in securing the requisite material, the experiment had to be postponed for the time. I took advantage of this delay to work out the details of the following improvements, which were introduced into the method on resuming the work in October, 1897, with Mr. KING's assistance.

(11.) *Duplex Scale Reading.*

For greater accuracy in observing the deflections and measuring the scale distance, which is generally one of the weakest points in a deflection method, a duplex system of reading was adopted. The apparatus was erected on a suitable pier, which had been provided for it in a basement room, with copper fittings and heaters, where the temperature was very steady and the ground free from vibration. A plane parallel mirror, $\frac{1}{8}$ inch thick, and 2 inches in diameter, silvered on *both* faces, was fitted to the suspended coils. A pair of metre scales, accurately divided on plane milk-glass, were mounted with suitable adjustments on a rigid frame of copper tubes at a distance of 3 metres apart, 150 centims. east and west of the mirror respectively. A circulation of water was maintained through the copper tubes. The distance between the scales and the thickness of the mirror could be measured with great accuracy. The deflections were observed simultaneously from either side with a pair of very perfect reading telescopes of 2 inches aperture, and about 2 feet long. These were fitted with filar micrometers, and adjusted so that one turn of the micrometer screw was very nearly equal to 1 millim. on the scale. The mirror and telescopes were specially made by BRASHEAR for this work. The coils and suspension were completely enclosed to screen them from draughts, and observations were taken through a pair of thin mica windows. With this arrangement, it was optically possible to read with certainty to a fiftieth of a millimetre on a steady deflection of 50 centims. on either side of the zero. This method of reading eliminates a number of small uncertainties, and makes it possible to approach an order of accuracy of 1 part in 100,000 in the deflection measurements.

(12.) *The Bifilar Suspension.*

In order to minimise the effect of imperfect elasticity, the wires of the suspension were made of hard drawn copper of high conductivity, as fine as was consistent with constancy of length (safety factor 5), and were rigidly clamped at a distance of 3·2 centims. apart, after the tensions had been adjusted to equality. The length of the suspension was 80 centims., and the effect of torsion of the wires was comparatively small. The directive force of the bifilar depended almost entirely on gravity, and remained constant to 1 in 20,000 for several months. The effect of current heating of the suspension was tested by observing the time of oscillation with the working current of ·5 ampere flowing in opposite directions in the two windings of the small coils, and was found to be less than 1 part in 20,000.

To determine the moment of inertia, the small coils were fitted with a co-axial brass tube about 2·5 centims. in diameter, and 50 centims. long, containing a pair of cylindrical inertia weights, 150 grammes each, which could be clamped at the centre of the tube, or at the ends. The distance between the weights in their extreme position is the most important measurement. This was determined by a very accurate pair of steel callipers by Brown and Sharpe, reading to ·01 millim., with a range of 50 centims. This gave sufficient accuracy for the preliminary measurements, but it was intended to employ a Whitworth measuring machine for the final series. In observing the oscillations, the times of passage were recorded on an electric chronograph with a standard clock rated from the observatory. The periods o oscillation, with the ends of the weights flush with the ends of the tube, and with the weights in contact at the centre of the tube, were 11·5385 and 6·7857 seconds respectively, and the observations on different days, when corrected for temperature, did not vary by more than two or three in the last figure.

(13.) *Mean Radius of the Large Coils.*

The mean radius of the pair of large coils was determined from the length of the copper tape with which they were wound. This method is not satisfactory with soft annealed copper wire owing to stretching, but the hard rolled copper tape could be wound without any tension, and did not undergo any change of length. This was verified by graduating the tape itself on a 50-foot comparator, the errors of which were known; then winding the coil for trial, and unwinding and measuring the tape again, which was found not to have changed in length by more than a tenth of a millimetre in each 50 feet. The tape was supported horizontally on the polished surface of the comparator, and measured under a tension of 6 kilogs. Young's modulus was determined for each section. The tape was wound on each coil in two lengths of 19 turns each, starting at opposite ends of a diameter, with two thicknesses of paraffined paper between each turn, so that the insulation could be tested with absolute certainty at any time. There were 38 complete turns, and nearly 6000 centims. of tape, on each coil. The probable error of the measurement was less than 1 millim. on the whole length, *i.e.*, less than 1 part in 100,000. The coils could not be boiled in paraffin after winding, as this would subject the tape to uncertain strains owing to the contraction of the wax. It was found necessary to re-wind the coils two or three times with minor improvements before the insulation proved to be perfect. Finally, silk ribbon was adopted in place of paper.

(14.) *Distance between Mean Planes of Large Coils.*

The coils were fitted to the frame at a distance between their mean planes equal to the mean radius of either coil. For this purpose, the original frame, which was insufficiently rigid, was strengthened with heavy rings of brass turned to fit the coils, and carefully tested for non-magnetic quality. The distance between the mean planes, though four times less important than the mean radius, must be known with considerable accuracy. This was effected by making the coils reversible and measuring their thickness. Each coil when in position rested against the points of three screws, which were adjusted to the right distance apart, and clamped in position. The distances between the points of opposite screws were measured with the callipers, and also the thickness of the coils themselves at the points of contact. The coils were connected to their respective terminals by eight pairs of flexible conductors, twisted together in pairs so as accurately to compensate, and arranged so that the coils could be rapidly removed, reversed and replaced at any moment. This appears to be the only satisfactory method of determining the distance between the mean planes, as the winding of the coils and the distribution of the current in the tape cannot be assumed to be perfectly symmetrical with respect to the channels.

(15.) *Area of the Small Coils.*

The most difficult part of the work was the determination of the area of the small coils by comparison with the large coils. A thick brass tube, carrying a delicately suspended magnet and mirror at its centre, was rigidly fixed to the framework so as to be co-axial with the large coils. The small coils could be mounted co-axially on this tube at a mean distance of 30 centims. on either side of the centre. Currents were passed in opposite directions through the large coils and small coils in parallel, and the resistances of the circuits were adjusted until the magnetometer showed no deflection. The ratio of the resistances was then immediately determined in a manner similar to that employed by Lord Rayleigh in measuring the mean radius of the small coil in his current balance. The chief difficulties were due to change of resistance of the coils with change of temperature. These changes were considerably reduced by employing copper resistances for the adjustment, and by arranging the details so as to secure the greatest rapidity of observation. Readings were taken in each position with the large and small coils severally reversed, and interchanged, and replaced, the complete series each night including 36 independent readings of the ratio. The distance between the two positions of the small coils on either side of the centre is the most important measurement. This was determined by two shoulders turned on the thick brass tube, the distance between which was measured with the callipers. It was necessary to make all these comparisons at night between the hours of 2 and 5 A.M. in order to avoid disturbance from the electrical railway, two lines of which passed within about a quarter of a mile of the building. The values of the ratio obtained from observations on three different nights, when there was no magnetic disturbance and the conditions were otherwise satisfactory, showed extreme differences, amounting to nearly 1 part in 5,000. These may have been partly due to temperature, as the small coils had been boiled in paraffin, which must have affected the expansion.

(16.) *Ratio of the Currents in the Coils.*

In the usual method of employing the electrodynamometer, the same current is passed through the large coils and small coils in series. This method has the advantage of simplicity, but it is essential, in order to obtain steady deflections and secure the maximum accuracy of reading, that there should be no appreciable heating of the small coils by the current. The latter condition, however, cannot be satisfied if the currents are equal, unless the large coils are wound with very fine wire, which is for many reasons objectionable. In the present case, the windings were designed to secure approximately equal current heating when the currents are in the ratio of 1 to 10 in the small and large coils respectively. The ratio of the currents was adjusted to this value at each observation by having a standard ohm in series with the small coils, and a standard tenth-ohm in series with the large coils. The whole arrangement formed a Wheatstone bridge, the balance of which was adjusted by means of some copper coils and a high-resistance shunt in series with the small coils. The standard coils were of manganin immersed in oil, and the ratio remained extremely constant, owing to the equality and smallness of the current heating, and the perfection of the insulation. Thus, although the division of the current involved an additional adjustment of the ratio of the resistances, no appreciable error was thereby introduced, and great advantages were secured by the equable distribution of the heat developed, and the steadiness of the observed deflections.

(17.) *Electromotive Force of the Clark Cells.*

The electromotive force of the Clark cells was determined by simultaneous observations with the potentiometer of the difference of potential on either of the standard manganin resistances while the currents were being measured by the electrodynamometer. This observation depended to some extent on the accuracy of calibration of the potentiometer, but this was repeatedly tested with results consistent to 1 part in 50,000. Owing to the great steadiness of the current, there being no silver voltameter in circuit, the potentiometer readings could easily be taken to this order of accuracy. The Clark cells were of the hermetically sealed type described in the 'Proceedings of the Royal Society' for October, 1897, and were kept in a well-stirred water-bath at a constant temperature.

The results of the first series of observations on the absolute value of the E.M.F. of the Clark cell in terms of the ohm, taken with this apparatus during the spring and summer of 1898, were sent in by Mr. R. O. KING as the report of his third year's work as 1851 Exhibition Scholar. When certain minor corrections are applied for the values of the resistance coils and for the higher harmonics in the series representing the force between the fixed and suspended coils, the result found for the E.M.F. of the Clark cell at 15° C is,

$$\text{Clark cell} = 1{\cdot}4334 \text{ volts},$$

the volt being defined as the potential difference due to a current of one-tenth of a C.G.S. unit through a standard ohm. This result was not immediately published, because Mr. KING hoped to be able to secure an order of agreement higher than 1 part in 10,000 in the comparison of the small coils with the large coils, which was much the most difficult part of the measurements. But it may be questioned whether a higher order of accuracy could reasonably be expected in this determination, and although the value above given was not at the time intended to be final, I feel that it may be regarded with considerable confidence on account of the high order of accuracy of the individual measurements, and the many new devices which were introduced into the design of the apparatus.

The work of setting up the apparatus and taking the observations was performed almost exclusively by Mr. KING under my supervision, with occasional assistance from other students in taking readings. I was able to assist him personally during the vacations in some of the more important measurements, such as the graduation of the copper tape on the comparator, the first winding of the large coils, and the first comparison of the small coils. I also verified the accuracy of most of the adjustments, and the perfection of the insulation, and am satisfied that the whole work was most carefully and systematically carried out. Mr. KING has since left McGill College, but I hope that he may yet find time to work out and publish in detail the final results of his observations, which should form a valuable contribution to absolute electrical measurement. It should be noticed that the result above deduced from the first series of observations by Mr. KING agrees with that deduced from the observations with the electrical calorimeter by comparison with ROWLAND and with REYNOLDS and MOORBY, namely, 1·4332, within the limits of probable error of the several methods.*

PART III.—THERMOMETRY.

(18.) *The Compensated Resistance Box.*

Nearly all the temperature measurements in this investigation were made with a special form of resistance box, which contains some devices which have not as yet been adopted in any other instrument of its class, or described in any scientific periodical. The most important feature in its construction was the system adopted for compensating the resistances to eliminate the effect of change of temperature. In the usual form of box the temperature of the coils is taken by means of a mercury thermometer, and the correction for change of temperature applied from a knowledge of the temperature-coefficient. The principal objection to this method is that the mercury thermometer cannot follow the temperature changes of the coils with sufficient exactness, and that the temperature is generally far from uniform throughout the box. In the method of compensation which I patented in 1887 (Complete Specification No. 14,509) the temperature correction is automatically eliminated by combining with each of the resistance coils proper, which are made of platinum-silver or some other alloy possessing a small temperature-coefficient, a compensating coil of copper or platinum having a large coefficient. The resistance of the compensating coil is adjusted so that its change of resistance per degree is equal to that of the coil it is intended to compensate, while its actual resistance at any temperature is much smaller, the ratio of the resistances being inversely as the temperature-coefficients. Each compensator is placed in the box in close proximity to the coil it is intended to compensate, so as to be always at the same temperature, but coil and compensator are connected on opposite sides of the bridge-wire, so that the balance depends only on their difference, which remains constant for any change of temperature, provided that the adjustment has been properly effected. The advantage of the method lies in the fact that this adjustment can be made with extreme accuracy, by testing coil and compensator together over the required range of temperature before they are connected in their places in the box. But the method has not come into general use, partly on account of the labour involved in the adjustment of the coils, and also in part owing to the discovery shortly afterwards of manganin and other alloys of small temperature-coefficient, which are fairly satisfactory for ordinary work though inferior, in my opinion, to the compensation method for work of precision The objections to manganin, for instance, are—(1) That it cannot be perfectly

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* The details of the construction and comparison of the Clark and cadmium cells employed are sufficiently described in the 'Proc. Roy. Soc.,' 1897, vol. 62, p. 117, and by Dr. BARNES, Section 3A, p. 159.

annealed after winding, and that its resistance is consequently liable to change for some time. (2) That the temperature-coefficients of different specimens are often different, and vary for different sizes according to the method of annealing, so that it is desirable to test the temperature-coefficient of each coil in the box, and to apply the corrections separately in the most accurate work. (3) That the temperature correction cannot be satisfactorily applied, as there is generally some hysteresis in the change of resistance with temperature, and the values of the resistances depend to some extent on previously existing conditions of temperature. (4) That it cannot be hard soldered without burning, and that soft solder connections to manganin are frequently found to be defective, unless they have been most carefully made. (5) That it is liable to corrosion if exposed to damp or gas fumes, although the usual coating of shellac is sufficient protection in most cases. These defects have been noted by other observers, notably by HARKER and CHAPPUIS, who employed a box with manganin coils in their recent comparison of the platinum and gas-thermometers The majority of other alloys of this class are inferior to manganin in constancy; they are also frequently objectionable (*e.g.*, "constantan") on account of their great thermoelectric power, which produces inconvenient disturbances if the temperature of the box is not uniform. The advantage of platinum-silver lies in the perfection with which it may be annealed, and in the absence of lag or change when properly annealed.

If *uncompensated* coils of platinum-silver are used, it is necessary to keep them in an oil-bath to secure sufficient certainty of temperature. It is also desirable to employ a thermostat for regulating the temperature of the oil-bath, and a stirrer for keeping the temperature uniform throughout. This adds considerably to the cumbersomeness and expense of the apparatus, and to the difficulty of using it. It is really simpler in the end to use compensated coils, as the individual temperature-coefficients of the coils must otherwise be determined and corrected separately, at least for work of the highest accuracy.

The first apparatus constructed on this principle was made in 1887, shortly before applying for the patent, and was figured in the specification. All the parts of this apparatus were made interchangeable in pairs, by an extension of the CAREY-FOSTER principle, with a view to facilitate testing and calibration. There were two exactly similar bridge-wires, each a metre long, and three pairs of compensated coils, which could be inserted singly or in series, with resistances on the binary scale equal to 1, 2, and 4 times that of either bridge-wire. The platinum-thermometers were also made in pairs, after the pattern described and figured in the 'Phil. Trans.,' A, 1890, but were generally contained in separate tubes, which greatly facilitated construction, and permitted them to be used differentially by a simple change in the connections of the bridge. In the instrument used for the boiling-point of sulphur (*loc. cit.*) it was necessary to have both thermometers in the same tube. This construction was also adopted in 1887 for comparison coils in which it was necessary that both wires should be accurately at the same mean temperature. The necessary changes of connection were effected by means of mercury cups and thick copper connectors, similar to those employed for standard resistance coils. The mercury cups were made by boring suitable holes in a flat plate of ebonite, to the under side of which thick copper plates were screwed, the joint being made mercury tight with a thin sheet of rubber.

The apparatus above referred to was first used for some determinations of the linear expansion of standard yards at the Standards' Office in 1887. It was subsequently employed by Dr. A. S. LEA, F.R.S., and Dr. W. H. GASKELL, F.R.S., and later by Dr. ROLLESTON, in some physiological experiments on the heat produced in muscle and nerve by electrical and other stimuli. For this purpose a very delicate pair of differential thermometers were constructed of ·001-inch wire wound on mica, weighing a few milligrammes each, and sensitive to the ten-thousandth of a degree C. One of these thermometers was described and figured in the specification (No. 14,509, 1887). This apparatus is still in the possession of the Physiological Laboratory, Cambridge.

The chief defect of the original form of apparatus was the uncertainty of the temperature correction of the platinum-silver bridge-wire owing to its length. In making a new form of apparatus in October, 1890, bridge-wires of manganin were employed, annealed at a red heat in coal gas. The pair of bridge-wires could be very accurately calibrated throughout their length by the Carey-Foster method, but owing to the trouble of determining and applying the bridge-wire correction, it was eventually decided to use a bridge-wire of low resistance in conjunction with a larger number of resistance coils. It also proved to be unnecessary in practice to make all the coils interchangeable in pairs, provided that the ratio coils were tested for equality of temperature-coefficient. In this case, it was sufficient to calibrate the bridge-wire and resistances by a method of substitution, which was much simpler than the Carey-Foster method. Apparatus constructed on this principle was described in the 'Phil. Mag.,' July, 1891, and figured in the patent specification (No. 5342, 1891). As the resistance coils were no longer required to be interchanged, they were permanently connected to the copper plates in a single box instead of being connected to copper rods in separate boxes like standard coils. The mercury cups, however, were still retained, in preference to plugs for short circuiting the resistance coils in accurate work, and were constructed precisely as originally described. The simplification consisted in connecting the resistance coils permanently in series, and using simple bridges of thick copper connected in pairs for short-circuiting each resistance coil and its compensator simultaneously.

The particular resistance box employed in this investigation is shown in the accompanying fig. 2. It was made to my designs by the Instrument Company, Cambridge, at the beginning of 1893, but I had personally to undertake the delicate work of compensating and adjusting the resistance coils. It contained 9 resistance coils, A, B, C, D, &c., on the binary scale, ranging from 2560 to 10 units, constructed of platinum-silver annealed at a red heat, and compensated with similarly annealed platinum. The box measured 15″ × 6·5″ × 3·5″. The bridge-wire was of platinum-silver, nearly 34 centims. long, but only 5 centims. on either side of the middle were actually used in the measurements. The scale was of brass, divided by Troughton and Simms to half millimetres, with a vernier reading to a hundredth of a millimetre. To secure this order of accuracy in the readings, the contact piece, consisting of a short length of the same platinum-silver wire with a nearly sharp edge, was rigidly fixed to the sliding piece carrying the vernier. The bridge-wire was stretched at such a height as to clear the contact edge by about ·01 inch, and contact was effected by pressing down the bridge-wire on to the contact wire by means of an india-rubber finger. This finger was provided with a screw adjustment, so that the contact could be set and held at any desired point. To keep the tension of the bridge-wire constant, which is most important in accurate work, the wire was stretched between parallel bars of brass and iron in an intermediate position corresponding approximately to its coefficient of expansion. Connection was made to the galvanometer through a similar wire stretched parallel to the bridge-wire, in order to eliminate thermal effects at the sliding contact. All the connecting wires throughout the box were accurately paired and compensated, and the thermometer connections were made by means of mercury cups at PP′ CC′. Screw terminals were used in the galvanometer and battery circuits only, where changes of resistance are immaterial. The ratio coils were adjusted to equality by the method of interchanging, and were tested and compensated for equality of temperature-coefficient before being fixed in their places in the box. They were *not* wound up together, as is usual in apparatus of this class, but were merely fixed side by side, as it is most important to secure the most perfect insulation of the ratio coils for delicate differential work.

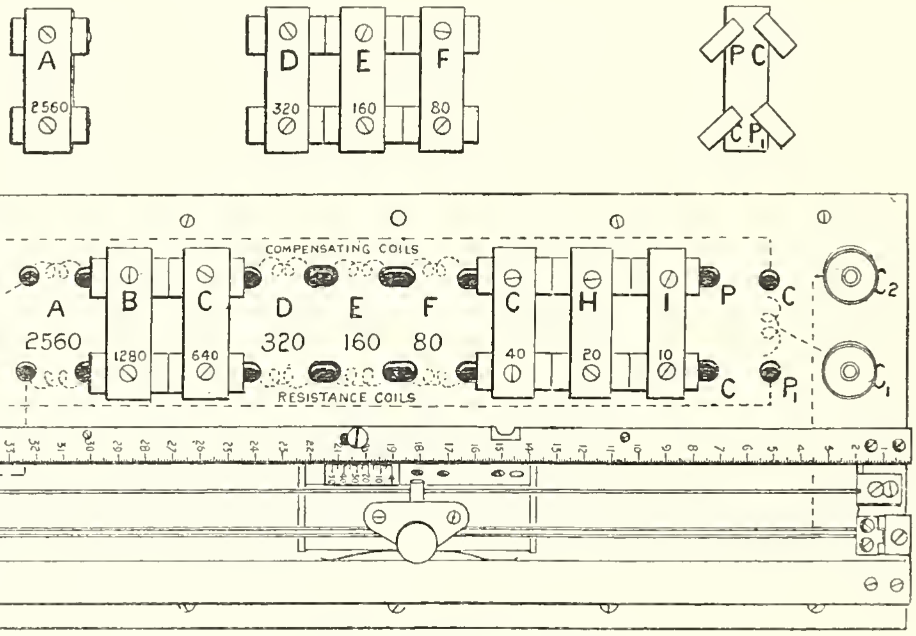

Fig. 2. Compensated Resistance Box.

The box was originally intended for working chiefly with thermometers of pure platinum having a zero resistance equal to the largest coil, *i.e.*, 2560 box-units, and a fundamental interval of 1000 box-units, or nearly 10 ohms. This gave a very convenient scale of 10 centims. of the bridge-wire to the degree, and made it possible to take readings to the ten-thousandth part of a degree. Thermometers of double the resistance, having a scale of 20 centims. to the degree, were employed for some differential work, *e.g.*, for demonstrating the lowering of the melting point of ice due to one atmosphere of pressure (·0075° C.) at the May Soirée of the Royal Society in 1893, where this box was first exhibited. But for ordinary temperature measurements, unless the insulation were extremely perfect, it was found that very little could be gained in point of accuracy by going beyond 10 ohms for the fundamental interval. For the boiling-point of sulphur, a fundamental interval of 5 ohms was found to be preferable; and 1 or 2 ohms for higher temperatures where the insulation was necessarily less perfect and the conditions less steady. As the portion of the bridge-wire actually utilised never exceeded 5 centims., and averaged only 2·5 centims., or $\frac{1}{4}$ of a degree, it was seldom necessary to take any account of the calibration correction of the bridge-wire, the errors of which proved to be less than one part in 500, or one two-thousandth part of a degree, without correction. In the best mercury thermometers it is unusual to calibrate closer than 2° intervals, and the corrections are necessarily uncertain to two or three thousandths, even if the interpolation formulæ can be trusted to one part in a thousand, which is very doubtful. It is easy to see how great is the advantage of the platinum-thermometer in point of ease and accuracy of calibration.

The comparison of the 9 coils of the resistance box, which were arranged on the binary scale, could be carried out and the relative values calculated in less than an hour. The peculiar advantages of the binary scale for this purpose are frequently misunderstood or misrepresented. The most important of these advantages are: (1) That a given resistance can be represented only by one particular combination of coils, so that there can never be any doubt as to which combination was employed for any given reading; (2) That the least possible number of separate coils are required, and that the complete calibration requires the least possible number of readings, and can be effected in the least possible time. It is often urged as an advantage of less simple and symmetrical arrangements, that each resistance can be made up in a great variety of ways, which act as checks in case of doubt; and that the relative values of the coils can be compared in a number of different combinations, so that several equations can be obtained for evaluating each resistance. This is, no doubt, an advantage in cases where the accuracy of calibration depends on micrometric *estimation*, as in calibrating a mercury-thermometer. But, if a good galvanometer is available, the accuracy of comparison of resistances is not limited in this way. We may, therefore, fairly consider the disadvantage of the excessive expenditure of time in the observations and calculations; moreover, the risk of error due to changes of condition or temperature, which is the really important point to be considered in work of this kind, is increased by the greater complexity and want of symmetry of the system of comparison. Examples of the calibration of this box on the binary method are given by BARNES, p. 187.

(19.) *Heating of the Thermometers by the Measuring Current.*

It is generally assumed in the construction and use of apparatus for comparing standard resistance coils, that the conditions of greatest sensitiveness are obtained when the resistance of the ratio arms is equal to that of the resistances to be compared. This, however, is certainly not the case in platinum-thermometry, and seldom in other cases, unless the heating of the resistances by the measuring current can be safely neglected. In platinum-thermometry the heating of the thermometer by the current is the limiting consideration which determines the amount of power available for the test. For a given rise of temperature with a given thermometer the current must not exceed a certain value, *e.g.*, about a hundredth of an ampere for a rise of temperature of a hundredth of a degree, with an average platinum-thermometer of ·006″ wire ('Phil. Trans.,' A, 1887, p. 184). With this limiting condition it is easy to see (1) that if the ratio coils are in parallel with the thermometer, the sensitiveness is doubled by making the ratio coils very small; (2) that if the ratio coils are in series with the thermometer, the sensitiveness is doubled by making the ratio coils as large as possible. In every case it is necessary, in order to secure accurate compensation for the variation of the leads, that the ratio coils should be equal, and that the bridge-wire should be inserted in the circuit between the thermometer and the adjustable balancing coils. The arrangement (2) with the ratio coils in series with the thermometer, involves leading the battery current in through the bridge-wire sliding contact, which is generally unadvisable on account of possible disturbance produced by variation of resistance at the contact, or by breaking the circuit to readjust. The first arrangement is therefore generally adopted, and some advantage is gained in this case by making the resistance of the ratio coils considerably *smaller* than that of the thermometers, provided that they are not made so small as to be appreciably heated when the working current is passed through the thermometer. In this particular box the ratio coils had a resistance of 6·4 ohms, or about a quarter of the normal thermometer at 0° C. They were each constructed of two ·008″ platinum-silver wires in parallel, and adjusted for equality of temperature-coefficient. With a working current of ·002 ampere through a 25·6 ohm. thermometer constructed of ·004″ wire, the heating effect in the thermometer would be nearly a thousandth of a degree, and the current through the ratio coils would be nearly one-hundredth of an ampere, which would not produce any material rise of temperature.

In differential work it is seldom necessary to take any account of current heating of the thermometers, unless the difference of temperature is considerable, or the thermometers are very differently situated. With a single thermometer, it is desirable to measure the heating effect occasionally, especially if a galvanometer of suitable sensibility is not available, or an excessive current is employed for any other reason. The simplest method of determining the rise of temperature due to the current in any case is to use two similar cells of low resistance, preferably storage cells, which can be connected in series or parallel by changing a switch. The normal measurements are effected with the cells in parallel. On putting the cells in series, the current through the thermometer is very nearly doubled, and the heating effect is nearly quadrupled, provided that it is small. The correction for current heating is obtained by subtracting from the first reading one-third of the difference between the two readings. I have used this method in all accurate work for the last ten years, and it appears to be worth recording, as there is some conflict of opinion with regard to the proper method of procedure. HARKER and CHAPPUIS measured the heating effect of the current on one of their thermometers at 0° C., and, assuming that the effect would vary as the watts expended on the coil, they adjusted the external resistance in the battery circuit so as to give always *the same watts* in the coil at different temperatures. This is not quite correct, since the cooling effect of conduction and convection-currents of air in the tube increases nearly in proportion to the absolute temperature. The effect of radiation also becomes important at high temperatures, and the cooling is then more rapid. If, therefore, the watts are kept constant, the heating effect will diminish as the temperature rises, and a small systematic error will be produced. Assuming that the rate of cooling increases as the absolute temperature θ, and that the watts are kept constant, the heating effect at any temperature θ is $273h/\theta$, where h is the heating effect in degrees of temperature at 0° C. It is easy to see that the corresponding systematic error in the temperature t on the centigrade scale, would be approximately $ht(t-100)/373(t+273)$. In the case described by HARKER and CHAPPUIS (‘Phil. Trans.,’ A, 1900, p. 62), the heating at 0° C. was ·014° C. The systematic error at 50° C. would be only ·0003°, and at 445° C. only ·008°.

A better rule is to keep the *current* through the thermometer constant. In this case the heating effect is nearly constant, since the resistance of the thermometer increases very nearly as fast as the rate of cooling, *i.e.*, a little faster than the absolute temperature. In this case it is evident that the error would be negligible, even if the heating effect at 0° C. were as large as a hundredth of a degree. In any case, provided that a galvanometer of suitable sensibility is used, the error due to the heating effect will be practically negligible, even if no account is taken of it, *i.e.*, if the resistance in the external battery circuit is kept constant. It is assumed, of course, that the current is kept flowing through the thermometer continuously, so that the heating effect is steady. Some writers have advised keeping the circuit closed for the shortest possible time. This method should never be used in accurate work. Other writers have apparently found more serious difficulties, and appear to have considered that the heating effect was fatal to accurate work. This view has arisen merely from the use of unsuitable apparatus or faulty arrangements.

(20.) *Ice-point Apparatus.*

In accurate work the heating effect should never exceed a hundredth of a degree, and the correction can be readily applied if required, in case the current through the thermometer is not kept constant. It is possible, however, to obtain consistent results, even if the heating effect amounts to several tenths of a degree, provided that the conditions are steady, and that the heat generated is not allowed to accumulate. This condition is generally satisfied in a bath of saturated steam or vapour, or in a well-stirred bath of liquid, but not at the freezing or melting point of a bad conductor. Errors due to variation of the heating effect are most common in observing the ice-point. The density of the water at this point is nearly constant, so that the convection currents are feeble, and the thermometer, if the current is excessive, or if there is considerable conduction of heat along the stem, as in the case of thick porcelain tubes, may become surrounded by a layer of water at a temperature appreciably above the freezing-point. Some advantage is gained in this case by employing a stirrer to make the water circulate vigorously through the ice. For this purpose I devised the following apparatus, which proved very useful for investigating the heating effects of large currents at the freezing-point, where accurate results could not be obtained by merely surrounding the thermometer with ice. The apparatus consists of two concentric cylindrical vessels. The thermometers are placed in the inner vessel. The whole apparatus is filled with melting ice, with enough water from previously melted ice to fill up the interspaces. The bottom and top of the inner vessel are fitted with gauze strainers to prevent circulation of the ice. The water is caused to circulate through the ice by means of a centrifugal stirrer below the middle of the inner vessel, worked by a shaft passing up through the centre of the apparatus. The thermometers should be deeply immersed, if they have thick tubes, or copper or silver leads, in order to minimise the effect of conduction along

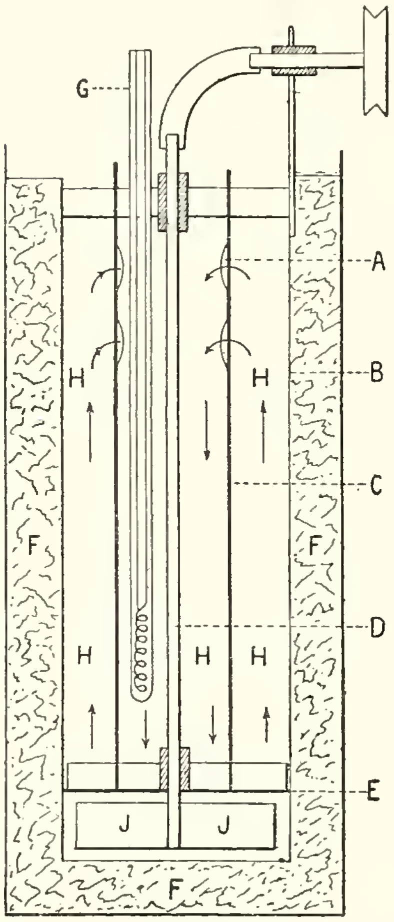

Fig. 3. Ice-point Apparatus.

A, gauze-covered apertures; B, outer vessel; C, inner vessel; D, shaft of stirrer; E, gauze strainer; F, lagging; G, thermometer; H, ice; J, stirrer blades.

the stem. It is probable that a similar method would give the most accurate results in all cases, but if the current heating is small its variation may generally be neglected, so that no special apparatus is required.

(21.) *Insulation of Thermometers.*

Defective insulation due to moisture condensed in the tubes is sometimes a source of error in accurate work at the ice-point with thermometers of high resistance, if the tubes are not sealed. To avoid this, the instruments may be fitted with a small inner tube leading to the bottom, through which dry air may be forced occasionally. A better plan, which I first adopted in 1893, for accurate work at low temperatures, is to seal the platinum leads through the glass so that the whole thermometer is air-tight. In this case the platinum leads may conveniently terminate in glass cups, and may be connected to the external leads by mercury or by fusible alloy,[*] as indicated in fig. 4. If the tubes are made of lead-glass, there is no difficulty in fusing the four leads through the tube. The joint will even stand sudden exposure to high-pressure steam without cracking, if properly annealed. All the thermometers employed in my experiments on the temperatures of steam in the cylinder of a steam-engine ('Proc. Inst. C.E.,' November, 1897), were made in this manner in order to make the joint perfectly steam-tight at high pressures. The method cannot be applied to porcelain tube pyrometers, but in this case the employment of a high resistance is out of the question for other reasons. I recommended hermetic sealing for the Kew thermometers ('Nature,' October, 1895), but it was not adopted, as the instruments were of low resistance, intended primarily for high temperature work. With such an instrument it is easy, as the recent report of the Kew Observatory shows ('Proc. Roy. Soc.,' November, 1900), to obtain an order of accuracy of a hundredth of a degree on the fundamental interval, which is all that is required for work at high temperatures; but it would be unreasonable to expect to be able to work to the thousandth of a degree, except under the best conditions, with the most skilful observers.

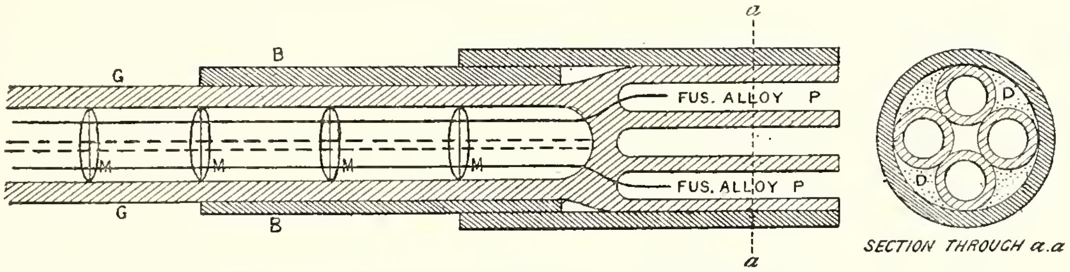

Fig. 4. Hermetically-sealed Thermometers.

B, brass tube; C, compensator; D, plaster of Paris; G, glass tube; M, mica discs; P, pyrometer leads.

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[*] I originally employed common solder, but the fusible alloy, first suggested by GRIFFITHS, appears to make a good connection and is more easily managed, though it could not be used in the steam-engine experiments.

(22.) *Differential Measurements.*

The only thermometric measurement requiring the highest accuracy in the present investigation was the difference of temperature between the inflowing and outflowing water at the two ends of the calorimeter. As this difference was obtained by a single reading of a pair of differential thermometers, all the minor errors and corrections were practically eliminated. Further, as there was no particular advantage to be gained by observing the fundamental interval with greater proportionate accuracy than the differential measurement, many special precautions, such as measuring the current heating, or keeping the current constant, were rendered superfluous. For the same reason it was unnecessary to secure the highest possible accuracy in the comparison of the coils of the box (as only a few of the smallest were used for the differential measurement), and no attempt was made to keep the temperature of the box approximately constant (to minimise possible errors due to imperfect compensation, or variation of temperature), although such precautions would naturally be adopted in many other investigations. It was sufficient to make sure that the vernier was correctly set and read, and that the sensitiveness of the galvanometer was suitable for the differential measurement.

The galvanometer employed in this investigation was specially made for the work by Messrs. Nalder Bros., to my order, in 1896. It was an astatic instrument, with four small coils of 5 ohms each. It had a fairly small and light magnet system, and a light plane mirror about 4 millims. in diameter, and was fitted with a long silk suspension, and a symmetrical system of control magnets above and below. The suspension might have been more delicate, and the magnet and mirror system lighter, with a smaller moment of inertia, but as the sensitiveness proved to be ample for the purpose, no alterations were made. The most important point for our work was the astaticism of the magnets. It was quite impossible to work with a sensitive non-astatic galvanometer owing to disturbance from the electric railway. But the astatic instruments, if properly adjusted, were very little affected. It was necessary to keep the time of swing short to secure sufficient rapidity of observation, but even with this restriction there was no difficulty in adjusting the galvanometer to give a deflection of four or five scale-divisions for a thousandth of a degree with a current of about one two-hundredth of an ampere through the thermometers. The deflections were observed with a microscope carrying a fine scale and a micrometer eye-piece. No attempt was made to adjust the contact to the exact balance point. It was merely set to the nearest millimetre division of the bridge-wire, and the galvanometer deflection observed on reversing the battery current. The exact balance reading could be easily calculated from this by observing the deflection per millimetre of the bridge-wire, which remained fairly constant. The mean temperature difference was worked out to the ten-thousandth of a degree. It appears probable from the observations that the error very rarely amounted to as much as one two-thousandth of 1° on a rise of temperature of 8°.

(23.) *Reduction of Results to the Hydrogen Scale.*

A most important factor in the variation of the specific heat of water, as ROWLAND was the first to point out, is the correction to the absolute scale of the readings of the particular thermometer employed in the research. In the present case, the temperature observations were taken with platinum-thermometers of standard wire, and were approximately reduced to the absolute scale by the difference-formula,

$$t - pt = dt\,(t - 100)/10{,}000 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

The recent observations of Messrs. HARKER and CHAPPUIS ('Phil. Trans.,' A, 1900) with a constant-volume nitrogen thermometer have confirmed my conclusion that a formula of this type represents the deviation of the platinum-thermometer from the absolute scale within the limits of error of observation over the range 0° to 600° C. A similar conclusion follows from the comparison by GRIFFITHS ('Phil. Trans.,' 1893) and by WAIDNER and MALLORY ('Phil. Mag.,' July, 1899) of mercury-thermometers standardized at the International Bureau with platinum-thermometers from 0° to 25°, and from 0° to 50°.

The value of the difference-coefficient d in this formula was assumed to be 1·50 from the mean of a number of observations taken at different times with different samples of the wire. The thermometers themselves were not directly tested, as the variation of the difference-coefficient for different specimens of the pure wire is in nearly all cases less than the probable error of a single determination. The particular sample of wire employed for thermometers E, on which most of the results depend, was tested by Mr. TORY ('Phil. Mag.,' 1900) by comparison with the original standard wire from which it was drawn, and found to be identical.

The limits of variation of the difference-coefficient for pure platinum wire, as tested by competent observers, assuming the normal boiling-point of sulphur to be 444°·53 C., on the scale of the constant-pressure air-thermometer, is only 1·49 to 1·51. The greater part of this variation is probably due to errors of observation and differences of annealing. A variation of 0·01 in the value of d would affect the specific heat of water by only 1 part in 10,000 at 0° or at 100° C., and by much less at intermediate points of the range. If we had assumed the boiling-point of sulphur to be 445°·27 C.,* as found by HARKER and CHAPPUIS with a constant-volume nitrogen-thermometer, the value of d would have to be increased to 1·54, which would increase the values of the specific heat of water by only 4 parts in 10,000 at 0° C., and by 2 in 10,000 at 25° C. The difference in the above values of the boiling-point of sulphur may possibly be explained as due to a real difference in

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* CHAPPUIS has recently ('Phil. Mag.,' 1902) accepted the results of HOLBORN and DAY for the expansion of Berlin porcelain, which reduce his value for the boiling-point of sulphur to 444°·7 C.—*Added March* 11, 1902.

the scales of the constant-volume and constant-pressure thermometers, as we have little direct experimental knowledge of the relation of the scales at these temperatures. It may be equally due to systematic differences of reduction of the observations, as for instance in the application of the correction for the expansion of the envelope of the gas-thermometer. The correction applied by CHAPPUIS,* obtained by extrapolation of a formula deduced from observations over the range 0° to 100° C., is much larger than similar corrections found by CALLENDAR and BEDFORD for hard glass and porcelain from observations over the range 0° to 600° C. The lower value of the boiling-point of sulphur obtained by CALLENDAR and GRIFFITHS in 1890 was confirmed by CALLENDAR with a different instrument in 1893, and later by EUMORFOPOULOS. Since the uncertainty of the correction for the expansion of the envelope is so great (CALLENDAR, 'Phil. Mag.,' December, 1899), it was decided to adopt the older value, which has been in use for 10 years, rather than to attempt a special correction based on the probable scale difference of the constant-pressure and constant-volume thermometers.

The uncertainty of this correction is mainly due to the difficulties of gas thermometry. The scale of a platinum-thermometer constructed of pure wire is so easily and so accurately reproducible, that it appears practically certain, as I have already explained at some length in a previous paper ('Phil. Mag.,' December, 1899), that it would afford a more convenient standard of reference than the hydrogen thermometer for scientific purposes. By employing a standard difference-formula, such as (1) for reduction of platinum temperatures to the absolute scale, we should obtain results in sufficiently close agreement with the thermodynamical scale for all practical purposes, and we should be saved the trouble and confusion incidental to small uncertain corrections. From this point of view it would be more scientific to omit any further reduction to the hydrogen scale, but it may be of interest to indicate the nature and the probable magnitude of the correction.

Since the parabolic difference-formula (1) was established and verified by means of observations with air- or nitrogen-thermometers, it would be most natural to assume that the scale obtained by its application coincided very closely with that of the nitrogen-thermometer, and to reduce the results to the hydrogen scale by the application of the table of corrections given by CHAPPUIS, deduced from the following formula for the difference,

$$t_n - t_h = t\,(t - 100)\,(+\,6{\cdot}318 + {\cdot}00889t - {\cdot}001323t^2) \times 10^{-6} \quad . \quad . \quad (2).$$

This formula has been applied to our results by GRIFFITHS ('Thermal Measurement of Energy,' Cambridge, 1901), who gives a table of the corrected values. But there

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* CHAPPUIS has recently ('Phil. Mag.,' 1902) accepted the results of HOLBORN and DAY for the expansion of Berlin porcelain, which reduce his value for the boiling-point of sulphur to 444°·7 C.—*Added March* 11, 1902.

are some objections to be considered. CHAPPUIS' formula (2) refers to the constant-volume nitrogen-thermometer at 100 centims. of mercury initial pressure, whereas the difference-formula (1) was obtained with a constant-pressure air-thermometer at 76 centims. pressure. Moreover, formula (2) makes the difference negative between 73° and 100°, as shown in the second column of Table IV., so that the correction to the specific heat would change from -2 in 10,000 at 80° to $+6$ in 10,000 at 100°. The negative differences are of the same order as the probable errors of the observations. CHAPPUIS himself considered them to be impossible, and gave a revised formula for the mean coefficient of expansion of nitrogen, from which the "corrected" values in the third column have been calculated. He has since recalculated the values on a slightly different assumption, namely that the pressure-coefficient $(dp/dt)/p_0$ of nitrogen at an initial pressure $p_0 = 100$ centims., reaches a minimum value ·0036738 at 80° C., and then remains constant at all higher temperatures. Taking the fundamental coefficient $(0° - 100°)$ as being ·00367466, the difference of the scales above 100° C. would be linear, and would amount to ·023° per 100°. The effect of this assumption between 0° and 100° does not differ materially from M. CHAPPUIS' first "corrected" results.

It is interesting to compare CHAPPUIS' results with those calculated from the observations of JOULE and THOMSON. In order to represent the results of these observers more accurately, especially in the case of hydrogen, I have added a term b to their formula, to represent the "co-volume," as in the later equations of HIRN and VAN DER WAALS. The equation of JOULE and THOMSON then becomes

$$v - b = \mathrm{R}\theta/p - \mathrm{A}/\theta^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which is practically equivalent for moderate pressures to the formula devised by CLAUSIUS to represent the divergences of CO_2 from VAN DER WAALS' formula. The differences calculated from this formula for nitrogen and hydrogen at constant-volume and 100 centims. initial pressure, are of the same order of magnitude, but not quite so large, as the "corrected" differences of CHAPPUIS. On the whole the agreement appears very satisfactory. It would have been still closer if the nitrogen-differences observed by CHAPPUIS in the second series of his observations between 0° and 25° had not been raised by ·007° in order to make the curve pass through the zero point. (See CALLENDAR, 'Proc. Phys. Soc.,' March, 1902, where the subject is more fully discussed.) It should be remarked, on the other hand, that the observations of JOULE and THOMSON can be represented well within the limits of experimental error by the formula of VAN DER WAALS. According to the latter formula the pressure at constant-volume is a linear function of the temperature, and the differences between the scales of all constant-volume thermometers should be identically zero. The evidence of the experiments of JOULE and THOMSON taken alone is therefore inconclusive, but it may be stated that the observations of AMAGAT, WITKOWSKI, and others on the compressibility of gases over considerable ranges of temperature and pressure, indicate a real difference between the scales, similar to that calculated from the observations of JOULE and THOMSON by the modified equation (3).

The differences between the nitrogen and hydrogen scales at a constant pressure of 1 atmosphere calculated from the observations of JOULE and THOMSON by the same equation are given in the same table. In each case the difference between the hydrogen scale, t_h, and the absolute scale, θ, is added. In the case of the constant-pressure thermometer the correction is larger than at constant-volume, but there is less uncertainty in its value, as the results calculated by different formulæ (*e.g.*, VAN DER WAALS and CLAUSIUS) are very nearly the same.

TABLE IV.—Difference between Scales of Nitrogen and Hydrogen Gas-Thermometers.

Temperature, Centigrade.	CHAPPUIS, formula (2).	CHAPPUIS, corrected.	JOULE-THOMSON, constant-volume, 100 centims.		JOULE-THOMSON, constant-pressure, 76 centims.	
°	$t_n - t_h$.	$t_n - t_h$.	$t_n - t_h$.	$t_h - \theta$.	$t_n - t_h$.	$t_h - \theta$.
10	+ ·0057	+ ·0053	+ ·0030	+ ·0005	+ ·0062	+ ·0011
20	+ ·0095	+ ·0087	+ ·0050	+ ·0009	+ ·0103	+ ·0019
30	+ ·0113	+ ·0105	+ ·0065	+ ·0012	+ ·0131	+ ·0024
40	+ ·0110	+ ·0110	+ ·0073	+ ·0013	+ ·0143	+ ·0026
50	+ ·0086	+ ·0103	+ ·0073	+ ·0013	+ ·0144	+ ·0026
60	+ ·0049	+ ·0090	+ ·0066	+ ·0013	+ ·0130	+ ·0025
70	+ ·0010	+ ·0069	+ ·0055	+ ·0011	+ ·0112	+ ·0020
80	− ·0023	+ ·0045	+ ·0044	+ ·0008	+ ·0083	+ ·0015
90	− ·0032	+ ·0022	+ ·0025	+ ·0004	+ ·0044	+ ·0008

In order to reduce the value of the specific heat of water expressed in terms of any scale of temperature t' to the corresponding value expressed in terms of any other scale of temperature t'', it is only necessary to multiply by the factor dt'/dt''. This factor is readily obtained if the formula giving the relation between t' and t'' is known. For instance, in order to reduce from the platinum scale by means of the difference-formula, we obtain at once by differentiation of the formula the factor

$$dpt/dt = 1 + (100 - 2t)\,d/10{,}000 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Since the specific heat of water varies so little from unity, the correction to be added at any point may be taken as being practically equal to the excess of the correction factor above unity. The corrections from the nitrogen to the hydrogen scale, obtained by differentiation from the table of differences above, are very uncertain, and are for this reason given only to the nearest part in 10,000. The platinum-scale correction is given for comparison in the last line of the table.

Table V.—Corrections (Parts in 10,000) to be added to reduce the Value of the Specific Heat of Water from the Nitrogen to the Hydrogen Scale.

Temperature, Centigrade	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°	100°
Chappuis, formula (2)	+6	+5	+3	+1	−1	−3	−4	−4	−2	+1	+6
,, corrected	+6	+4	+3	+1	+0	−1	−2	−2	−2	−2	−2
Joule-Thomson, constant-volume, 100 centims.	+4	+3	+2	+1	+0	−0	−1	−1	−2	−2	−3
Joule-Thomson, constant-pressure, 76 centims.	+7	+5	+3	+2	+1	−1	−2	−2	−3	−4	−5
Platinum scale correction by difference-formula (1)	+150	+120	+90	+60	+30	0	−30	−60	−90	−120	−150

It will be observed that the correction in any case is very small, and that the uncertainty of the correction is nearly as large as the correction itself. A change of nearly 1 in 1000 in the correction at 100° is produced, if we adopt the "corrected" results of Chappuis instead of the table taken by Griffiths. On the whole, as the difference-formula (1) was obtained by comparison with a constant-pressure air-thermometer at 76 centims., we shall probably be most nearly correct if we apply the corrections calculated from the observations of Joule and Thomson for air under the same conditions. The corrections thus obtained do not differ materially from those applied by Griffiths (they agree to 1 in 5000), except at 90° and 100°, where they differ by 5 and 11 in 10,000 respectively. I have therefore assumed the corrections calculated from Joule and Thomson in reducing the results to the hydrogen scale in Table XII., Section 37.

The value 1·54 for the difference-coefficient already referred to was obtained by Harker and Chappuis with a constant-volume nitrogen-thermometer at 56 centims. initial pressure. The corrections for this case can be calculated from the observations of Joule and Thomson by reducing those for the constant-volume thermometer given in Table IV. in proportion to the initial pressure, namely, in the ratio 56 to 100. It happens that if our results are reduced by employing Chappuis and Harker's value of the difference-coefficient, 1·54, and are then corrected to the hydrogen scale by applying the correction for the constant-volume nitrogen-thermometer at 56 centims., the results are identical with those obtained by using the difference-coefficient, 1·50, and then applying the correction for the constant-pressure air-thermometer. This agreement, however, is not really so satisfactory as it appears at first sight, because, according to the theory on which it is based, the correction to the hydrogen scale does not follow the same function as the difference-formula, and the difference in the values of the coefficients assumed, namely, 1·50 and 1·54, cannot be entirely explained by the difference of the scales at the boiling-point of sulphur.*

Part IV.—Calorimetry.

(24.) *Temperature Regulation.*

The question of temperature regulation was particularly important in this method of calorimetry. It also presented exceptional difficulties on account of the form of the calorimeter, and the large range of temperature to be covered. The apparatus employed for this purpose was made in the summer of 1895, and I spent a good deal of my leisure time during the session 1895–96 experimenting with various forms of regulator before I was able to obtain a satisfactory arrangement.

On account of the extreme length of the calorimeter (over 1 metre), and since it was necessary to have both the ends accessible for inserting leads and thermometers, I decided to employ a tube form of water-jacket open at both ends in place of the more usual bath and stirrer. The most convenient method of maintaining such a jacket at a constant temperature appeared to be by means of a vigorous water circulation maintained by a centrifugal pump. The apparatus constructed for this purpose is shown diagrammatically in fig. 5. It was intended to serve as heater, regulator and circulating pump simultaneously. The annular bulb AB was filled with oil, the expansion of which actuated a gas regulator in the usual manner. The revolving blades CC of the centrifugal pump were connected through the gland D with a water motor by means of a short piece of stiff rubber tubing. The circulating

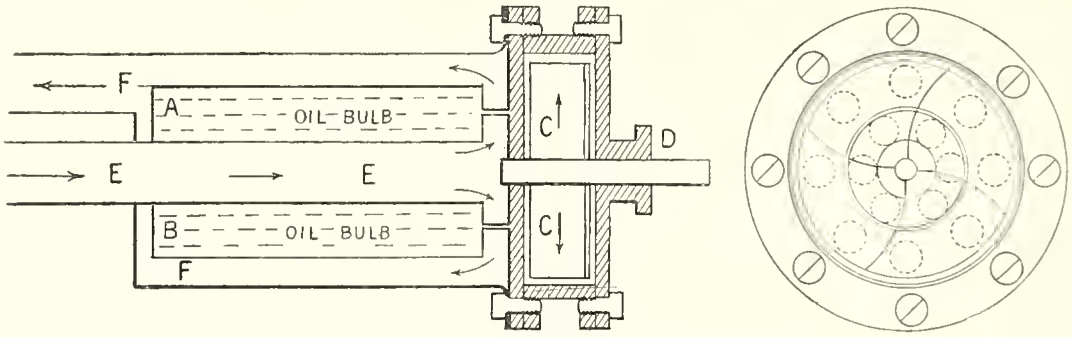

Fig. 5. Heater, Circulator, and Regulator.
AB, oil bulb; C, stirrer blades; D, gland; E, inflow; F, F, outflow.

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* The Joule-Thomson equation, extrapolated to 445°, would make the constant-volume thermometer read two or three-tenths of a degree higher than the constant-pressure thermometer, which would account for the difference between Chappuis' corrected result, 444°·7 C., for the sulphur boiling-point, and the value, 444°·53 C., obtained by Callendar and Griffiths.—*Added March* 11, 1902.

water was sucked in through the central tube E, 1 inch in diameter, and ejected through the annular space surrounding the bulb of the regulator by the tube F. The whole was mounted on a large gas burner, and shielded with an asbestos screen.

The object of placing the regulator bulb *inside the heater*, and in close proximity to the pump, was to secure quickness of action in response to any change in the gas-pressure. The violent stirring, and the comparatively small capacity of the heater in proportion to the bulb favoured this result. It was most important that the regulator should be very sensitive, and that there should be no forced oscillations of temperature, because the jacket-temperature determined that of the inflowing water-supply to the calorimeter, and did not merely affect the external heat-loss. Any temperature oscillation would produce a serious effect on the results, especially on the smaller flows, in which the total mass of water passing, about 250 grammes in 15 minutes, was not very large compared with the effective thermal capacity of the calorimeter, which was about 50 grammes.

When the regulator was made sufficiently sensitive to cut off the gas for a very small change of temperature, I found it necessary at the higher points of the range, where a large supply of gas was required, to adjust the by-pass so that, if the regulator were cut off, the temperature would very nearly reach the required point. Forced oscillations could only be avoided if the regulator controlled a very small fraction of the heat supply, acting merely as a fine adjustment on the temperature of the system. Under these conditions, however, when the total gas-supply was large, any small accidental change in the gas-pressure might exceed the limits of control of the regulator. A rapid change in the quality of the gas produced similar effects. It was therefore absolutely necessary at the higher temperatures to keep the gas-pressure very constant. The best forms of gas-governor were tried, but did not prove sufficiently delicate. I therefore fitted up a large copper gas-holder, delicately suspended and counterpoised by means of a steel tape passing over a wheel with ball bearings so as to move with very little friction. This arrangement proved to be capable of regulating the pressure to within a tenth of a millimetre of water. The large capacity of the gas-holder tended also to minimize the effect of sudden small variations of quality of the gas, such as might be produced by air in the pipes, &c.

The action of this constant-pressure gas-supply was so perfect that for many purposes no other temperature-regulator was required, and as a matter of fact none was used in many of the preliminary experiments. Since variations of gas-pressure were practically eliminated, it was found to be unnecessary to have the regulator bulb inside the heater, and the fine adjustment-regulator was placed in the tank C, (Barnes, figs. 14 and 15, pp. 211, 213). This regulator was employed to operate an electric heating arrangement, as described by Dr. Barnes in Section 4, in which slow period oscillations were prevented by the device of the reciprocating contact suggested by Gouy ('Journ. de Phys.,' 1897, p. 479). I found it necessary to introduce a few modifications into the arrangement as described by GOUY, the most important of which was to make the relay put another lamp in series, instead of breaking the circuit. This prevented the destructive sparking at the break, which was a serious matter with a 100 candle-power lamp. Of course, the greater part of the work still fell on the constant-pressure gas-supply, which was mainly responsible for the excellence of the results at high temperatures.

(25.) *Preliminary Experiments on the Specific Heat of Mercury.*

Our first experiments by the steady-flow electric method of calorimetry were made on the specific heat of mercury, as it presented fewer experimental difficulties than water. Since mercury is itself a conductor of suitable specific resistance, it was unnecessary to insert a heating conductor in the fine flow-tube, which greatly simplified the fitting together of the apparatus. The conducting properties of mercury were also utilised in the design of an electrical device for maintaining a constant head so as to secure uniformity of flow. The level of the mercury in the reservoir was regulated by a platinum wire contact which actuated an electro-magnet compressing a small rubber tube which supplied mercury to the reservoir. As soon as the level fell below the platinum point, the contact was broken, the armature released, and more mercury supplied. The inflow was arranged to keep the mercury near the platinum point in perpetual agitation, so that there was no sticking or hunting of the regulator. The whole arrangement was fitted to a wooden bracket belonging to a Geissler pump, which could be hung up on the wall at different levels when it was required to alter the flow of mercury in a given ratio. The flow was regulated and steadied by passing the mercury through fine glass tubes immersed in a tank of water before entering the calorimeter. In measuring the flow of mercury, the time of switching over was automatically recorded on an electric chronograph by the momentary contact of the mercury thread with an edge of platinum foil, which diverted the flow from one beaker to another.

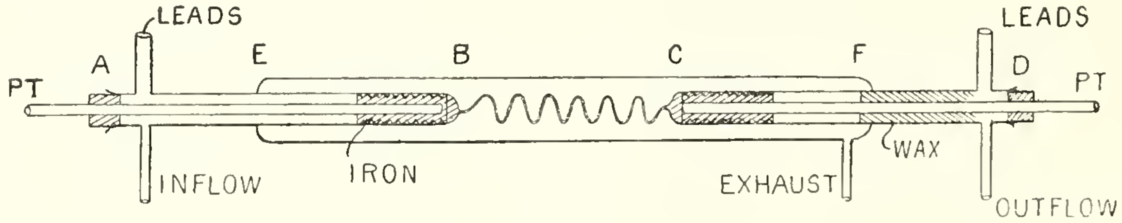

Fig. 6. Diagram of Mercury Calorimeter.

The design of the calorimeter itself will be readily understood from the accompanying diagram (fig. 6). The inflow and outflow tubes AB and CD are exactly similar, about 2 centims. internal diameter and 25 centims. long. They are connected by the fine flow-tube BC, of 1 millim. bore and 1 metre long, coiled in a short spiral of about 2·5 centims. diameter. The vacuum jacket EF extends about 13 centims. along the inflow and outflow tubes, and is provided with a side tube for exhausting. The inflow and outflow tubes are provided with two side openings, the smaller of which was intended for the inflow or outflow of mercury, and the larger for the leads conveying the electric current. In some of the earlier experiments the larger tubes were fitted with a pair of delicate mercury-thermometers for watching the progress of the experiment, and observing when the conditions became steady. But these mercury-thermometers were found to be of little or no use, and the large side-tubes were subsequently removed to facilitate the fitting of the calorimeter in a tubular form of water-jacket.

(26.) *Method of Determining the True Mean Temperature of Outflow.*

By far the most important point in this method of calorimetry is the device adopted for obtaining the true mean temperature of the outflowing liquid, and securing a definite measurement of the electrical watts expended in heating it. If a thermometer were merely inserted in the outflow-tube, leaving a free space all round for the circulation of the liquid, it is evident that the heated liquid would tend to flow in a stream along the top of the outflow-tube, and that the thermometer might indicate a temperature which had little or no relation to the mean temperature of the stream. It is easy to make an error of 20 per cent. in this manner, as I found in my preliminary experiments in the summer of 1896. A fairly uniform distribution of the flow might be secured by making the space between the thermometer and the outflow-tube very narrow. But this leads to another difficulty in the case of mercury. As the space is narrowed, the electrical resistance is increased, and an appreciable quantity of heat, which cannot be accurately estimated, is generated in the vicinity of the thermometers.

Both the difficulties above mentioned were overcome in the mercury experiment by fitting the inflow and outflow tubes with soft iron cylinders, 6 centims. long, turned to fit the tubes, and bored to fit the thermometers. The soft iron had a conductivity about ten times that of mercury for both heat and electricity. The heat generated by the current in the immediate vicinity of the thermometer bulbs was so small that the watts might fairly be calculated from the difference of potential between the iron blocks at the middle points of the bulbs. The mercury stream was forced to circulate in a spiral screw thread of suitable dimensions cut in the outer surface of the blocks, which prevented the formation of stream-lines along one side of the tube, and secured uniformity of temperature throughout the cross section of the outflow-tube. The high conductivity of the iron also assisted in securing the same result.

A precisely analogous device for averaging the outflow temperature was applied in the water calorimeter. The bulb of the thermometer was fitted with a copper sleeve of high conductivity, on the outside of which a rubber spiral was wound to fit the outflow-tube as closely as possible. The accuracy of fit was found to be much more important in the case of water than in the case of mercury. The reason of this is that, the thermal conductivity of water being 10 or 15 times less than that of mercury, the accurate averaging of the outflow temperature is more dependent on the uniformity of the spiral circulation and the complete elimination of asymmetric stream-lines.

In order to obtain a perfect fit for the sleeves with their spiral screws, it was necessary that the bore of the outflow-tube should be as nearly uniform as possible, and accurately straight. It was most essential that there should be no constriction at the points of junction E and F with the vacuum-jacket, and that the external portions of the tubes AE, FD should not be of smaller bore than the portions inside the vacuum-jacket, though it would not matter much if they were a little larger. These details of the design, which determined the choice of the dimensions of the tubes, had all been carefully worked out before the ordering of the first six calorimeters with vacuum-jackets in October, 1896, and the importance of the straightness and uniformity of the tubes was clearly explained in the specification. There was some difficulty in making the calorimeters accurately to specification, and when they arrived about three months later, it was found that this particular detail had been somewhat overlooked. It was consequently a difficult matter, even with a soft rubber spiral, to secure sufficient perfection of fit, and the accuracy of many of the earlier experiments was seriously impaired.

The effect of an imperfect fit was to permit part of the heated stream to escape directly past the thermometer, so that the temperature indicated by the outflow thermometer was lower than the true mean of the flow. This defect was less apparent with a large flow or a large rise of temperature, either of which conditions tend to promote mixing of the liquid and the attainment of a proportionately greater uniformity of temperature. A good illustration of this is afforded by the results quoted by Dr. BARNES in Section 7 of his paper, p. 237, which were obtained with one of the first three calorimeters in which the bore was undoubtedly defective. The apparent diminution of the heat-loss per degree rise with increase in the rise of temperature is probably due in part to the more perfect mixing of the stream caused by the greater differences of temperature, which promote instability of flow and increase the formation of eddies. I may add that I have repeatedly observed the same effect in my experiments on steam by a similar method. With steam it is much more difficult than with water to secure a true average of the outflow temperature. Any imperfection of fit or circulation immediately produces the observed effect in an exaggerated form.

The greater irregularity of the results (BARNES, Section 7) for the small flows is probably in part accidental, but is also characteristic of imperfect fitting of the rubber spiral in the outflow-tube, which is obviously more detrimental in the case of the smaller flows. As a consequence of this irregularity of the small flows, I do not think these results can be fairly treated by the somewhat artificial method adopted by Dr. BARNES. The extrapolation of the heat-loss per degree for zero rise of temperature is too uncertain in the case of the small flow. The natural method of treatment would be to take the difference between the sum of the electrical watts ΣEC, and the sum of the heat-watts $\Sigma JQd\theta$, and divide by the sum of the temperature differences $\Sigma d\theta$, to find D for each flow. Combining the two flows in the usual manner, without any arbitrary assumptions, we thus obtain practically the same result as that deduced by Dr. BARNES.

(27.) *Design of the Water Calorimeter.*

The design of the water calorimeter presented certain points of difficulty which were not settled without some preliminary experiments on the conditions of flow in fine tubes. The greater part of these experiments were carried out in the summer of 1896, in the Thermodynamical Laboratory of the Engineering Building of McGill College, with the kind permission of Professor NICOLSON, who erected for this purpose a large supply-tank of water on an upper floor in a room at a very constant temperature. The results of some of these experiments were mentioned in a paper on the 'Law of Condensation of Steam,' which was communicated to the Institution of Civil Engineers in September, 1896, and read in the following year.

Since water is practically a non-conductor of electricity, it was necessary either to make the fine flow-tube of platinum instead of glass, or else to thread a conducting wire or strip of platinum through it. A fine bore *metallic* flow-tube would have presented some advantages in point of smallness of radiation loss, but in the end I decided to use a glass flow-tube and a central conductor, chiefly on account of the importance of securing the greatest possible constancy and perfection in the vacuum-jacket. This could be most easily and certainly attained by making the vacuum-jacket entirely of glass.

The glass-work of the water calorimeter differed from that of the mercury calorimeter (fig. 6) only in having a straight flow-tube 50 centims. long and 2 millims. bore, instead of a spiral flow-tube 100 centims. long and 1 millim. bore. It was necessary to make the flow-tube straight on account of the difficulty of threading the conductor through it as well as the connecting wires to which it was attached. This operation would have been facilitated by using a larger tube, but, apart from this necessity, it was desirable to have the flow-tube as fine as possible to secure uniformity of temperature of cross-section and other advantages. From one point of view, it was desirable to make it as short as possible, in order to minimise the heat-loss, which depended chiefly on the surface of the flow-tube; but on the other hand it was necessary to have sufficient length to eliminate leakage of the current through the water, and to secure a suitable resistance for the conductor, and sufficient surface to prevent excessive superheating by the current. It was found that the dimensions above given satisfied the required conditions very fairly, and although there were a few minor details which could not be satisfactorily settled until the complete apparatus had been fitted up, it was not found necessary to make any changes in the essential features of the design. The three calorimeters ordered two years later by Dr. BARNES were of the same design in all important points, except that two of them had 3 millims. bore flow-tubes; but these were found to be less suitable, and were employed in very few of the tests.

(28.) *Improvements in the Design of the Calorimeter.*

Although Dr. BARNES was naturally unwilling to introduce any radical changes in the original pattern, which had proved to be capable of giving very good results, there can be no doubt that it was capable of improvement, and I had in fact already noted several points in which alterations were desirable.

The importance of uniformity of bore in the flow-tube, and particularly in the outflow-tube, has already been referred to (§ 26). This was remedied in the later apparatus. Two of the side tubes were also removed, and the other two bent parallel to the flow-tube, to facilitate insertion in the cylindrical form of jacket. These modifications were of small importance, and were made in the first calorimeters after the apparatus was received. A more important improvement in the same direction would be to have the tube for exhausting the vacuum-jacket inserted at F, fig. 6, in a direction *parallel* to the flow-tube, which would permit the water-jacket to be made much smaller, thus securing a more vigorous and uniform circulation.

It would be most important for future work to endeavour to reduce (1) the risk of error from conduction at the outflow end of the calorimeter at high temperatures; (2) the correction for the heat-loss, which amounted to 4 per cent. at the higher points of the range.

The conduction error might be reduced by including a greater length of the outflow-tube in the vacuum-jacket. This would be much more effective than lagging the exposed parts with flannel, since the flannel lagging is exposed to the temperature of the laboratory, which is much lower than that of the jacket. Besides, the lagging is apt to become damp, and takes a long time to reach a steady state. The length of outflow-tube inside the vacuum-jacket might easily be increased to 25 centims. instead of 12, with 5 centims. outside. This would greatly diminish the possible uncertainty of the conduction loss.

The heat-loss depends chiefly on the extent of surface of the flow-tube and thermometer bulb. The thermometer bulb could not be made much smaller, but the greater part of the loss arises from the flow-tube, which might be reduced to about half the external diameter, although the bore could not conveniently be made less than 1·5 millims. This would also be an advantage as diminishing both the heat capacity of the tube and the difference of temperature between the inside and outside of the glass. In heating the apparatus during exhaustion, there is some risk of breaking the flow-tube, as it heats and cools very slowly in a good vacuum. The difference of temperature between the thick flow-tube and the jacket in some cases caused the tube to bend so as nearly to touch the sides of the jacket. This effect would be reduced by making the tube thinner.

It does not appear that very much could be gained by taking excessive precautions to improve the vacuum. With a less perfect vacuum there would probably be less variation of the heat-loss, due to the evolution of minute traces of gas during exposure to a high temperature. The greater certainty of the correction in that case might compensate for its larger magnitude. The first three calorimeters, one for mercury and two for water, were exhausted in the laboratory on a five-fall Sprengel pump which I had set up some time previously for experiments on radiation and on X-ray tubes. This pump gave a very perfect vacuum, but the tubes were merely heated by hand with a bunsen burner during the process. They showed, however, approximately the same rate of heat-loss as the best of the calorimeters which were subsequently exhausted by Messrs. EIMER and AMEND in an asbestos oven. The vacuum in one of the calorimeters exhausted in the laboratory was also tested by means of a powerful oscillating discharge from a battery of Leyden jars passed through a coil surrounding the tube. This failed to induce a ring discharge inside the vacuum-jacket, although the same test would produce a brilliant discharge in the majority of commercial vacuum vessels for liquid air.

Probably the most effective method of reducing the heat-loss would be to silver the inside of the vacuum-jacket. I have tried this method in my experiments on the specific heat of steam by the electrical method with a vacuum-jacket calorimeter, and have found it very advantageous, owing to the low radiative power of the silver. The vacuum-jacket in this case requires very careful evacuating on account of the difficulty of drying the silver film.

With these improvements, the heat-loss could probably be reduced to about one-quarter of its value in the existing apparatus, and the uncertainty of the correction would be greatly diminished, though perhaps not quite in the same proportion. In any case the results obtained with a calorimeter having a very different value of the heat-loss could not fail to be a valuable confirmation of the previous work.

(29.) *Effect of Variation of Viscosity.*

The rise of temperature of the water due to friction in its passage through the tube, can be easily estimated from the observed difference of head at the inflow and outflow. I made this observation for each of the conductors mentioned on p. 117, with a flow of half a gramme per second in a tube very slightly less than 2 millims. diameter and 50 centims. long. The difference of head was found to vary from

20 to 30 centims. of water at 20° C., for different arrangements of the conductor, and different conditions of flow, being greater when the flow was non-linear. Since 1° C. corresponds to a fall of 42,700 centims. under gravity, the rise of temperature due to the friction would be less than a thousandth of a degree. This is a quantity which ought not to be neglected in working to a ten-thousandth of a degree, but the effect was practically eliminated by the method of observing the difference of temperature, which was expressly intended to eliminate small residual sources of error of this character. For each value of the flow, the difference of temperature was observed "cold" before turning on the electric current, and the "cold reading" was subtracted from the difference observed with the current passing. We are therefore concerned only with the change in the head due to diminution of viscosity with rise of temperature when the current is turned on. I found by calculation from the known variation of the viscosity, and also verified by direct observation in each case, that this amounted to only 10 per cent. of the head for a rise of 8° C. at 20° C. This would be equivalent to 2 or 3 centims. fall, or less than a ten-thousandth of a degree, a quantity which might safely be neglected. The correction would be much smaller at higher temperatures, owing to the great diminution in the viscosity.

In the final apparatus, as employed by Dr. BARNES, the difference of head would be somewhat greater owing to the rubber spirals on the copper sleeves, and the rubber cord on the central conductor. The question was raised at the Dover meeting of the British Association, and I wrote to Dr. BARNES asking him to measure the head under the actual conditions of experiment, but the apparatus happened to be dismounted at the time. We may safely conclude, however, that the difference of head could not have exceeded 1 metre of water, in which case the correction would be less than 1 in 40,000 at 20° C., and might be fairly neglected. This correction corresponds with that for the heat generated by stirring in the GRIFFITHS and SCHUSTER methods of calorimetry. It amounted in GRIFFITHS' apparatus to about 10 per cent. of the heat-supply, but was apparently negligible in SCHUSTER'S experiments.

(30.) *Radial Distribution of Temperature in the Fine Flow-Tube.*

We assume in the elementary theory of the experiment that the temperature is uniform across the section of the flow-tube at any point. It is important to consider how far and under what conditions this is true. Given the rate of external heat-loss at any point it is easy to calculate the difference of temperature between the inside and outside surfaces of the glass tube, but the distribution of temperature in the liquid can only be calculated if we assume the flow to be in straight lines parallel to the axis of the tube, and the conductor to be circular in section and concentric with the tube. Even in this simple case the solution cannot be made complete, owing to the variations of viscosity and conductivity with temperature;

but it is possible to estimate the order of magnitude of the differences involved, which is all that is really required for our purpose.

Assuming that the internal and external diameters of the flow-tube are 2 and 6 millims. respectively, and length 50 centims., and that the conductivity of the glass is ·0020 cal. C.G.S., it is easy to calculate that the mean difference of temperature between the internal and external surfaces would be of the order of one-tenth of a degree only when the final rise of temperature is 8°, and the heat loss ·050 watt per degree, as in the majority of our experiments. It will therefore evidently be unnecessary to take account of this in any of the calculations.

To find the radial distribution of temperature in the liquid, assuming the flow to be linear, I will take first the case of the metallic flow-tube, which is much the simplest. The differential equation of the radial distribution of temperature, neglecting the minute effect of longitudinal conduction, is

$$d\,(kr\,d\theta/dr)/dr = +\,vcr\,d\theta/dx \quad \ldots \ldots \ldots \quad (1),$$

in which k is the thermal conductivity of the liquid, and c the specific heat per unit volume, v the velocity of the stream, θ the temperature, r the distance from the axis, and x the distance along the tube. The velocity v is a function of r, which can be easily calculated if the viscosity is assumed constant. As a matter of fact, both the viscosity and the conductivity vary rapidly with change of temperature. The viscosity at 100° is nearly six times less than at 0° C., and its variation is accurately known. But if we assume both conductivity and viscosity constant (as we are practically compelled to do, since the variation of conductivity with temperature is quite uncertain) we shall obtain a solution which is sufficiently simple to be useful, and which can be strictly applied to small changes of temperature.

To simplify the solution still further, I shall assume the longitudinal temperature gradient $d\theta/dx$ constant over the cross-section of the tube at any point, and equal to θ'/l, where θ' is the rise of temperature observed in a length l. This will not be true near the inflow end of the tube, where the radial distribution of temperature is rapidly changing, but it will very fairly represent the *limiting state*, which is attained when the liquid has flowed along the tube for some distance.

If the flow is linear, and the viscosity constant, the velocity at any point of the cross-section is given in terms of r by the equation

$$v = 2\mathrm{V}\,(1 - (r/r_0)^2) = 2\mathrm{Q}\,(1 - (r/r_0)^2)/\pi r_0^2 \quad \ldots \ldots \quad (2),$$

where V is the mean velocity, Q the flow in cub. centims. per second, and r_0 the internal radius of the flow-tube.

Making this substitution in (1) and integrating, we obtain

$$k\,r\,d\theta/dr = \frac{\mathrm{Q}\theta'}{\pi l}\left(\frac{r^2}{r_0^2} - \frac{r^4}{2r_0^4}\right) + \mathrm{B} \quad \ldots \ldots \ldots \quad (3).$$

The constant of integration B is determined by the consideration that the temperature-gradient vanishes at the centre of the tube. Putting this condition in (3), we find $B = 0$, which materially simplifies the solution of the equation. Integrating from the temperature θ_0 of the surface of the tube, we find

$$\theta_0 - \theta = Q\theta' \left(r^4/4r_0^4 - (r/r_0)^2 - \tfrac{3}{4}\right)/2\pi lk \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

The temperature θ_1 at the axis of the tube where $r = 0$, is given by

$$\theta_0 - \theta_1 = 3Q\theta'/8\pi lk \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

The mean temperature θ_2 of the flow, allowing for variation of velocity over the cross-section, is given by the expression

$$\theta_0 - \theta_2 = 11Q\theta'/48\pi lk \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

(31.) *Electrical Method of Measuring the Thermal Conductivity of a Liquid.*

The remarkable simplicity of this expression induced me to attempt a method of measuring the conductivity of a liquid, based on the observation of the difference of temperature $\theta_0 - \theta_2$ between the tube and the mean of the flow at any point; the temperature θ_0 of the tube and the gradient θ'/l being deduced from observations of the changes of resistance of the flow-tube itself. Although this may appear at first sight a difficult and out of the way method, it possessed special attractions for me as an application of the electrical resistance method of measuring temperature, and it really offers several advantages which more than counterbalance the difficulty of the electrical measurements. The longitudinal distribution of temperature in the flow-tube was deduced from observations of the resistance of consecutive sections by the same method which I had already applied in 1886 to the determination of the conductivity of platinum. The difficulty of this part of the work was therefore largely discounted by previous experience. The advantage of the method is that the tube is its own thermometer; the temperature measured is that of the tube itself, and not that of a thermo-couple or water-bath assumed to be at the same temperature as the tube. This avoids the most common and insidious source of error in all conductivity measurements.

As compared with the plate-method of measuring the conductivity of liquids, which has been practised by WEBER and many other observers in different forms, the tube-method possesses several important advantages. (*a*) It avoids the difficulty of measuring accurately the small distance between the bounding surfaces of the liquid, or the thickness of the sheet, since the expressions (5) and (6) already given are independent of the radius of the tube, and contain only lengths and differences of temperature which are easily observed. (*b*) All uncertainties with regard to the area from which the heat is conducted, and all difficulties of boundary conditions, which cannot satisfactorily be eliminated in the plate-method, even by the employment of a guard-ring, are easily avoided in the tube-method by making the tube small in proportion to its length. (*c*) The error of the plate-method due to direct radiation through the liquid, which is quite important with a thin transparent stratum, is completely eliminated, since all the heat which is lost by the inner surface of the tube must be absorbed by the liquid itself.

GRAETZ, ('Wied. Ann.,' vol. 18, p. 79) has applied a non-electrical steady-flow method to the determination of the conductivity of a liquid, which bears a close superficial resemblance to that above described, but in reality differs from it in several fundamental points. In his method a stream of liquid at a temperature between 30° and 40° C. flows through a thin capillary tube, 10 centims. long, and 0·6 millim. bore, immersed in a water-bath at a temperature of 7° C. to 10° C. The mean outflow temperature is observed, and is also calculated in terms of the conductivity on the assumption that the flow is linear. The temperature of the external surface of the tube is *assumed* to be the same as that of the water-bath. This is the most obvious defect of his method, as the assumption could not be even approximately true unless the current of liquid through the tube were extremely slow. Unfortunately in that case the difference of temperature between the outflow and the bath, on which the measurement depends, tends to vanish; it is also more difficult to obtain the true mean temperature of a small stream owing to defective mixing in the outflow tube, and accidental sources of error due to end-effects are exaggerated. These defects might be avoided in various ways. The true mean temperature of the tube itself might be determined by making the tube very thin, and observing its expansion, or preferably its electrical resistance. Or the temperature of the outside surface might be indefinitely approximated to that of the bath by making the tube very thick, and supplying a vigorous circulation around it. The true mean temperature of the outflow might also be determined for small flows by adopting a spiral circulation similar to that employed in the present investigation. There would remain, however, a most essential point of distinction between the two methods.

In the electrical method, heat is continuously supplied by the current at a nearly constant rate as the liquid flows along the tube. The observation depends on the *limiting* difference of temperature at the end of a long tube when a *steady* radial distribution has been reached. The advantage of this is that the solution is independent of the initial or variable state, the calculation of the effect of which is much less certain on account of the steep gradients and excessive differences of temperature involved, which tend to produce disturbances in the flow. In GRAETZ' method the initial differences, amounting to 20° or 30° C., were much larger than in the electrical method, and the result entirely depends on the correctness of the assumptions made in the solution of the initial state. The final or limiting state in his method is one of uniform temperature, and cannot be utilized at all.

In carrying out the electrical method, advantage was taken of the increase of resistance of the tube with temperature in order to secure a constant temperature gradient in the latter part of the flow-tube by suitably adjusting the current, as explained below in § 34. The results were not quite as good and consistent as I had hoped to obtain, on account of want of uniformity in the platinum-tube employed. I therefore thought it best to defer publication till I could find time to repeat the observations under better conditions, but the preliminary work was distinctly encouraging, and was particularly valuable as an indication of effects to be expected in steady-flow electrical calorimetry.

(32.) *Superheating of the Central Conductor.*

The case of a glass flow-tube with a concentric conductor, which more nearly approaches the arrangement actually employed in the present investigation, leads to nearly the same differential equation, but the solution is much less simple. In the course of designing the experiment, I worked out the complete solution for this case also, including the initial state, on similar assumptions of constant viscosity and conductivity. But since the conductor cannot be held exactly central in practice, and the other theoretical conditions cannot be realized, the method cannot conveniently be applied with a central conductor to the measurement of the conductivity of liquids. For the purposes of the present investigation, moreover, since we are only concerned with the approximate estimation of a small correction, a less elaborate calculation will be more appropriate. In order not to overburden the paper with purely mathematical difficulties, it will suffice to give the solution of the limiting state for the simpler case in which the velocity of flow is assumed to be constant over the cross-section of the tube and equal to its mean value. This simplification does not materially alter the general character of the solution, and the numerical results which it gives for the calorimeters actually employed are within a few parts per cent. of those obtained when allowance is made for the variation of the velocity.

If we integrate the differential equation (1) on the assumption of a constant velocity $V = Q/(r_1^2 - r_0^2)$, where r_1 is the radius of the glass-tube, and r_0 the radius of the conductor, writing A for $Vc\theta'/2lk$, we obtain the solution

$$d\theta/dr = \mathrm{A}r - \mathrm{A}r_1^2/r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7),$$

$$\theta_0 - \theta = \mathrm{A}r_1^2 \log_e (r/r_0) - \mathrm{A}\,(r^2 - r_0^2)/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8),$$

in which the constant is determined by the condition that, neglecting external heat-loss, the gradient is zero at the surface of the glass. This gives for the difference of temperature between the surface of the wire and the surface of the glass,

$$\theta_0 - \theta_1 = \mathrm{A}r_1^2 \log_e (r_1/r_0) - \mathrm{A}\,(r_1^2 - r_0^2)/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9).$$

The mean temperature θ_2 of the outflow deduced from (8) is given by

$$\theta_0 - \theta_2 = \mathrm{A}r_1^4 \log_e (r_1/r_0)/\mathrm{S} - \mathrm{A}r_1^2/2 - \mathrm{AS}/4 \quad . \quad . \quad . \quad . \quad (10),$$

where S is the sectional area $\pi(r_1^2 - r_0^2)$ of the flow, and $\mathrm{A} = \mathrm{Q}\theta'/2\pi lk\mathrm{S}$. Equation (10) gives the superheating of the conductor above the mean temperature of the outflow. The difference (9)–(10) gives the error of the assumption that the glass is at the same temperature as the mean of the outflow at the outflow point. The limiting value of the latter error, if r_0^2 is negligible in comparison with r_1^2 (the most unfavourable case), is $\theta_2 - \theta_1 = \mathrm{AS}/4 = \mathrm{Q}\theta'/8\pi lk$.

Although the above formulæ cannot be directly applied to the experiments on the specific heat of water, it is interesting to make an estimate of the superheating of the conductor, and of the difference of temperature between the glass and the water under the assumed conditions of linear flow and concentric conductor. It is obvious from the formulæ already given, that the differences of temperature in each case are directly proportional to the heat supplied by the electric current, and inversely proportional to the length of the tube and the conductivity of the liquid. To estimate the effects numerically, we may take the rate of heat supply as $\mathrm{Q}\theta' = 5$ calories per second, or 21 watts, for the larger flows. The conductivity k of water at 25° C. may be taken as ·0016 C.G.S., but is much too uncertain to permit the estimate to be extended to other temperatures. Since $l = 50$ centims., we have $4\pi lk = 1{\cdot}00$ very nearly.

For the metallic flow-tube from equation (6) the superheating of the tube above the mean temperature of the flow in the limiting state would be about 5° C., and would be independent of the diameter. For the glass flow-tube, from equations (9) and (10), the temperature of the glass would be from 1°·5 to 2°·0 below the mean of the outflow for tubes of the dimensions employed, increasing to 2°·5 as a limit for a very large flow-tube with a very small conductor. In spite of its higher temperature the metallic flow-tube would have the advantage of a smaller heat-loss, owing to its smaller surface (1 millim. diameter instead of 6 millims.), and far lower radiative power. It would also be possible to measure the actual temperature of the metallic flow-tube at any time from its resistance, without any knowledge of the conductivity of the liquid, and without assuming the flow to be linear.

The superheating of the conductor in the glass flow-tube would naturally depend on the size of the conductor as well as that of the tube, as given by equation (10). With a wire ·8 millim. in diameter, and the flow-tube 2 millims., the superheating of the wire would be about 4°·5 for a heat supply of 21 watts. With a wire ·4 millim. diameter, and a 3 millims. flow-tube, the superheating would be about 13°·2. This illustrates the importance of having a large surface for the wire and a small flow-tube. It is probable, however, that the superheating would not directly affect the radiation loss, as platinum is a bad radiator, and water is very opaque to heat-rays from heated water.

(33.) *Methods of Eliminating Stream-Line Motion.*

It was evident from the equations above given that, since the conditions of linear flow gave rise to a systematic variation of the temperature of the flow-tube, which was directly proportional to the flow for a constant rise of temperature, it would be necessary to adopt some device for mixing the water in its passage through the tube so as to produce a nearly uniform distribution of temperature over the cross-section of the tube. The obvious method of securing this result was to employ a *stranded conductor*. This would diminish the superheating by increasing the available surface of the conductor, and would distribute the heat evenly over the cross-section of the tube, provided that the strands were separated and arranged in such a manner as to break up the stream-lines.

In order to verify the theory and observe the nature of the effects to be expected, I made some rough preliminary experiments on the superheating of various conductors in a 2 millim. tube with a steady flow of water. The general character of the flow, and the degree of mixing attained, were observed by the introduction of a colour-band of blue ink, after the method employed by OSBORNE REYNOLDS, and generally practised in hydraulic laboratories in studying the flow of liquids. The most instructive results were obtained with a stranded conductor consisting of 5 strands of ·006″ pure platinum wire. My reason for selecting this particular size of wire was that I happened to possess a considerable quantity of it, and that its temperature-coefficient was accurately known, as it was regularly employed for making thermometers.

The resistance of the stranded platinum conductor, when carrying the heating current, was measured by the Wheatstone-bridge method, by comparison with a specially constructed platinoid resistance connected in series with it. The two were connected in parallel with a post-office box, by means of which the ratio of the resistances was observed. The resistance in the arm connected to the platinoid strip was 2000 ohms, the resistance in the adjustable arm corresponding to the platinum conductor was about 6000 ohms. As the platinoid strip remained practically constant, the resistance of the platinum could be taken as proportional to the resistance in the adjustable arm. The watts on the conductor were observed by means of a Weston ammeter and voltmeter of suitable ranges.

The platinoid strip resistance, which was subsequently utilised for regulating the current, is shown very clearly at L in the bird's-eye view (BARNES, fig. 15, p. 213). It consisted of a number of strips of platinoid about 1 foot long, one-half inch broad, and $\frac{1}{32}$ inch thick, having a resistance of nearly $\frac{1}{50}$th of an ohm each. The ends of the strips were bent at right angles and amalgamated. They could be connected in series or parallel in a great number of different combinations by means of the mercury cups and copper connectors shown in the plate. For this particular experiment they were arranged two in parallel, and 19 in series, giving a resistance of nearly $\frac{1}{5}$th of an ohm, capable of carrying a current of upwards of 60 amperes without excessive heating. The maximum currents used in this experiment were about 8 amperes.

The rise of temperature of the platinum conductor in each case was found to be nearly proportional to the watts expended. This was verified by varying the number of cells employed, and keeping the water-flow constant, for each arrangement of the conductor to be tested. The superheating of the conductor was estimated by deducting from the observed rise of temperature half the calculated rise of temperature of the water, making a suitable allowance for the heat-loss. The value of the water-flow was nearly half a gramme per second in all cases, and the results were reduced to a value of $Q\theta' = 5$ calories per second to render the experiments with the different conductors strictly comparable. The actual heat-loss from the flow-tube could not be measured by this comparatively rough method, but I made some attempts to obtain comparative estimates of the temperatures of the outside of the flow-tube by winding a platinum wire round it, covering the spiral with flannel, and observing its resistance. These measurements could not lay claim to any accuracy, but were useful as an indication of effects to be expected.

TABLE VI.—Superheating of Stranded Conductor.

Form of Conductor employed.	Conditions of Flow.	Superheating.
		°
Five strands, irregular	Mixed	2·8
Same, annealed and straightened . . .	Linear	6·5
,, twisted into a rope	Linear	8·5
,, spiral fitting tube	Mixed	3·0

In the first case the wire was taken as it came from the reel. The strands were well separated, and crossed each other irregularly, so that the colour-band was completely broken up and mixed to a uniform tint in a space of 10 or 15 centims. The flow was not precisely turbulent or eddying, but the stream-lines were so quickly sub-divided and mixed that the same effect was produced. When the wire was annealed and straightened,* the colour-band remained practically unbroken from end to end of the tube, but as the strands were still separate, the heat was more or less distributed over the cross-section. The twisting of the wire into a rope in the third experiment diminished the effective surface and increased the superheating, the value of which closely approached that calculated for a central conductor in a 2 millim. tube assuming the conductivity of water ·0016 C.G.S. The great diminution of the superheating in the fourth case, in which the wire was wound into

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* It is probable that the failure of Dr. BARNES to obtain consistent results with a stranded conductor may have been due to the use of annealed wire, which would inevitably become straightened in fitting up the apparatus unless special care were exercised. I was not aware of this mistake at the time.

a spiral of about 1 centim. pitch, closely fitting the tube, was chiefly due to the breaking up of the stream-lines. The colour-band rapidly became mixed to a uniform tint as in the first experiment. I found, however, from the indications of the platinum thermometer wound round the outside of the tube, that the glass was considerably heated by the close contact of the spiral. The simpler arrangement of the loose stranded conductor was equally effective in mixing the stream-lines, and appeared to be free from this defect.

An excellent illustration of the possible effects of a faulty arrangement of the conductor is given by Dr. BARNES in § 6, p. 234. In this case it is possible to calculate the actual heat-loss from a knowledge of the correct value of J for the temperature of the experiment.* The conditions were purposely chosen to exaggerate the errors as much as possible, and it must not be imagined that such large differences could be obtained without special pains in the arrangement of the heating conductor. The normal heat-loss for this calorimeter at a temperature of 26° with a constant gradient of temperature along the flow-tube was approximately ·070 watt per degree rise. Starting from this value, it is possible to calculate the limiting values of the heat-loss for either condition of flow, that of the metallic tube or the small concentric conductor, by drawing the curves representing the actual distribution of temperature in either case, and making a suitable allowance for the loss of heat from the thermometer. Dr. BARNES has given a pair of imaginary curves for these two cases in § 2, p. 152, but it should be observed that these curves are not drawn to scale, being merely intended to illustrate the general nature of the difference, which is considerably exaggerated in order to make it clearer.

TABLE VII.—Superheating of Straight Conductor in 3 millim. Flow-Tube.

Number of experiment.	Position of conductor.	Flow, Q.	Watts, EC.	Superheat of wire.	Heat-loss, observed.	Limit, calculated.
(1)	At side of tube	·600	21·7	8°·0	·1108	·1140
(2)		·277	10·4	4·1	·0909	·0920
(3)	In middle of tube	·600	21·7	12·8	·0482	·0530
(4)		·271	10·7	7·0	·0773	·0610

The observed values of the superheat and of the heat-loss agree in a general manner with those calculated by the theory given in § 32, but there are some difficulties. The limit in the last column of lines (1) and (2) is estimated for a *metallic* flow-tube, and it is difficult to see how the heat-loss for a *glass* flow-tube could approach this value so closely when the conductor is in imperfect contact with the glass over a small fraction of its surface. The superheat 12°·8 in line (3) agrees

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* In discussing these observations Dr. BARNES takes $(EC - 4 \cdot 2\, Q\, d\theta)$ in place of the actual heat-loss, which unduly exaggerates the difference. The conductor had evidently been *annealed*, otherwise it would have filled the tube instead of resting along the side.

very closely with the value 13°·3, calculated for a similar case in § 32, but the heat-loss is *less* than the limit for a small conductor in a large tube. On the other hand, the observed heat-loss in line (4) is greater than the normal value ·0700 instead of being less, as theory requires. It is possible that there may have been some other source of error in this experiment due to shifting the thermometer in the outflow-tube or similar causes.

When the first apparatus was set up with the vacuum-jacket in June, 1897, only three strands of ·006″ wire were employed, as it was necessary that the resistance of the heating conductor should be of the same order as that of the manganin current-standard. The latter had been made of 1 ohm resistance to suit the mercury experiment, and there was not time to make another, as the experiment had to be tried before the meeting of the British Association at Toronto. In order partially to compensate for this defect, I took pains to exaggerate the irregularity of the wire by bending it into a zigzag before pulling it through the tube, but the superheating of the wire (4° at 14 watts) proved to be somewhat excessive. In spite of this the readings were extremely steady, and could be taken easily to 2 or 3 parts in 100,000. The accuracy of this preliminary series of experiments was seriously impaired by the bad fitting of the thermometers in the inflow- and outflow-tubes, but the results showed that the method was capable, under suitable conditions, of attaining a very high order of precision on account of the great steadiness of the readings, which was much more perfect than anyone could have anticipated without actual trial.

Shortly after the British Association meeting, another manganin current-standard of 1 ohm resistance was made, and placed in parallel with the first. The platinum conductor, was composed of 6 strands of ·006″ wire, which gave a much better distribution of the heat. After numerous preliminary difficulties of temperature regulation, of leakage, and of bad fitting and connections had been overcome, the results, though often very consistent, still showed occasional discrepancies, especially after refitting. I was inclined to attribute these difficulties at the time either to bad fitting of the thermometer in the outflow-tube as previously explained, § 26, or to variable contact between the conductor and the walls of the glass tube, or possibly to bad solder joins on the manganin current-standards, one of which had actually broken away on one occasion.

With the view of preventing the uncertainty of contact with the walls of the glass tube, I thought at one time of trying a conductor in the form of a twisted strip, which I had employed some years previously in experiments on the viscosity of liquids by the Wheatstone-bridge method, for which I required a continuously variable resistance analogous to a slide-wire in the electrical method. I found that a round wire sliding in a tube would not do for this purpose owing to the impossibility of centering. A twisted strip, sliding in a tube which it closely fitted, evaded this difficulty, but led to further anomalies, which proved, on investigation by the colour-band method, to be due to the fact that the motion of the liquid became turbulent if the pitch of the twist was too steep. This change in the character of the flow was a serious defect in the viscosity experiment, but was exactly what was required for the calorimeter. As the calorimeters were already made, and I could not choose the flow-tube to fit the strip, I procured a special pair of rolls about the end of 1897 for rolling a wire to fit the flow-tube as closely as possible. But after carefully rolling a wire to fit one of the calorimeters at one end, I found that it would not go through the tube, on account of want of uniformity of diameter, and in particular on account of a join near one end which unduly constricted the bore. I accordingly abandoned the attempt at the time, as I did not feel at all certain of the necessity of making any change in the form of the conductor. But the twisted strip was subsequently employed by Dr. BARNES at my suggestion with great success in two other calorimeters, the tubes of which were probably more uniform.

The method independently devised by Dr. BARNES for eliminating the effect of the stream-lines, and at the same time preventing all contact between the conductor and the glass, was to wind a rubber cord round the conductor so as nearly to fit the tube, after a similar manner to that employed in fitting the copper sleeve of the outflow thermometer. This is undoubtedly a very simple and effective method, and unlikely to get out of order. It is quite possible that some of the discrepancies in the earlier experiments may have arisen from the accidental disarrangement of the stranded conductor, which might be pulled tight along the side or middle of the tube in refitting the apparatus, either of which contingencies would lead to serious errors. There were many other sources of error and difficulties in the earlier experiments which might have accounted for the effects observed, but Dr. BARNES' opinion on this point is entitled to the greatest weight, as he was personally responsible for the greater part of the fitting-up of the apparatus. With proper care I have no doubt that it would be possible to obtain as accurate results with the stranded conductor as by any other method, but I should be inclined to prefer the rubber-spiral method as being safer and more certain.

A possible objection to the rubber-spiral is that, since the wire is held central and considerably superheated, the temperature of the surface of the glass must necessarily be less than the mean of the flow, in spite of the mixing of the stream-lines. This would not matter if the difference of temperature were independent of the flow. Since it is impossible to calculate what the effect would be in the case of turbulent flow, the question can be answered only by trial. The experiments with the twisted strip, which was partly in contact with the glass and gave a higher heat-loss, were undertaken, at my suggestion, with the object of testing this important point. The extremely close agreement of the results with those obtained with the rubber-spiral at 30° C. are sufficient proof that the error, if any, must be extremely small. It is unlikely that it could amount to more than two or three parts in 10,000 at 30°, and there is no reason to think that this type of error should increase largely at higher temperatures, where the viscosity of water is much smaller and the conductivity probably much larger.

(34.) *Correction for Variation of the Temperature-Gradient in the Flow-Tube.*

The elementary theory of the elimination of the heat-loss in the steady-flow method of calorimetry assumes that, if the electric current and the flow of liquid be simultaneously varied in such a manner as to keep the rise of temperature the same, the heat-loss by radiation, &c., will remain constant. Dr. BARNES (p. 225) has quoted experiments to show that this condition is very closely satisfied in the present method, and has calculated all the results of the investigation on this assumption. It will be noticed, however, that there are small systematic divergences in the experimental verification for the small flows, which, though amounting only to a few parts in 10,000, require careful examination as possible indications of constant errors.

So long as the distribution of temperature throughout the apparatus is accurately the same for the same rise of temperature, whatever the flow, the heat-loss must also be identical. But if there is any systematic change in the temperature distribution with change of flow, then there must be a corresponding systematic difference in the heat-loss, which will lead to constant errors in the calculation if no account is taken of it. A possible source of error of this type is loss of heat by conduction along the outflow-tube. When the flow is large, the heated liquid passing along the tube will keep it nearly at a uniform temperature, so that the gradient in the outflow-tube will be small, and the conduction loss correspondingly minute. As the flow is diminished, supposing the temperature of the outflow to remain the same, the gradient in the outflow-tube must increase in proportion to the reciprocal of the flow, since the radiation-loss remains nearly the same. The conduction-loss will vary directly as the gradient, or inversely as the flow, for a given rise of temperature.

A small error of this kind, due to conduction, was detected at an early stage in the mercury-calorimeter, owing to the large mass of mercury in the flow-tube, the small rate of flow, and the relatively high thermal conductivity of the liquid. It was practically eliminated by filling the greater part of the outflow-tube from the end of the vacuum-jacket with paraffin wax, leaving only a small passage for the outflow of mercury. This made the conduction-loss very small, and nearly independent of the flow. In the water experiment it is easy to see that the conduction loss must be practically negligible in any case, but special pains were taken to make it as small as possible, and to verify its non-existence.

A more important correction of this type is that due to variation of temperature gradient in the fine flow-tube, which can be estimated with considerable precision. As the liquid flows along the tube it is receiving heat at a nearly uniform rate from the electric current, but it is also losing heat more and more rapidly by radiation as its temperature rises. As a result, the mean temperature of the fine flow-tube, upon which the radiation-loss chiefly depends, usually exceeds the mean between the initial and final temperature by an amount which varies, to a first approximation, inversely as the flow.

In order to calculate the value of this correction in terms of the heat-loss and the flow, it is necessary to consider the differential equation of the distribution of temperature in the flow-tube. We assume, as a first approximation, that the temperature of the surface of the flow-tube, on which the loss of heat depends, is at each point nearly the same as that of the liquid flowing through it. This is very nearly true in the case of mercury, and to a sufficient approximation in the case of water under suitable conditions.

The rate of evolution of heat by a current C amperes in a length dx of the tube is $C^2r\,dx$ watts, where r is the resistance in ohms per centim. The rate of loss of heat is $f\theta p\,dx$, where p is the perimeter of the flow-tube in centims., and f the emissivity in watts per sq. centim. per degree of temperature excess θ. The rate of gain of heat by the liquid is $JsQ\,d\theta$, where J is the number of joules in one calorie; s the specific heat of the liquid in calories per gramme degree C; Q the flow of liquid in grammes per second; and $d\theta$ the rise of temperature in a length dx. Since it is necessary to take account of the change of resistance with temperature, we must substitute for r the value $r_0(1 + a\theta)$, where a is the temperature-coefficient of the increase of resistance, and r_0 the value of r when $\theta = 0$. We thus obtain the linear differential equation

$$JsQ\,d\theta/dx + (fp - C^2ar_0)\,\theta = C^2r_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

Writing for brevity, $A = (fp - C^2ar_0)/JsQ$, and $B = C^2r_0/JsQ$, and observing that $\theta = 0$ when $x = 0$, since the liquid flows into the tube at the jacket-temperature, the solution of this equation is

$$\theta = (1 - e^{-Ax})\,B/A \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

Since A is very small compared with B in the actual experiment, we may obtain a sufficient approximation for our purpose by expanding the exponential and neglecting the terms beyond A^2, which gives

$$\theta_x = Bx\,(1 - Ax/2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.)$$

If the whole length of the fine flow-tube is l, the temperature at the end of the flow-tube will be approximately

$$\theta_l = Bl\,(1 - Al/2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4),$$

and the mean temperature θ_m from 0 to l, will be

$$\theta_m = Bl\,(1 - Al/3)/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

It will be observed that the value of A is zero, and that the gradient is constant throughout the tube for a particular value of the current, $C^2 = fp/ar_0$, which may be called the critical value of the current. In this case the radiation-loss along the flow-tube is exactly compensated by the increase of resistance of the conductor with rise of temperature. I made use of this relation in some experiments on conduction of heat in metals by an electrical method with Mr. KING in 1895, and also in some experiments on the conduction of heat in liquids, § 31, in which the elimination of the heat-loss was a matter of some importance as simplifying the differential equation. In the calorimetric experiment, the constancy of the gradient along the tube was not a matter of primary importance, provided that the temperature distribution was approximately the same for different flows. Moreover, the relation could not apply accurately to both the flows required in the experiment. Nevertheless, I thought it worth while, in designing the dimensions of the calorimeter and the details of the experiment, to arrange that the compensation might hold for a value of the flow between ·5 and 1·0 gramme per second in the water experiment, as nearly as it could be estimated beforehand. The gradient would then be nearly constant, and the mean temperature of the flow-tube nearly half the rise of temperature observed with the differential-thermometers.

(35.) *Application to the Mercury Experiments.*

Neglecting for the present that part of the heat-loss which occurs in the outflow-tube before the liquid reaches the middle of the thermometer bulb where its temperature is measured (which loss is a comparatively small fraction of the whole in the mercury experiment), the systematic error of the elementary theory given by Dr. BARNES, p. 152, consists in assuming that the mean temperature of the flow-tube is always the same for the same rise, or that the gradient is independent of the flow. This is equivalent to assuming the mean temperature of the flow-tube equal to $\theta_l/2$ instead of θ_m. The error of this assumption may be approximately estimated from equations (4) and (5) above, which give

$$\theta_m = (1 + \mathrm{A}l/6)\,\theta_l/2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

If we write (as in BARNES, p. 242) $d\theta$ for the whole rise of temperature observed by the differential thermometers, and $h\,d\theta$ for the heat-loss, we must then regard h as variable with the flow, since the heat-loss is really $fpl\theta_m$. We thus arrive at the expression,

$$\text{Heat-loss} = fpl\theta_m = fpl\,(1 + \mathrm{A}l/6)\,\theta_l/2 = h_0\,(1 + \mathrm{A}l/6)\,d\theta \quad . \quad . \quad . \quad (7),$$

in which $d\theta$ is written for θ_l, and h_0 is the value of the heat-loss per degree rise when the gradient is constant ($\mathrm{A} = 0$), namely $fpl/2$. We have also, to the same order of approximation,

$$\mathrm{A}l = 2h_0/\mathrm{J}s\mathrm{Q} - a\,d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8).$$

Hence, the complete equation of the method, when corrected for the effect of the variation of the temperature gradient in the fine flow-tube, becomes

$$EC = JsQ\,d\theta + h_0\,(1 + h_0/3JsQ - a\,d\theta/6)\,d\theta \quad . \quad . \quad . \quad . \quad . \quad (9).$$

If we divide through the equation by $d\theta$, and write $s = s_0\,(1 + d)$, since our object is to determine the variations of s, we obtain

$$EC/d\theta - Js_0Q = D = Js_0Qd + h_0\,(1 - a\,d\theta/6) + h_0^2/3JsQ \quad . \quad . \quad (10),$$

in which D is employed as an abbreviation for the expression on the left-hand side, which it is most convenient to calculate as the first stage in the reduction of the observations.

By combining the observations for two different flows, Q' and Q'', for which the current is adjusted to give approximately the same rise of temperature, $d\theta$, if D' and D'' are the corresponding values of the difference observed, we obtain

$$(D' - D'')/(Q' - Q'') = Js_0d - h_0^2/3JsQ'\,Q'' \quad . \quad . \quad . \quad . \quad . \quad (11).$$

Since the last term, which represents the effect of the correction sought on the variations of the specific heat, is generally very small, the equation may be readily solved by approximation, employing the value of h found in the first instance by neglecting the term involving h^2.

As an example of the order of magnitude of the correction, and of the method of application, we may take the following experimental results, which were given as an illustration of the method at the meeting of the British Association in 1897, and were quoted in the 'Electrician' of that date. In all the earlier series of observations, three independent flows were taken, with the same rise of temperature at each point, with the object of verifying the theory of the method, and detecting possible sources of error. If the values calculated from the largest and smallest flow disagreed with the observation on the intermediate flow, it was a sure sign of some error or defect in the work. I thought at first that it might be possible to determine the conduction error experimentally in this manner, but the effect proved to be too small.

TABLE VIII.—Example of Calculation of Specific Heat of Mercury.*

	Flow, Q.	Rise, $d\theta$.	Watts, EC.	EC/$d\theta$.	·1400Q.	D.	$h^2/3JsQ$.	Results, corrected.
(1)	8·753	11°·764	14·862	1·2632	1·2255	·0377	·0008	$h =$ ·0546
(2)	6·740	11·8720	11·696	·9851	·9435	·0416	·0010	$Jsd = -$ ·00202
(3)	4·594	12·301	8·488	·6901	·6433	·0468	·0015	$Js =$ ·13798

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* These results are given merely as an illustration of the method: they were not corrected for the absolute values of the resistances and other minor sources of error.

In working out these results, the standard value of the specific heat was taken as $Js_0 = \cdot 1400$ joule per gramme degree, since the specific heat of mercury is approximately $\frac{1}{30}$th of that of water. If we take only the values of the difference D corresponding to the first and third flows, and calculate the values of h and Jsd, according to the elementary theory, neglecting the correction term $h^2/3JsQ$, we find

$$Jsd = (D' - D'')/(Q' - Q'') = - \cdot 0091/4 \cdot 159 = - \cdot 00219,$$

$$\text{whence, } h = \cdot 0568, \; Js = \cdot 1400 - \cdot 00219 = \cdot 13781 \text{ joule per gramme degree.}$$

As a verification, we may calculate the value of D for the intermediate flow (2). We find $D_2 = \cdot 0420$, in place of the observed value ·0416. The difference is only four parts in 10,000, on $EC/d\theta$, and might well be attributed to errors of observation in these preliminary experiments.

Inserting the correction for the variation of the temperature gradient in the flow-tube, by subtracting $h^2/3JsQ$ from each of the corresponding values of D, and then calculating as before, we find the corrected results given in the last column, which exceed those calculated on the elementary theory by nearly one part in 700. It should be remarked that this correction can be deduced with certainty from (1) and (3) without reference to (2). It cannot be calculated satisfactorily from three flows, as it depends on small differences.

(36.) *Correction of Results with Water Calorimeter.*

In applying the correction to the water calorimeter, it is necessary to take some account of the heat-loss from the outflow-tube round the thermometer bulb, as well as that from the fine flow-tube. This changes the numerical factors, which depend to some extent on the dimensions of the tubes, but the theory of the correction is otherwise unchanged. Assuming the heat-loss from the thermometer bulb to be two-fifths of the whole, which is sufficiently exact, since the whole correction is very small and a change of one-tenth in the ratio would not alter the result by more than 2 or 3 per cent. of itself, equation (10) becomes

$$EC/d\theta - Js_0Q = D = Js_0Qd + h_0(1 - ad\theta/10) + h_0^2\, 11/25JsQ \quad . \quad . \quad (12),$$

and the correction to be added on this account to the value of the specific heat in joules, as calculated by Dr. BARNES, is given by the expression

$$\text{Correction for Variation of Gradient with Flow} = + 11h_0^2/25JsQ'Q'' \quad . \quad (13)$$

In calculating this correction it is desirable to use the corrected value of h_0, which is obtained from that of h as given by Dr. BARNES by adding the terms

$$\text{Correction to value of } h = + ah\, d\theta/10 - (11h^2/25Js)(1/Q' + 1/Q'') \quad . \quad (14).$$

The standard value of Js_0 assumed in reducing the tables in the case of water for calculating the value of D, was the British Association unit of 4·200 joules. Inserting this value, and putting $a = \cdot 0039$, we have the numerical formulæ

$$\text{Correction to } h = + \cdot 00039 h \, d\theta - \cdot 105 h^2/Q' - \cdot 105 h^2/Q''.$$

$$\text{Correction to J} = + \cdot 105 h_0^2/Q'Q'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15).$$

These formulæ are to be employed in correcting the results for the specific heat of water given in the summarized tables (BARNES, p. 243).

In cases where more than two flows are available at the same time and under the same conditions, it is naturally possible to obtain a more reliable value for the result by utilising all the flows, so as to minimize the effect of accidental errors. The accuracy of the work may then be verified by comparing the observed values of D for each flow with those calculated by equation (12). As an illustration we may take observations I. and II. with calorimeter D (BARNES, p. 243), which are also selected by Dr. BARNES as an experimental verification of the elementary theory.

TABLE IX.—Correction for Variation of Gradient in Flow-Tube.
Specific Heat of Water. Observations I. and II. (BARNES, Table XVIII., p. 243), Calorimeter, D.

Number of flow . . .	(1)	(2)	(3)	(4)	(5)	Mean of 2, 3, 4
Flow, Q, gramme per second	·6741	·3993	·3902	·4967	·2482	·4287
h_0, watts per degree . .	·06975	·06975	·06975	·06975	·06975	·06975
$\cdot 0039 h_0 \, d\theta/10$	− ·00021	− ·00022	− ·00022	− ·00022	− ·00022	− ·00022
$\cdot 105 h_0^2/Q$	+ ·00076	+ ·00128	+ ·00132	+ ·00103	+ ·00207	+ ·00120
$- \cdot 0190Q$	− ·01281	− ·00758	− ·00741	− ·00944	− ·00471	− ·00815
D, calculated	(·05749)*	·06323	·06344	·06112	·06689	(·06258)*
D, observed	·05749	·06317	·06318	·06135	·06691	·06257
$\cdot 07145 - \cdot 00207Q$ . . .	(·05749)*	·06318	·06337	·06117	·06631	(·06257)*

The last column gives the mean of the three intermediate flows, which has been combined with the first flow in the calculation of the results. The second line gives the approximate values of the flows, which are required in working out the results.

The next four lines give the values of the several terms in equation (12) for the calculation of D. The two unknown quantities h_0 and Jsd are calculated by assuming the values of D enclosed in brackets for (1) and the mean of (2, 3, and 4).

The values of D "calculated" are obtained by adding the numbers in the four lines above, and are corrected for the effect of variation of the gradient in the fine flow-tube. The values D "observed," given in the next line, are taken from the tables, and are found by subtracting 4·2Q from $EC/d\theta$.

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* Assumed in the calculation of h_0 and d.

The last line contains the values of D calculated on the elementary theory, neglecting the variation of the gradient, assuming the same two values (1) and (2, 3, 4), and taking the heat-loss per degree constant. This assumption gives $h = \cdot 07145$ for the heat-loss, and $Jsd = - \cdot 00207$ joule per gramme degree for the defect of the specific heat from 4·200.

Comparing the observed and calculated values of D on the two assumptions, we see that the relatively large discrepancy of ·00060 on the elementary theory in the value calculated for the small flow (5), is exactly accounted for by the correction for variation of the gradient in the flow-tube.

The effect of applying the correction in this particular case is to increase the value of the specific heat from 4·1793 to 4·1810, *i.e.*, by 4 parts in 10,000. This correction is very small, but it cannot be neglected, because it is systematic. Besides, it is much larger than the errors of observation, which rarely amount to so much as 1 in 10,000 on a single flow with a rise of 8°.

In the discussion of these observations, Dr. BARNES (§ 5, p. 226) concludes, from the close agreement of the observed and calculated values of the heat-loss for the larger flows, that the elementary theory is valid and requires no correction, provided that the flow exceeds a certain limit, about ·35 gm./sec. But the agreement for the larger flows results merely from his method of calculation, and is no evidence that the correction is negligible. The need for the correction could not arise *per saltum* below a certain limit, as he suggests.

The existence of the correction is obviously required by theory, and it is a remarkable verification of the accuracy of his observations that the small apparent discrepancy on the smaller flows, which he was prepared to attribute to some unknown source of error, should be so nearly accounted for by the variation of temperature distribution with flow, which is a necessary consequence of the method adopted.

In going through the summary of observations (BARNES, Table XVIII.), it may be noticed that there is generally a small systematic error of this nature in the results, as calculated on the elementary theory, tending to make the value of the specific heat smaller, the smaller the flows from which it is calculated. It would not, however, be worth while to recalculate the whole in detail as above illustrated, because the correction is so small that it may reasonably be applied to the observations as a whole.

In any particular case, for a pair of flows, the correction can most easily be applied by means of the numerical formulæ (15) already given. This will not give the best results, if more than two flows are available, but the residual errors will then be accidental, so far as this particular correction is concerned. A few examples of this method of correction, taken from the first few experiments at 29°·10 C. with calorimeter C, are given in the following table. The heat-loss in this calorimeter was much smaller than in calorimeter D, owing to a better vacuum and a smaller flow-tube. The correction is consequently smaller, and its effect is more obscured by accidental errors, but so far as it goes, it tends to bring the observations into better agreement.

TABLE X.—Correction for Variation of Gradient in Flow-Tube, Calorimeter C.

Number of Experiment.	Values of Flow.		Heat-Loss h per 1°.		Specific Heat in Joules.	
	Q′.	Q″.	Table.	Reduced.	Table.	Corrected.
III.	·665	·399	·04944	·04859	4·1803	4·1813
IV.	·501	·258	·05123	·04989	4·1771	4·1791
V.	·660	·392	·04937	·04859	4·1795	4·1805
VI.	·590	·375	·04965	·04882	4·1790	4·1802

The general effect of the correction here is to raise the values by about 1 in 4000 for the larger pairs of flows. The discrepancy between Experiments III. and IV. is mainly due, as the values of D show, to accidental errors of the small flows in opposite directions. The mean value 4·1803 agrees very well, allowing for the difference of temperature, with the value 4·1810 deduced from observations I. and II. with calorimeter D at 28°·0 C., which would give 4·1805 at 29°·10 C.

(37.) *Variation of the Gradient-Correction with Temperature.*

The importance of this correction arises chiefly from the fact that the value of the heat-loss increases with rise of temperature for any calorimeter. As a result, the correction, which depends on the square of the heat-loss, is considerably larger at higher temperatures, and thus affects the curve of variation of the specific heat as well as the absolute values. If the correction were constant, it would affect only the absolute values, which would matter little owing to the uncertainty of the electrical units.

As an illustration of the greater importance of this correction at higher temperatures, the last four observations (BARNES, Series 8, Table XVIII.) are given in the next table, reduced and corrected in a similar manner. Although these observations do not include any exceptionally small values of the flow, the correction at the higher points nearly reaches 1 in 1000 owing to the larger value of the heat-loss.

Table XI.—Correction for Variation of Gradient in Flow-Tube, Calorimeter C, Series 8.

Number of Experiment.	Temperature, Centigrade.	Values of Flow.		Heat-Loss per 1°.		Specific Heat in Joules.	
		Q'.	Q''.	Table.	Reduced.	Table.	Corrected.
	°						
LII.	74·05	·621	·384	·08469	·08198	4·1920	4·1950
LIII.	91·55	·644	·402	·10011	·09643	4·2017	4·2055
LIV.	80·38	·617	·388	·09218	·08891	4·1951	4·1986
LV.	68·21	·603	·388	·08283	·08011	4·1890	4·1919

The effect of the correction on the curve of variation of specific heat is most readily appreciated by taking the approximate formula for the variation of the heat-loss with temperature, given by Dr. Barnes, p. 253, which, when slightly reduced to allow for the correction of the value of h given in equation (15), becomes

$$h = \cdot 0300 + \cdot 00070t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16).$$

This formula represents the experimental results very fairly, except for the lower temperatures in the neighbourhood of 0° C. It leads to the following values of the corrections for the specific heat in joules and calories.

Table XII.—Variation of Gradient-correction with Temperature, and Corrected Values of Specific Heat of Water.

Temperature, Centigrade.	Heat-Loss.		Correction ·105 $h_0^2/Q'Q''$.		Results, 1900, Corrected.	Reduced to H scale.
	Formula (16).	$E\theta^4$.	Joules.	Calories.		
°						
0	·0300	·033	·00038	·00009	1·0080	1·0084
10	·0370	·039	·00058	·00014	1·0029	1·0031
20	·0440	·045	·00082	·00019	1·0000	1·0000
30	·0510	·051	·00109	·00026	0·9987	0·9986
40	·0580	·058	·00141	·00034	0·9986	0·9984
50	·0650	·066	·00177	·00042	0·9993	0·9989
60	·0720	·074	·00218	·00052	1·0005	1·0000
70	·0790	·083	·00263	·00063	1·0018	1·0013
80	·0860	·094	·00312	·00074	1·0033	1·0027
90	·0930	·105	·00364	·00087	1·0048	1·0041
100	·1000	·117	·00420	·00100	1·0062	1·0055

In calculating the correction, the value of the product $Q'Q''$ is taken as $\cdot 64 \times \cdot 39 = \cdot 25$, which represents fairly the values of the larger pair of flows on which the results mainly depend. The corrections calculated from the actual numbers in the tables are, as a rule, slightly larger than those calculated from the formula for the heat-loss, but the latter are usually within 1 in 10,000 of those observed.

It may be interesting to remark that formula (16) gives a mean rate of increase of the heat-loss which is proportional to the fourth power of the absolute temperature over the range 0° to 80°. The fourth power law is well known to represent heat-loss by radiation with considerable accuracy over a moderate range at ordinary temperatures under conditions similar to those of this experiment. Values of the heat-loss calculated according to the fourth power law starting from the same value at 30° C., are given, for comparison, in the third column, headed $E\theta^4$. They represent the experimental numbers rather better than the linear formula (16) at temperatures below 30°, but give results which are a little too high at 80° and 90°. The corrections in the table have been calculated from the linear formula, but the difference would be very slight over the greater part of the range.

The values of the specific heat given in the column headed "Results, 1900, Corrected," are obtained from those calculated by the formulæ given by BARNES, 'Proc. Roy. Soc.,' 1900, p. 242, by adding the correction in calories given in the previous column, and expressing the results in terms of a unit at 20° C., instead of the unit at 16° employed by BARNES. Although the values of the corrections are worked to the next figure, I have not considered it desirable to give the values of the specific heat beyond 1 part in 10,000.

It happens, by a curious coincidence, that the correction for the variation of the temperature gradient is very nearly equal and opposite to the correction required to reduce the results to the hydrogen scale, if calculated, as previously explained in Section 23, from the observations of JOULE and THOMSON for air at a constant pressure of 76 centims. The values given in the last column, reduced to the hydrogen scale, are practically identical with those calculated directly from BARNES' formulæ without correction, except that they are expressed in terms of a unit at 20° C., and are corrected for an obvious misfit of the formulæ at 55° C. (see §46).

PART V.—DISCUSSION OF RESULTS.

(38.) *Meaning of the Term "Specific Heat."*

The term "specific heat" is here employed as an abbreviation for the phrase "specific capacity for heat," or "thermal capacity of unit mass,' *i.e.*, the quantity of heat per unit mass per degree required to raise the temperature of a substance. In a similar manner, "specific electrical resistance" or "resistivity" of a substance is understood to mean the resistance of the material per unit area of section per unit length. On this understanding, specific heat may be measured in terms of any convenient unit, either in joules per gramme per degree Centigrade, or in foot-pounds per pound per degree Fahrenheit, without any implied reference to the properties of water. On the other hand, it is not unusual in elementary text-books to define specific heat as the *ratio* of the thermal capacity of a given mass of the substance considered to that of an equal mass of *water* at a standard temperature. The two definitions lead to the same numerical results, provided that the unit of heat is the thermal capacity of unit mass of water at the standard temperature. But there is nothing in the derivation of the term "specific heat" to imply that it denotes a ratio with respect to water at a standard temperature, and I think that this definition unduly restricts the meaning, and has given rise indirectly to a good deal of confusion.

(39.) *Choice of a Standard Temperature for the Thermal Unit.*

In addition to the absolute unit of heat, which is naturally the same as the unit of mechanical energy, it is necessary for practical calorimetry to adopt as a standard of reference a thermal unit equal to the quantity of heat required to raise unit mass of water one degree at a standard temperature. For purely academic purposes, it would suffice to adopt either of the time-honoured standards at 0° C. or 4° C., which have been frequently proposed, and are still to be found in the majority of text-books. But it has been conclusively shown that the specific heat of water at these low temperatures is considerably higher than over the range which is commonly employed for calorimetric determinations. The units at 0° and 4° would be practically inconvenient on this account. A still more serious objection is that the specific heat at these temperatures cannot readily be determined with the same order of accuracy as at ordinary temperatures. The unit of 4·200 joules proposed by the British Association Committee, which was supposed at that time to represent the specific heat of water in joules per gramme degree at 10° C., is open to the additional objection that it is really an absolute unit in disguise, and that, as such, it is superfluous, and does not satisfy the requirement of a thermal unit defined in terms of the specific heat of water at a definite temperature.

For practical purposes, it is evidently necessary to define the thermal unit in terms of the mean specific heat *over a range* of temperature rather than at a definite point. The range of 1°, which is generally taken in definitions, is evidently too small for the accurate measurement of the rise of temperature in terms of the fundamental interval. These very small ranges of temperature have frequently been employed in calorimetry, as in JOULE's earlier experiments, for the purpose of reducing the uncertain correction for external heat-loss; but with modern appliances for accurate thermal regulation, and provided that the duration of the experiment is not unduly prolonged, it is quite possible to employ a rise of 10° or more without the uncertainty of the heat-loss exceeding the probable theormometric error.

So far as the thermometric error alone is concerned, the obvious interval to select is the fundamental interval itself. For this reason, the "mean calorie," which is equal to one-hundredth part of the quantity of heat required to raise the temperature of a gramme of water from 0° to 100° C., has been often proposed as the most suitable thermal unit. But in this case the calorimetric difficulties due to the large range of temperature are so exaggerated that the relation of the mean calorie to the practical unit employed in calorimetry cannot be determined with the same order of accuracy as the practical unit itself can be realized. This point is further illustrated in Section 45 below. An equivalent proposition is to select as the standard temperature for the definition of the thermal unit that temperature at which the specific heat is equal to its mean value over the fundamental interval. The objection to this is that it leaves the standard temperature uncertain. If, however, a definite temperature of either 15° or 20° C. were selected, we should have a definite unit, which would probably be within one part in a thousand of the mean calorie, or near enough for all practical purposes.

On the whole, a range of 10° appears to be the most appropriate to adopt for the practical definition of the thermal unit. ROWLAND'S results for the specific heat were calculated in this manner by taking the mean value over each interval of ten degrees. GRIFFITHS also adopted a range of ten degrees, 15° to 25°, in his experiments, and his results may be held to refer to the mean of this range, which is also very close to the mean of the range, 18° to 20°, of SCHUSTER and GANNON'S experiments. For this reason, I have been in the habit for some years of expressing results in terms of the mean specific heat of water over the range 15° to 25° C., which is, within 1 part in 20,000, the same as the value *at* 20° C. The mean thermal unit over this range may conveniently be called the "calorie *at* 20° C.," although of course it cannot be practically realized except as the mean over a range.

The preliminary results for the variation of the specific heat of water communicated to the British Association at the Dover meeting in 1899, were expressed in terms of the calorie at 20° C. I have thought it important to retain this unit in the present paper to avoid confusion, although Dr. BARNES and Mr. GRIFFITHS* have since proposed units at 16° and 15° respectively, as being probably closer in magnitude to the mean calorie between 0° and 100° C. From a scientific point of view there is little to choose between these units, and the relation between them is known with a high degree of accuracy; but as a question of practical calorimetry, I think the unit at 20° is undoubtedly superior. In all accurate calorimetric work it is necessary to employ thermal regulators, and there can be no doubt that from this point of view the range 10° to 20°, corresponding to the unit at 15° C., is too low. The range 20° to 30° would be better for temperature regulation than 15° to 25°, but I adopted the latter as corresponding to the mean of ROWLAND'S, and GRIFFITHS', and SCHUSTER'S experiments, and as agreeing more nearly with the mean range of an ordinary

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* More recently, GRIFFITHS ('Thermal Measurement of Energy,' Cambridge, 1901) has proposed to adopt the calorie at 17·5° C., or the mean value over the range 15°–20° C.

calorimetric experiment without a thermal regulator. It might be objected that SCHUSTER (range 18° to 20°) and LÜDIN (range 11° to 18°) found it necessary to keep the calorimeter always *below* the temperature of its surroundings, in order to avoid readings on a stationary or falling temperature, which are quite unreliable with a mercury-thermometer, owing to capillary friction. But even in this case it would be better to use a regulator at 25°, to avoid any risk of cooling the calorimeter below the dew-point, if a range of 10° is required.

(40.) *Choice of a Standard Scale of Temperature.*

An equally important question in the definition of the practical thermal unit is the choice of the scale of temperature to which it should be referred. There would probably be little hesitation in selecting the scale of the constant-volume hydrogen-thermometer at 1 metre initial pressure; but this necessitates the further consideration of the secondary standard by which the practical unit is to be realized, as it would of course be quite impossible to employ the hydrogen-thermometer at constant-volume *directly* in a calorimetric experiment. The mercury-thermometer, which is regarded at present as the representative of the normal scale, is a most unsatisfactory instrument for accurate calorimetric work. Some of its defects in this respect have already been incidentally mentioned, and it is impossible to regard with confidence results obtained by its use under conditions so different from those of the comparison with the ultimate standard. The only satisfactory method of standardizing a mercury-thermometer under the conditions of experiment, is by comparison with a platinum-thermometer. In the great majority of cases it would be far less trouble to discard the mercury-thermometer in accurate work and employ the platinum-thermometer itself. The results could be nominally reduced to the hydrogen scale in the manner described in the present paper, with an accuracy which is limited only by the gas-thermometer. But though nominally expressed in terms of the hydrogen scale, and subject to all the uncertainties of gas-thermometry, the results would have the advantage of being really referred to a practical scale which could be reproduced at any time with an accuracy depending only on that of the original observations.

Although it is very generally admitted that the platinum-thermometer is the most accurate instrument for scientific work, it is also commonly assumed that the mercury-thermometer is much easier to work with. This is quite a mistake if an accuracy of the order of ·001° C. is aimed at. If anyone wishes to realize the incalculable simplification introduced into accurate work by the employment of platinum-thermometers instead of mercury, even over the range 0° to 100° C., he should try to perform an experiment like the present. After endless labour, spent in calibrating and standardizing a suitable series of limited scale-thermometers, he would probably find all his observations spoilt by uncertainties of stem exposure and capillary friction, and more particularly by unknown changes of zero at the higher points of the range.

It is no exaggeration to say that this investigation could not have been carried out successfully without the direct employment of platinum-thermometers.

(41.) *The Work of* REGNAULT.

The work of REGNAULT ('Mémoires de l'Institut,' Paris, 1847) on the specific heat of water by the method of mixture at temperatures between 110° C. and 190° C., represents the only evidence at present available on the variation of the specific heat at high temperatures. It was carried out on a large scale with his usual experimental skill, and is undoubtedly entitled to great weight; but there are large discrepancies in several cases between the recorded data and the calculated results, and very little is known of the scale of the thermometers employed in the work.

The total capacity of the calorimeter employed was about 110 kilogs. At each experiment 10 kilogs. of cold water was drawn off, and the same amount of hot water, at a known temperature, was introduced from a high-pressure boiler. The rise of temperature varied from 8° to 15°, according to the initial temperature of the hot water, and was read to the hundredth of a degree. The discrepancies in the observations taken at any one point under similar conditions are of the order of ·5 per cent. The results have been recalculated from the data columns by J. M. GRAY ('Proc. Inst. Mech. Eng.,' 1889), who finds in several cases disagreements amounting to from 2 to 4 per cent. In all these cases it appears that the total recorded quantity of water considerably exceeded the capacity of the calorimeter. As the result of a careful enquiry, GRAY concludes that REGNAULT'S calculations are probably right, and that the apparent discrepancies in the data arise from deficient information or erroneous entries.

It would appear to be hopeless at the present time to make any corrections to the readings of the thermometers employed for observing the temperature of the hot water, beyond those which REGNAULT himself applied. The principal source of uncertainty lies with the calorimetric-thermometers, as REGNAULT was unable to obtain any consistent evidence of deviation from the scale of the air-thermometer between 0° and 100° C., and did not apply any correction from the mercurial to the absolute scale. Moreover, no allowance was made for the temporary depression of zero to which French "*cristal*" thermometers appear to be particulary liable. Some thermometers of this class show a depression of as much as half a degree after heating to 100° C. If such a thermometer is suddenly immersed in steam, its reading rapidly rises to a maximum, and then slowly falls for half an hour or so towards its steady reading. In using a mercury-thermometer in a calorimeter, where it is exposed to a sudden rise of temperature, the effect of this phenomenon is to make the observed rise of temperature too large. The maximum reading is always taken, with additive corrections to represent the subsequently observed rate of cooling. At the time of reading the maximum, the zero depression has not had time to produce its full effect, owing to the suddenness of the rise, and it therefore tends to increase slightly the subsequent rate of fall. In graduating the thermometer, or comparing it with an air-thermometer, the readings are taken at steady temperatures, so that the zero depression has time to produce its full effect. These steady readings will be systematically lower than the instantaneous readings obtained on suddenly heating the thermometer. Unless the method of variable zero is employed in taking the observations, it is quite impossible to apply an accurate correction, since the depression in any given case depends so much on the past treatment of the thermometer, especially in the case of French "*cristal*" glass. It is possible, however, to assert that the probable effect would be to produce an error in the observed rise of temperature approximately proportional to the rise, and therefore nearly proportional to the excess of temperature of the hot water, since the same weight of water was employed in all the experiments. The corresponding error in the value of the mean specific heat deduced would therefore be nearly constant on the average, although no doubt the variations of the zero depressions in consecutive experiments may be responsible for some of the individual discrepancies. The possible limit of error from this source would be about 5 parts in 1000, allowing for the effect of the zero depression in accelerating the apparent rate of cooling, which would tend to increase the error. The *probable* effect would be to make the specific heat, as calculated by REGNAULT, about 2 or 3 parts in 1000 too large.

The correction of REGNAULT's thermometers to the hydrogen scale cannot be applied with any certainty without recovering the original instruments, as different thermometers of the same glass often differ considerably, and so much depends on the exact method of treatment. But if we assume GUILLAUME's tables for modern thermometers of similar glass, the correction to the values of the specific heat would be of the order of 3 parts in 1000 in the direction of reducing REGNAULT's results, and would be nearly constant for the different observations.

Including both sources of error, we should infer that REGNAULT's values for the mean specific heat may require to be reduced by a constant correction of 5 or 6 parts in 1000.

Although it is evident that some correction is necessary, I should hesitate to assume the above estimate without experimental corroboration. I find, however, as explained in the 'Brit. Assoc. Rep.,' 1899, that a correction of precisely this order of magnitude is required to make REGNAULT's observations of the mean specific heat between 20° and 110° C., agree with those of REYNOLDS and MOORBY, between 0° and 100°, and with those of BARNES, between 40° and 90° C. The correction also makes REGNAULT's observations at 110° agree much better with his own observations at higher temperatures. It has the further advantage of being the simplest, as well as the most probable kind of correction to apply. I therefore proposed in 1899 to adopt REGNAULT's formula provisionally for the higher temperatures, merely subtracting the constant quantity ·0056 from his values of the specific heat, in order to make them agree with the curve of variation deduced from the present investigation at a temperature of 60° C. Thus modified, the formula for the specific heat s at a temperature t is as follows :—

$$\text{From } 60^\circ \text{ to } 200^\circ \text{ C. } s = \cdot 9944 + \cdot 00004t + \cdot 000{,}000{,}9t^2 \quad . \quad . \quad . \quad (1).$$

Regnault's formula for the *mean* specific heat would require further modification, as it is of course quite erroneous between 0° and 60°. But it is really of comparatively little use to tabulate the mean specific heat. The quantity most often required is the total heat h from 0° to t. If we adopt as unit the specific heat of water at 20° C., the total heat from 0° to 60° is 60·020. The value of the total heat h above 60° is then represented by the formula,

$$(\text{Above } 60^\circ)\ h = + \cdot 220 + \cdot 9944t + \cdot 000{,}02t^2 + \cdot 000{,}000{,}3t^3 \quad . \quad . \quad (2),$$

which differs from Regnault's formula only in the first two terms, and is deduced from the formula (1) for the specific heat at t by integration, and addition of a suitable constant to make the value right at 60° C.

To find the mean specific heat between any two arbitrarily selected temperatures, which is often required in reducing calorimetric observations, the simplest method of procedure is usually to take the difference between the values of h corresponding to the integral values nearest to the extremes of the range, and divide by the whole number of degrees between the values taken. This will generally give a result which is accurate to 1 in 10,000. If the range is less than 10° the order of accuracy will be proportionately less; but this is immaterial, as the same will probably be true of the observations themselves with which the comparison is required.

The work of Pfaundler and Platter, of Hirn, of Jamin and Amaüry, and of many other experimentalists who succeeded Regnault, appeared to indicate much larger rates of increase than he had found; but there can be little doubt that the discrepancies of their results, which often exceeded 5 per cent., were due to lack of appreciation of the difficulties of the problem. Before the time of Rowland's experiments in 1879, sufficient attention had not been paid to the thermometry, and the results were of comparatively little value.

(42.) *The Work of* Rowland.

It is unnecessary to give any description or criticism of Rowland's work, which is generally recognised as being the most accurate determination of the mechanical equivalent of the thermal unit at ordinary temperatures. Rowland himself considered that his results were probably correct to at least 1 in 500, and that the greatest uncertainty lay in the comparison of the scale of his mercury-thermometers with the air-thermometer, which was the most difficult part of the work. His thermometers have recently been compared with a mercury-thermometer standardized at Paris, and with a platinum-thermometer standardized by GRIFFITHS. The result has been to reduce the rate of change of specific heat shown by his original calculations by nearly one-half, but the absolute value of the specific heat about the middle of the range remains almost unchanged. The accuracy of his results in terms of the hydrogen scale has probably been raised to 1 in 2000 on the average by this correction; but it must be remembered that the thermometers were compared at steady temperatures, and not under the actual conditions of the experiment on a steadily rising temperature. This may affect the validity of some of the conclusions.

In ROWLAND's experiments, the most striking difference from ours is the sharp minimum at 30° followed by a rapid rise. ROWLAND himself considered that at 30°, owing to the increasing magnitude and uncertainty of the radiation correction, "there might be a small error in the direction of making the equivalent too great, and the specific heat might go on decreasing to even 40°." It should be remembered that his method gives directly the total heat reckoned from the start of each experiment, and that the values of the specific heat over shorter ranges would be more affected by thermometric errors, especially near the ends of the range. If our results are compared with his by means of the *total heat* starting from the same value at 5° C., it will be seen that, in spite of the apparent dissimilarity in the forms of our curves for the specific heat, our values of the total heat do not differ from those of ROWLAND by more than 1 in 5000 over the whole range of his experiments. This is shown in the following table:—

TABLE XIII.—Values of Total Heat of Water compared with ROWLAND.

Temperature, Centigrade.	Total Heat, CALLENDAR and BARNES.	Total Heat, ROWLAND.
° 5	5·037	5·037
10	10·056	10·058
15	15·065	15·068
20	20·068	20·071
25	25·065	25·067
30	30·060	30·057
35	35·052	35·053

(43.) *The Method of Mixture.* LÜDIN.

The experiments of BARTOLI and STRACCIATI ('Boll. Mens. dell' Acc. Gioenia,' 18, Ap., 1891), by the method of mixture between 0° and 30°, gave a curve very similar to ROWLAND's, but with a minimum at 20° C. This excessive lowering of the minimum may probably be attributed to constant errors inherent in their methods of experiment.

The later work of LÜDIN (Zurich, 1895), under the direction of Professor PERNET, extending from 0° to 100° C., requires further notice on account of the wider range of the experiments, and the great attention paid to the thermometry. He employed mercurial thermometers of the Paris type, with all the usual precautions. He adopted the method of mixture, adjusting the quantity of hot water in each case to give the same rise of temperature, from 11° to 18°, in the calorimeter. The discrepancies of individual measurements at any one point do not exceed ·3 per cent., but he did not vary the conditions of experiment materially, and it may be questioned whether the well-known constant errors of the method could have been eliminated by the devices which he adopted. His results (see Table XIV., p. 144) give a minimum at 25° and a maximum at 87° C., the values being ·9935 and 1·0075 respectively, in terms of the mean specific heat between 0° and 100°. The rapid rise from 25° to 75° may possibly have been due to radiation error from the hot water supply; and the subsequent fall between 90° and 100° to the inevitable loss of heat by evaporation of the nearly boiling water on its way to the calorimeter. His values, reduced to a unit at 20° C., are given for comparison in Table XIV. The agreement with our values is remarkably close at the lower temperatures; but the difference at 80° amounts to nearly 1 per cent. In addition to the fact that his curve cannot easily be reconciled with REGNAULT, there is this theoretical difficulty in accepting his values at higher temperatures. The quantity which he actually observed was the *mean* specific heat between the higher temperature and the final temperature of his calorimeter. His values of the specific heat itself were obtained by differentiating the curve, and really depend on small differences at the higher points between observations which are themselves difficult and uncertain. His values for the *mean* specific heat differ much less from ours. The peculiar advantage of the method we adopted is that the specific heat itself is determined over a range of 8° to 10° at each point by adding accurately measured quantities of energy to the water at the desired temperature. There is no possibility of evaporation or heat-loss in transference as in the method of mixture, and the protection from external radiation is much more perfect.

(44.) *The Work of* MICULESCU.

The work of MICULESCU ('Ann. Chim. Phys.,' XXVII., p. 202, 1892), though not directly affecting the question of the variation of the specific heat, is interesting as an example of a steady-flow method of calorimetry. The apparatus consisted of a Joule calorimeter mounted horizontally, with the paddles directly driven by an electric motor, the torque being observed by the "cradle-method" of DÉSPRETZ and BRACKETT. The heat generated was measured by passing a steady current of water round the calorimeter, and observing with a platinum-iron thermocouple the rise of temperature of the stream. The rate of heating was about 50 calories per second, the rise of temperature 2°, and the capacity of the calorimeter about 3 litres. The work has been criticised by Schuster, and also by Ames ('Paris Congress Reports,' 1900) on the ground that the length of the lever by which the torque was measured was apparently taken as 28 centims. without verification. M. Guillaume replies in a footnote that the length would probably in any case be accurate to a tenth of a millim., or 1 in 2800 (which is about the limit of accuracy claimed for the best absolute measurements of the mechanical equivalent), but regrets that the original lever cannot be found for the purpose of verification. It appears, however, from the description given by Miculescu, and also from the wood-cut of the apparatus, that the weight was not supported on a knife-edge but suspended from *a round hook* clamped to the lever with a screw, so that it would be a matter of some difficulty to estimate the effective length. Moreover, it would be very difficult with a platinum-iron couple to measure so small a difference as 2° with a degree of accuracy higher than ·01°, and Miculescu does not mention some of the necessary precautions. In addition, the correction for the external loss of heat from the calorimeter by radiation and conduction was regarded as being negligible in comparison with the heat-supply, and no correction was applied for it. It is easy to estimate, however, from the dimensions of the apparatus, that it could not have been much less than 0·5 per cent., and that it was probably larger on account of the smallness of the interval between the calorimeter and the jacket, which would considerably increase the heat-loss by conduction and convection through the air space. There are several other indications in the paper that the author did not really aim at a higher order of accuracy than 1 per cent., which is about the limit usually reached in engineering experiments, and that the work should be regarded rather as an illustration of a method than as a serious absolute determination.

(45.) *The Work of* Reynolds *and* Moorby.

The work of Reynolds and Moorby ('Phil. Trans.,' A, 1897), on the mean specific heat between 0° and 100° C. in absolute measure, stands in the same category as that of Rowland as an accurate determination of the mechanical equivalent. The two are not directly comparable, but if we assume the rate of variation of specific heat found in our experiments as the medium of comparison, the result of Reynolds and Moorby would give 4·179 for the number of joules in one calorie at 20° C., at which point Rowland's corrected results give 4·181. If we took Lüdin's table, we should find 4·157. The formula of Winkelmann[*] gives 4·133, and that of Regnault 4·167. The comparison of Reynolds and Moorby with Rowland is therefore a confirmation to some extent of the accuracy of the present experiments, as compared with Lüdin's, or with formulæ proposed by other writers. On the strength of this comparison, I have generally adopted the mean value 4·180 joules per calorie at 20° C. as the most probable estimate of the "Mechanical Equivalent," assuming that the absolute value cannot be certain to a higher order of accuracy than 1 in 2000.

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[*] Winkelmann, 'Handbuch der Physik,' Band 2, Abth. 2, p. 338.

It might, however, be claimed that either or both of the absolute determinations above cited were more accurate than this, and that the error lay with our comparison. It is a nice question whether the mean specific heat, which is practically independent of the scale of the thermometer employed, should be chosen as the standard of reference, rather than the specific heat at a particular temperature such as 20° C. on the scale of a particular thermometer. My own opinion is that the latter unit is the more practical, and the most accurately reproducible. It is not very difficult in a thermochemical experiment to measure a quantity of heat to 1 in 1000 with a suitable rise of temperature and a good thermometer with known scale errors. But it is quite impossible to realize the mean thermal unit to this order of accuracy without the most elaborate apparatus on a scale approaching that adopted by REYNOLDS and MOORBY.

The fundamental difficulty in the determination of the mean specific heat between 0° and 100° C. lies in the great range of temperature to be covered, and the consequent risk of excessive or uncertain loss of heat. REYNOLDS and MOORBY endeavoured to meet this objection by working on a very large scale, and succeeded in reducing the heat-loss to 5 per cent., even without the use of lagging. But in working on this scale they encountered peculiar difficulties, which were not overcome without great pains and ingenuity, and which must in any case have materially affected the order of accuracy attainable by their method. Owing to the employment of a steam-engine as motor, it was difficult to secure a high degree of steadiness in the conditions of running, and the outflow-thermometer could not be read more closely than a tenth of a degree owing to its incessant oscillations. The largest variation recorded in the two trials of which full details are given, was 4·9° F. in two minutes on the outflow temperature, and four or five revolutions per minute in 300 on the speed. The greater part of these variations being accidental would disappear in the mean, but it is probable that there would be systematic errors of the same order as the limit of accuracy of the instantaneous readings. In using so large a quantity of water, it was impracticable to deprive it entirely of air, which caused considerable trouble, owing to loss of heat by generation of steam in the air bubbles. Again it was naturally impossible to enclose the brake in a vacuum-jacket, or shield it from draughts and extraneous disturbances by means of an isothermal enclosure. The greatest uncertainty appears to have arisen from damp in the lagging, which caused the rejection of a number of trials. The correction for conduction along the 4-inch shaft was of much smaller magnitude, though probably more uncertain on account of the impossibility of determining the actual gradient in the shaft itself. The extreme limits of variation of the recorded results were from 776·63 to 779·46 foot-pounds, but considering that the main sources of error above mentioned were accidental, it is probable that the accuracy of the mean would be of a higher order than might be inferred from the separate experiments.

(46.) *Empirical Formulæ.*

The usual method of representing the results of a series of observations like the present is to adopt an empirical formula of the type,

$$s = 1 + at + bt^2 + ct^3 + dt^4 + \&c., \quad . \; . \; . \; . \; . \; . \; . \quad (3),$$

and to calculate the values of the coefficients a, b, c, d, &c., by the method of least squares. This was, in fact, the method adopted by LÜDIN. It has the advantage of providing a simple and ready rule, which is very generally recognized and applied; but it appears to me that it is in reality liable to several objections. Too much weight is given to the observations at higher temperatures, which are necessarily less accurate than the rest. The results obtained are in a great measure dependent on the particular type of formula assumed, which is frequently inadequate to represent the phenomenon, and is generally quite unsuitable for extrapolation. Moreover, the method gives a fictitious appearance of completeness and accuracy, which is quite misleading, as the calculated values of the probable errors contain no reference to possible sources of *constant* error. It also generally happens that the terms of the empirical formula are large and of alternate sign, so that the small variation required is given as the difference between large quantities, which must be calculated to several figures in applying the formula. The following formula of LÜDIN supplies a good illustration of some of these points:—

$$\left.\begin{array}{llll} s = 1 & - \;{\cdot}00076668t & + \;{\cdot}000019598t^2 & - \;{\cdot}000{,}000{,}1162t^3 \\ & \pm \;{\cdot}0000025 & \pm \;{\cdot}000004 & \pm \;{\cdot}000{,}000{,}03 \end{array}\right\} \quad . \; . \; . \quad (4).$$

The probable errors of the several coefficients, as calculated by LÜDIN, are given in the second line below the coefficients to which they apply. The value of the specific heat at 100° C. on LÜDIN's formula is made up as follows:—

$$\begin{array}{rll} s = 1 & - \;{\cdot}076668 & \pm \;{\cdot}00025 \\ & + \;{\cdot}19598 & \pm \;{\cdot}040 \\ & - \;{\cdot}1162 & \pm \;{\cdot}030 \\ \hline & \underline{1 + {\cdot}0031} & \end{array}$$

It is at once obvious that a formula of this type is quite unsuitable for the representation of the variation of the specific heat over the whole range 0° to 100° C. Moreover, since the maximum divergence of the specific heat from its mean value over the range 10° to 70° is only 2 parts in 1000, according to the present series of experiments, it is evidently desirable from a practical point of view to employ the simplest possible formulæ for its representation. The variation from unity over this range cannot be determined more closely than 2 or 3 parts in 10,000 (*i.e.*, 10 per cent. of the variation itself), so that it would appear ridiculous to employ coefficients with five significant figures in the formulæ.

For the above reasons, in the 'British Association Report,' 1899, the following simple formula was given as representing the results between 10° and 60° within the limits of accuracy of the observations, in terms of a unit at 20° C.—

$$s = \cdot 9982 + \cdot 000{,}0045\,(t - 40)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

It was stated that the variation of the specific heat near the freezing-point was apparently more rapid than the formula indicated, and could be approximately represented by the addition of the constant quantity ·020 calorie to the total heat. This correction to the formula has since been further verified, and may be represented by the addition of a small cubic term below 20°.

$$\text{Below } 20^\circ\text{ C. add to (5)} + \cdot 000{,}000{,}5\,(20 - t)^3 \quad . \quad . \quad . \quad . \quad (6).$$

At that time the observations had not been extended above 60°, and the formula of Regnault, emended as already described, was therefore adopted for the higher temperatures, namely,

$$\text{Above } 60^\circ \text{ to } 200^\circ\text{ C.} \quad s = \cdot 9944 + \cdot 000{,}04t + \cdot 000{,}000{,}9t^2 . \quad . \quad . \quad (7).$$

Shortly afterwards, Dr. Barnes succeeded in obtaining six observations at higher temperatures. One of these was vitiated by dissolved air, and another was incomplete. There remain four good observations, which could be represented within 1 part in 10,000 by the linear formula,

$$\text{From } 68^\circ \text{ to } 92^\circ. \quad s = 1 + \cdot 000{,}14\,(t - 60) \quad . \quad . \quad . \quad . \quad (8).$$

This formula gives a value nearly 1 part in 1000 lower than (7) at 90°, and it cannot be satisfactorily fitted on to Regnault's observations at higher temperatures. I think on the whole it would be better to retain Regnault's formula as previously emended, until further observations are available. Although the agreement of the four observations is so perfect among themselves, it is possible that they may be affected by a constant error of this order of magnitude, if all the difficulties of the work are rightly considered. Besides, the linear formula cannot represent the probable increase in the rate of variation of the specific heat at higher temperatures, which is theoretically required to account for the vanishing of the latent heat at 360° C., the critical temperature.

It would of course be easy to represent the observations a little more accurately in any particular part of the curve by using more complicated formulæ, but it is doubtful whether the advantage gained would be worth the extra complication, and the possible confusion caused by changing a formula already published and widely distributed.

Dr. BARNES ('Roy. Soc. Proc.,' vol. 67, p. 242) has proposed the following:—

From 5° to 37°·5,

$$s = \cdot 99733 + \cdot 000{,}0035\,(37\cdot 5 - t)^2 + \cdot 000{,}000{,}10\,(37\cdot 5 - t)^3 \quad . \quad . \quad (9).$$

From 37°·5 to 55°,

$$s = \cdot 99733 + \cdot 000{,}0035\,(37\cdot 5 - t)^2 - \cdot 000{,}000{,}10\,(37\cdot 5 - t)^3 \quad . \quad . \quad (10).$$

From 55° to 100°,

$$s = \cdot 99850 + \cdot 000{,}120\,(t - 55) + \cdot 000{,}000{,}25\,(t - 55)^2 \quad . \quad . \quad . \quad . \quad (11).$$

The first two formulæ differ only in the sign of the third term. They are not quite so simple and convenient for calculation as (5) above. The first formula does not represent the observations below 10° quite so accurately as formula (6), but both are probably within the possible limits of error. The mean divergence of the observations between 37°·55 and 5° from the second formula is about 3 parts in 10,000, and is rather greater than the mean divergence of the observations from the old formula (5). The agreement with the latter would be greatly improved if we reject the discordant observation No. XXII., in series 2 at 54°·61 (BARNES, p. 244), giving greater weight to the later observations, No. XXXII. in series 3 at 54°·57, and No. XLVIII., in series 6 at 51°·02. On the whole, the balance of probability appears to me to be in favour of retaining the older and simpler formula in preference to that since proposed by Dr. BARNES.

The third of the above formulæ, from 55° to 100°, does not fit with the second at 55°, the respective values being, (10) ·99893, and (11) ·99850. This is shown by the difference in Table XIV. between the values at 55° and 60° in the column headed "BARNES, Roy. Soc., 1900," which is only ·00016. The corresponding differences for five degrees on either side are 50° to 55°, ·00087; 60° to 65°, ·00061. There is also a considerable change of slope from ·000216 to ·000120 at 55°. It is, of course, necessary that the values should fit accurately at the point where the formulæ meet, and it is further desirable that there should *not* be a sudden change of slope. The first condition is accurately and the second very approximately satisfied by the old formulæ (5) and (7) at 60°.

The following table contains a comparison of the formula of LÜDIN and those of BARNES, with those previously published in the B.A. Report, 1899.

TABLE XIV.—Comparison of Formulæ.

Temperature, Centigrade.	LÜDIN, 1895.	BARNES, Roy. Soc., 1900.	B.A. Report, 1899.	Values of J.
°				
0	1·0084	1·0084	1·0094	4·219
5	1·0051	1·0055	1·0054	4·203
10	1·0026	1·0031	1·0027	4·191
15	1·0009	1·0012	1·0011	4·185
20	1·0000	1·0000	1·0000	4·180
25	0·9998	0·9991	0·9992	4·177
30	0·9999	0·9986	0·9987	4·175
35	1·0006	0·9984	0·9983	4·173
40	1·0017	0·9984	0·9982	4·173
45	1·0030	0·9986	0·9983	4·173
50	1·0046	0·9991	0·9987	4·175
55	1·0063	0·9999	0·9992	4·177
60	1·0079	1·0001	1·0000	4·180
65	1·0094	1·0006	1·0008	4·183
70	1·0109	1·0013	1·0016	4·187
75	1·0123	1·0020	1·0024	4·190
80	1·0131	1·0027	1·0033	4·194
85	1·0137	1·0034	1·0043	4·198
90	1·0136	1·0041	1·0053	4·202
95	1·0129	1·0048	1·0063	4·206
100	1·0117	1·0055	1·0074	4·211

For the reasons already stated, the values in the above table are all expressed in terms of a unit at 20° C. for comparison, and are given to 1 part in 10,000 only. I am inclined to regard the values and formulæ corresponding to the column headed "B.A. Report, 1899," as being the most probable. The corresponding values of J, the number of joules per calorie, are calculated assuming the value 4·180 at 20° C.

(47.) *Theoretical Discussion of the Variation of the Specific Heat.*

CLAUSIUS ('Mechanical Theory of Heat,' p. 180, translation, 1879) has calculated the specific heat of water at constant volume C_v from that at constant pressure C_p by means of the well-known equation,

$$C_v = C_p - T\,(dv/dT)_p\,(dp/dT)_v = C_p - T(dv/dT)_p^2/(dv/dp)_T \quad . \quad . \quad (12).$$

Taking REGNAULT's values of C_p, KOPP's values of the coefficients of expansion, and GRASSI's values of the compressibility, CLAUSIUS finds the values,

Temperature	0°	25°	50°
C_p, at constant pressure . .	1·0000	1·0016	1·0042
C_v, at constant volume . . .	0·9995	0·9918	0·9684

Dieterici ('Wiedemann's Annalen,' vol. 57, p. 333) has repeated the calculation, employing Rowland's values of the specific heat at constant pressure. He seems to argue that the variation of the specific heat at constant pressure as discovered by Rowland is of the character to be expected from the large variation of the specific heat at constant volume. I do not think, however, that we can fairly infer anything with regard to the variation of the specific heat at constant pressure from that at constant volume. The value of the latter can only be deduced by the aid of very uncertain data, and we have as yet no sure theoretical guide as to the way in which it ought to vary, apart from experiments on the specific heat at constant pressure.

The most remarkable facts about the specific heat of water are its great constancy over a considerable range, and its high value as compared with that of the solid or the vapour. The specific heat of liquid mercury is nearly the same as that of the solid, and both are about double that of the vapour at constant volume. The specific heat of water is double that of ice, and nearly three times that of steam at constant volume. If we adopt Rankine's hypothesis of a constant "absolute" specific heat for each kind of matter, we must admit that this absolute specific heat has a different value in different states.

J. Macfarlane Gray ('Proc. Inst. Mech. Eng.,' 1889), adopting Rankine's idea of a constant specific heat for "ideal" water, gives, without proof, the following formula for the total heat h of water reckoned from 0° C.,

$$h = 1{\cdot}0106\,(\theta - 273) + \theta v\, dp/d\theta \quad . \quad . \quad . \quad . \quad . \quad . \quad (13),$$

in which the constant is the ideal specific heat, and $dp/d\theta$ is the rate of increase of the steam-pressure with temperature. The term $\theta v\, dp/d\theta$ is evidently intended to represent the latent heat of expansion of the liquid from the ideal state against the steam-pressure. The value of v, however, is not the apparent expansion from 0° C., but is the "actual volume of unit mass of water less its absolute matter-volume, the pressure during the heating being that due to the higher temperature. Absolute matter is no doubt much more dense than platinum; and the reduction from the apparent volume, being very small, may therefore be disregarded." The value of v is therefore taken as the observed volume at the temperature θ of unit mass of water. The justification of this argument is not very clear, but the values calculated by the formula on this assumption agree fairly with the observations of Regnault on the specific heat between 110° and 190° C.*

W. Sutherland, in a recent paper "On the Molecular Constitution of Water," ('Phil. Mag.,' vol. 50, p. 460, 1900), has endeavoured to explain the properties of water on the assumption that it is a mixture of two kinds of molecules in varying proportions, "trihydrol," $3H_2O$, which is identical with ice, and "dihydrol," $2H_2O$, which constitutes the greater part of liquid water at higher temperatures. He

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* In a recent paper ('Proc. Inst. Civil Engn.,' vol. 147, 1902), Gray gives a further elucidation of this formula, and a detailed comparison with our experimental results.—*Added March* 11, 1902.

calculates the densities and proportions of the two ingredients on the assumption that each constituent follows the MENDELÉEFF law of expansion, or that the density is a linear function of the temperature. He thus finds that 1 gramme of water at 0° C. consists of liquid $3H_2O$, density ·88, ·375 gramme; liquid $2H_2O$, density 1·09, ·625 gramme. The latent heat of fusion of trihydrol, 16 calories, is calculated on the assumption that it would expand ·0366 on fusing, which is the mean expansion on fusion deduced from a number of metals. The remainder of the latent heat of fusion of ice is supposed to be made up of the heat of dissociation of ·625 trihydrol into dihydrol, and the solution of the remaining fraction ·375 in the dihydrol. As a starting-point for the explanation of the variation of the specific heat, he assumes that the specific heat of dihydrol is 1·00 at 200° C., at which temperature water contains ·167 of trihydrol. Taking "the usual rate of variation of the specific heat of a liquid as ·1 per cent. per degree," he finds ·83 for the specific heat of pure dihydrol at 0° C. He takes that of trihydrol to be ·6 with a similar rate of increase, and explains the remainder of the specific heat of water as due to the heat of dissociation of trihydrol and of solution in dihydrol, which he calculates on the above assumed values of the specific heats.

It is more natural to regard the high specific heat of water as due to internal work done against molecular forces, and as being closely related to the decrease of the latent heat of vaporization with rise of temperature. Whatever assumptions are made with regard to the molecular constitution of water, it was proved by RANKINE (in a slightly different form), in 1849, that the rate of decrease of the latent heat $dL/d\theta$ was equal to the difference between the specific heat of water s_w, and that of steam S_s at constant pressure.

$$dL/d\theta = S_s - s_w \quad \ldots\ldots\ldots\ldots \quad (14).$$

This is accurately and necessarily true if we assume that steam may be regarded as an ideal gas of constant specific heat, which is probably justifiable at low pressures. At higher pressures, it is necessary to make allowance for the co-aggregation of the steam molecules, which may be effected to a high degree of approximation by the method which I have explained ('Roy. Soc. Proc.,' Nov., 1900). If we write h for the total heat of water from 0° C. (without assuming the specific heat to be constant), we obtain the relation,

$$L - L_0 = S_0(\theta - \theta_0) - (n+1)(cp - c_0p_0) - h \quad \ldots\ldots \quad (15),$$

where S_0 is the limiting value of S_s at zero pressure, and c represents the defect of the actual volume of the steam from the ideal volume $R\theta/p$. This defect of volume is independent of the pressure p, but varies inversely as the nth power of the absolute temperature θ. It is clear that the rate of diminution of the latent heat is not constant, but increases at higher temperatures, on account of the co-aggregation of the molecules, as represented by the increase of the product cp, where p is the saturation-pressure.

Similarly, we might suppose that the rate of variation of the total heat h of the liquid would be constant for ideal water, but increases at higher temperatures for actual water on account of the existence of molecules of vapour in the liquid. The two phases in equilibrium at saturation-pressure may be regarded as a saturated solution of water in steam (the dissolved water being represented by the proportion of co-aggregated molecules $cp/\text{R}\theta$), the liquid phase conversely as a saturated solution of steam in water. On the one hand, the total heat of the steam is reduced below its ideal value by the amount $(n + 1)\,cp$, owing to the presence of dissolved molecules of water causing a diminution of volume c per unit mass of the solution; on the other hand, the total heat of the liquid is increased by the presence of a certain proportion of dissolved molecules of steam, which may doubtless account for part of the thermal expansion of the liquid. When the temperature is raised, the properties of the two phases continue to approach each other, as the proportion of water in the steam and of steam in the water increases At the critical temperature the two solutions mix in all proportions.

It is possible to estimate more or less perfectly the number of co-aggregated molecules present in steam at any temperature by observing the defect of volume from the ideal state; or to deduce the value theoretically on certain assumptions from experiments by the JOULE-THOMSON method on the cooling effect of expansion through a porous plug or throttling aperture (' Roy. Soc. Proc.,' 1900, vol. 67, p. 270). It is probable that the proportion of steam molecules present in the liquid is similarly related to its expansion, but there is no certain theoretical guide to the relation. The simplest hypothesis to make would be that the number of vapour molecules per unit volume of the liquid is the same as the number of molecules per unit volume of the saturated vapour at the same temperature. If we suppose the formation of vapour molecules in the interior of the liquid (specific volume w) to require the addition to the liquid of the latent heat corresponding to the same quantity of vapour (specific volume v) when formed outside the liquid (*i.e.*, if we neglect the heat of solution of the vapour in the liquid), the total heat h of the liquid would require to be increased by an amount $w/(v - w)$ of L to allow for the latent heat of the dissolved steam. It happens that this result, though obtained by a quite different line of reasoning, agrees with the expression given by GRAY, and approximately represents the experiments of REGNAULT at high temperatures. We thus obtain the simple formula,

$$h = s_0t + w\text{L}/(v - w). \qquad \qquad (16).$$

On similar grounds it would be natural to suppose that the increase of the specific heat, as we approach the freezing-point, was due to the presence of a certain proportion of dissolved ice molecules, which are also required to account for the anomalous expansion. But here there is no obvious guide to the proportion required, or to the latent heat of solution to be assumed. The basis adopted by SUTHERLAND appears to be too empirical, and the results to which it leads are too vague and inexact to permit of a profitable comparison with experiment. In order to place any such hypothesis as that represented by formula (16) on a sound experimental basis, it would be necessary to determine the variation of specific heat of several typical liquids with great accuracy over a wide range. The required data are not at present obtainable, but the suggestion appears to be worth recording as a possible physical interpretation of the variation of specific heat.

INDEX SLIP.

BARNES, Howard Turner—On the Capacity for Heat of Water between the Freezing and Boiling Points, together with a Determination of the Mechanical Equivalent of Heat in Terms of the International Electrical Units. Phil. Trans., A, vol. 199, 1902, pp. 149–263.

Calorimetry—Continuous Electrical Method.
BARNES, Howard Turner. Phil. Trans., A, vol. 199, 1902, pp. 149–263.

Heat—Mechanical Equivalent, Comparison of Mechanical and Electrical Methods.
BARNES, Howard Turner. Phil. Trans., A, vol. 199, 1902, pp. 149–263.

Specific Heat of Water—Variation determined by Electrical Method.
BARNES, Howard Turner. Phil. Trans., A, vol. 199, 1902, pp. 149–263.

III. *On the Capacity for Heat of Water between the Freezing and Boiling-Points, together with a Determination of the Mechanical Equivalent of Heat in Terms of the International Electrical Units.—Experiments by the Continuous-Flow Method of Calorimetry, performed in the Macdonald Physical Laboratory of McGill University, Montreal.*

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Communicated by Professor H. L. Callendar, *F.R.S.*

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Table of Contents.

Sec. 1.—*Introduction.*

The unsatisfactory state of our knowledge of the Mechanical Equivalent of Heat and, inseparably connected therewith, of the capacity for heat of water, is the more surprising when we consider the large number of physicists who have devoted their attention to this subject during the century just closed. Since the remarkable pioneer experiments of Count Rumford, undertaken just 100 years ago, to determine the nature of heat, the subject has been advanced step by step by different investigators. Conspicuous among these we may mention Regnault, who gave us the first idea of the mode of the variation of the specific heat of water with temperature, without, however, giving us any knowledge of the mechanical equivalent of heat; Joule, who gave us the first measurements of the mechanical equivalent without attempting to study the thermal unit at different temperatures; Rowland, who by the remarkable accuracy of his experiments gave us not only a direct determination

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of the mechanical equivalent, but also the variation of the thermal unit over a limited range. More recently we have the exceedingly careful experiments of MICULESCU, of GRIFFITHS, of SCHUSTER and GANNON, and of REYNOLDS and MOORBY.

It is evident from only a cursory glance at the work of these and the host of other investigators, that the science of calorimetry must be regarded as incomplete and approximate so long as its fundamental unit remains in doubt. To obtain, as is urgently needed, a complete series of determinations of the capacity for heat of water over the entire range of temperature is manifestly impossible by the older methods of calorimetry. A new method has long been required, more completely free from the influence of extraneous surrounding conditions.

During a conversation which I had with Professor CALLENDAR, in the autumn of 1896, we discussed the unsatisfactory state of our knowledge of the specific heats of water and mercury. Professor CALLENDAR pointed out that what was required was a new method of calorimetry, which would reduce to a minimum many of the larger corrections inherent in, and making uncertain, the older methods. Such he considered possible in a continuous, or steady, flow method, in which a stream of liquid could be made to continuously carry off a definite and measurable supply of heat. This method he considered capable of great accuracy and free from nearly all the errors in the older methods. I very gladly consented to assist Professor CALLENDAR in developing this method, which we commenced as a joint work early in 1897.*

The early experiments with mercury will be discussed in full in another paper, and cannot be more than mentioned in this place. They were satisfactory in many respects, but must be considered more as preliminary attempts, the experience of which served so much to aid in later measurements with water. A calorimeter, designed for the determination of the specific heat of water, was set up and tested just previous to the meeting of the British Association at Toronto, to which body a preliminary note was sent describing the method in general terms. On the re-opening of the College session, in September of that year (1897), Professor CALLENDAR was unfortunately obliged, through stress of work, to relinquish his connection as a joint observer in the experiments. My own duties, however, were such as to allow of a certain amount of time to be devoted to research, so that the work was carried on at intervals throughout the winter. During this session Mr. RUSSELL W. STOVEL, B.Sc., joined our graduate classes and devoted a large part of his time to assisting in the work. It is largely to his skill as an observer that it was possible to continue the work during this time.

In the spring of 1898 Professor CALLENDAR was called to London to fill the Quain Chair of Physics in University College, and was obliged to sever his connection entirely with the experiments. It was with extreme regret that we realized this, as

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* For theory of experiment and work done prior to 1897, see the paper by Professor CALLENDAR above, pp. 55–148.

so much was due to his kind supervision in perfecting different portions of the apparatus. Mr. STOVEL also was obliged to leave at this time, so that the work was somewhat delayed.

During the summer of 1898, Mr. CHARLES SHEFFIELD, B.Sc., was kind enough to devote his entire time to the work, and made himself exceedingly useful through his untiring efforts until late in the autumn. University duties being closed, it was possible for us to devote all our time to the work. The measurement of the mechanical equivalent we obtained will be described further on, but it must be regarded as a preliminary attempt owing to a source of error in the method, which was not discovered until some time after. We made a careful study of the general theory of the method, which, as will be explained in its place, was affected somewhat by the error above mentioned. On comparing these determinations with later ones, and more particularly in applying the theory of the method to different calorimeters, we met with such large discrepancies, much larger than any possible error in the instrumental readings, that we were forced to abandon the greater part of our earlier results, and re-organize the experiment.

Unfortunately Mr. SHEFFIELD was called away at this time and was unable to continue his work on the method. It is with extreme regret that I have to record the death of Mr. SHEFFIELD, since leaving this laboratory, which occurred recently at Niagara Falls, where he occupied a position in the capacity of electrical engineer. His death at so early an age and under such trying circumstances is all the more sad, as he had proved his worth and ability in so many ways as an accurate observer and faithful worker.

During the winter of 1898–99 I was obliged to undertake the sole responsibility of the work, with the exception of some temporary assistance in taking observations from my colleague, Mr. H. M. TORY, M.A., to whom I am also indebted for many helpful suggestions. As at that time there was no prospect, until the close of the session, of finding an experienced observer who could devote sufficient time to help in taking observations, it was necessary for me to arrange the conditions of the experiment so as to be able to take all the observations, both thermal and electrical, myself. With a little practice I was soon satisfied that this could be done, although not quite so quickly as with two observers, yet with sufficient accuracy to satisfy the conditions of the experiment. It became chiefly necessary to produce perfectly steady and uniform conditions, over a more extended period of time, conditions which demanded greater refinements in the apparatus. The experiments from this time on, as they became little by little improved and extended, were so steady and consistent, and fulfilled the conditions demanded by the theory so perfectly, that it was deemed unnecessary to break the continuity of the work by introducing a second observer. From January, 1899, to the close of the work, the complete set of observations for nearly every experiment was taken by one observer.

The results of the work from 4° C. to 60° C., obtained between January and June of that year, were communicated by Professor CALLENDAR and myself to the meeting of the British Association, at Dover, in September. A reprint of this communication, slightly modified, to contain some later determinations above 60°, was published in the 'Physical Review' of April, 1900.

In the present communication I desire to record the complete set of experiments obtained for the mode of variation of the specific heat of water over the entire range 0° C. to 100° C., feeling confident that they represent, to an order of accuracy approaching 1 in 10,000, the true values, and to point out the wonderful verification they give of the work of REGNAULT over the range where his experiments are the most trustworthy, a verification so complete that the present work may be said to extend over the entire range where it is possible to maintain water in the liquid phase.

I desire, at this time, to record my thanks to Professor JOHN COX, Director of the Macdonald Physical Laboratory, for placing every facility at my disposal that could aid me in the work; to Mr. J. W. FRASER, B.Sc., Demonstrator in Physics in this laboratory, for his observations on the comparisons of our 1-ohm resistance standards; and to Mr. G. W. SCOTT for his kindness in helping me prepare figures for this paper.

I am also indebted to Messrs. EIMER and AMEND, of New York, for the very efficient way in which they made three glass calorimeters, and the great trouble they took to exhaust very perfectly the vacuum-jacket connected with each one.

Sec. 2.—*General Theory of the Method of Continuous Calorimetry.*

If we have a flow of liquid, Q per second, continuously heated by an electric current in a fine tube enclosed in a vacuum-jacket, the walls of which are maintained at the temperature of the liquid flowing into the fine tube, then, when equilibrium has been established,

$$\mathrm{J}s\,\mathrm{Q}t\,(\theta_1-\theta_0)+(\theta_1-\theta_0)\,ht=\mathrm{EC}t,$$

where

J is the mechanical equivalent of heat,
s, the specific heat of the liquid,
θ_0, the temperature of the inflowing liquid,
θ_1, the temperature of the outflowing liquid,
h, the heat-loss per degree difference in temperature between the surface of the fine tube and the walls of the vacuum-jacket,
EC, the electrical energy generated per second, and
t, the time of flow.

If the liquid be a conductor of electricity, such as mercury, then E represents the difference of potential maintained across the column of liquid in the fine tube, and C represents the current flowing through the tube. If the liquid be a non-conductor, such as water, then E represents the difference of potential across a conducting wire passed through the tube in which the current C flows.

We will deal entirely in this place with the method as applied to this latter case, such as a steady flow of water, and replace J*s* in the general equation by J, or the number of joules in one calorie.

Let $J = 4{\cdot}2\ (1 \pm \delta)$, where δ is a small quantity varying with the thermal capacity of the water, then we may write the general equation,

$$4{\cdot}2\ (1 \pm \delta)\ Qt\ (\theta_1 - \theta_0) + (\theta_1 - \theta_0)\ ht = ECt.$$

Dividing through by t, and re-arranging the terms, we have

$$4{\cdot}2\ Q\ (\theta_1 - \theta_0)\ \delta + (\theta_1 - \theta_0)\ h = EC - 4{\cdot}2\ Q\ (\theta_1 - \theta_0).$$

This we will call the general difference equation.

The total heat-loss from the water will be made up of radiation from the surface of the tube through which the water is flowing, conduction from the ends of the tubes containing the thermometers for measuring the temperature of the inflowing and outflowing water, and convection currents due to insufficient stirring around the thermometer bulbs. There will be a small gain in heat due to work done by the water in flowing through the fine tube. To study the effect of these upon the general difference equation it will be necessary to refer to the diagram of the continuous-flow electric calorimeter in its simplest form, given in fig. 1.

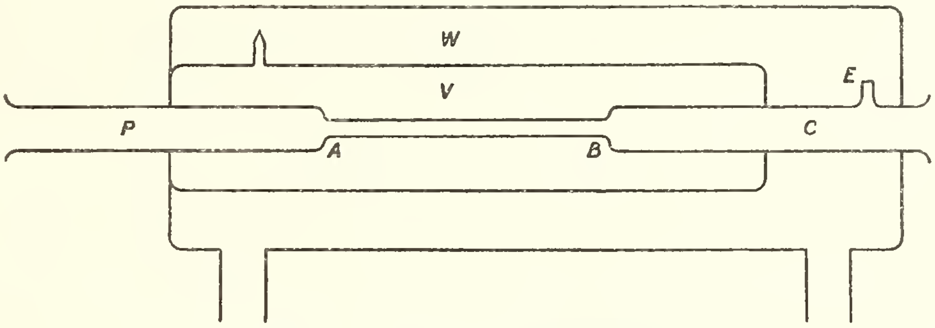

Fig. 1. Diagram of Calorimeter.

In this AB represents the fine tube in which the water is heated while flowing through, V, the vacuum-jacket, and C and P the inflow and outflow tubes connected to AB, in which the thermometers are placed. The water-jacket is shown at W, and includes the vacuum-jacket and inflow-tube C. The water enters the calorimeter at E from a reservoir separate from that supplying the water for the jacket, but maintained at the same temperature. The electric heating current passes through the fine tube AB through a platinum wire extending the whole length, but is arranged so as not to generate heat in the vicinity of the thermometer bulbs. The thermometer in C measures the temperature θ_0 of the inflowing water, and that in P the temperature θ_1 of the outflowing water, warmed by the passage of the electric current. The temperature of the water increases rapidly from B to A, and gradually decreases from A towards P.

Radiation.—The loss of heat through the vacuum-jacket will consist of the cooling of the surface of the glass in the flow-tube by radiation, by convection currents of residual vapour in the jacket, and by radiation from the molecules of the water itself. Provided the vacuum is good, these are all included in the h term of the general difference equation. This radiation term obviously should not vary, but should remain independent of the quantity of water flowing, provided it can be assumed that the temperature gradient from B to A remains the same for all flows. This assumption can be justified only if the temperature gradient is linear. If it is not linear then we may have either one of two conditions:—

1. When the distribution of heat in the water column AB is such that the water is hotter in the centre than the sides, in which case the temperature of the glass surface of the fine tube will be that represented in (1) fig. 2, and will depend on the thermal conductivity of the different layers of water between the centre and the sides, which will be conditioned by the rapidity of flow. This condition is fulfilled perfectly when the water column is receiving heat from a central wire conductor and flowing at velocities less than the critical velocity for the tube in question. In this case the water flows in parallel stream-lines, and does not mix. The higher the velocity of flow up to the critical velocity, the more gradual will be the slope of the temperature gradient of the glass surface from B to A. At A, the water is mixed around the thermometer bulb and the temperature of the glass suddenly increases. For any given temperature θ_1 of the water, as indicated by the outflow-thermometer, the total heat-loss from the water will decrease with increasing velocity of flow in proportion to the slope of the temperature gradient along BA.

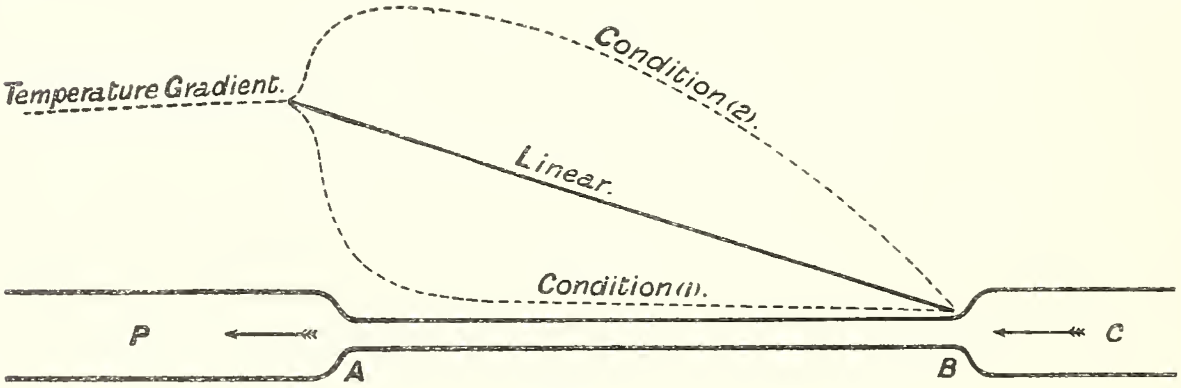

Fig. 2.

2. The case where the sides of the water column are hotter than the interior, or where the water is receiving heat from the surface of the fine tube. The

temperature gradient will then be represented by (2) fig. 2. The water flowing through the interior of the tube will receive less and less heat from the layers along the sides as the velocity of flow increases. To attain the given temperature θ_1 on the outflow-thermometer, the temperature gradient from B to A will rise rapidly, and suddenly decrease as the water is mixed around the bulb. The total heat-loss from the water will then increase with increasing flow in proportion to the slope of the temperature-gradient from B to A. This condition would be perfectly fulfilled by replacing the fine glass tube by one of metal through which the electric heating current could be made to flow. Less perfectly it is fulfilled when the heating wire lies along the sides of the tubes, and supplies heat to the layers of water nearest the walls of the tube.

In both these cases the heat-loss would not be independent of, but would depend on, some function of the flow. To ensure a perfectly uniform temperature, equal to that of the flow-tube, throughout any section of the water column, it is necessary to produce thorough mixing at all points, and avoid the formation of stream-lines. If this is fulfilled, we can be safe in assuming the temperature gradient at least approximately linear from B to A in both the above cases. Also that the total quantity of heat lost per second by radiation from the water in its passage through the length of tube included in the vacuum-jacket is the same, quite independent of the velocity of flow.

An experimental study of the two cases above given, where the water flowing in parallel stream-lines receives heat from a platinum wire, which may be moved from the centre to the sides of a 3-millim. bore flow-tube, will be given in Section 7.

Conduction.—The heat-loss by conduction from the ends of the calorimeter will evidently be very small where a bad thermal conductor, such as water, is used. Where metal wires are introduced to convey the electric current to the central heating wire, the conduction of heat from the water by the wires assumes a much more serious character, more especially when the calorimeter and jacket are maintained at a temperature very different to that of the surrounding air. At the inflow end the effect, when the calorimeter is at a higher temperature than that of the air, is to lower the temperature θ_0 of the inflow water by a small amount. The effect at the outflow end is similar, but smaller, on account of the direction of flow. It is evident that this can always be measured and eliminated for any given flow by recording the temperatures of the inflow and outflow thermometers before the electric heating current is turned on. The only conduction effect that these "cold" readings will not take account of is the conduction from the outflow-tube due to the rise of temperature $(\theta_1 - \theta_0)$. This must be separately measured in other ways. It can be estimated and its maximum effect obtained, for any given difference in temperature, by surrounding the outflow-tube beyond the water-jacket by a water circulation, the temperature of which can be changed at will. If it is made as small as possible by replacing the water circulation by heavy lagging; its effect can be measured by varying the flow of water, as will be shown further on. This conduction effect will be independent of the difference in temperature between the jacket water and the outside air, and depend on the rise of temperature $(\theta_1 - \theta_0)$ directly, and on the velocity of flow inversely.

Convection.—We have already discussed the effect of the stream-line flow on the radiation correction, when the water is not stirred in its passage through the flow-tube. It is proposed further on to treat this more in detail, as it has an important bearing on the general validity of this method applied to a non-conducting liquid. The effect of convection currents around the thermometer bulbs is avoided by suitably stirring the water. Strictly speaking, the thermal stream-lines in the flow-tube should not be classed as convection currents, but I have included them here for the sake of convenience.

Gain of Heat.—The work done by the water in flowing through the fine tube may be measured by determining the difference in water-pressure between the inflow and outflow-tubes, for any given flow. The work done by any other flow can then be determined by measuring the change in temperature on the outflow-thermometer due to the change in flow.

If W_1 be the work done by the flow Q_1 per second,
W_2 ,, ,, ,, Q_2 ,,
then

$$W_1 = JQ_1(\theta_1 - \theta_0) + (\theta_1 - \theta_0)h \quad \text{and} \quad W_2 = JQ_2(\theta_2 - \theta_0) + (\theta_2 - \theta_0)h,$$

where θ_0 is the temperature of the inflowing water as before,
θ_1 and θ_2 the temperatures of the outflowing water for the flows Q_1 and Q_2 respectively, and
h the heat-loss per degree rise, as before.

Then $W_1 - W_2 = J(Q_1 - Q_2)(\theta_1 - \theta_2) + h(\theta_1 - \theta_2)$.

But h is small, and $(\theta_1 - \theta_2)$ is small, so that we may neglect it in comparison to $(Q_1 - Q_2)$. If we find that $(\theta_1 - \theta_2)$ is negligible for a large value of $(Q_1 - Q_2)$, then we have $W_1 = W_2 = 0$.

For the limits of flow and the size of flow-tubes I adopted in the present experiments, no measurable effect could be obtained on the outflow-thermometer. Even if the work done was appreciable, the method adopted of obtaining the "cold" readings for each flow would eliminate it, except if it varied with the change in the viscosity of the water, heated through the temperature $(\theta_1 - \theta_0)$.

Method of Measuring the Specific Heat.—Referring to the original difference-equation, we see that

$$4{\cdot}2\,Q(\theta_1 - \theta_0)\delta + (\theta_1 - \theta_0)h = EC - 4{\cdot}2\,Q(\theta_1 - \theta_0),$$

in which there are the two terms δ and h to be determined. If we take two flows of water, Q_1 and Q_2, for the same inflow temperature θ_0, then we have the two equations

$$4{\cdot}2\, Q_1 (\theta_1 - \theta_0)\, \delta_1 + (\theta_1 - \theta_0)\, h = E_1C_1 - 4{\cdot}2\, Q_1 (\theta_1 - \theta_0),$$
$$4{\cdot}2\, Q_2 (\theta_2 - \theta_0)\, \delta_2 + (\theta_2 - \theta_0)\, h = E_2C_2 - 4{\cdot}2\, Q_2 (\theta_2 - \theta_0).$$

If the electric current is adjusted for the two flows so that $\theta_1 = \theta_2$, then

$$(\theta_1 - \theta_0)\, h = (\theta_2 - \theta_0)\, h,$$

and $\delta_1 = \delta_2 = \delta$, and hence by direct subtraction and writing $d\theta = (\theta_1 - \theta_0) = (\theta_2 - \theta_0)$,

$$4{\cdot}2\, (Q_1 - Q_2)\, d\theta\delta = (E_1C_1 - 4{\cdot}2\, Q_1\, d\theta) - (E_2C_2 - 4{\cdot}2\, Q_2\, d\theta),$$

and
$$\delta = \frac{(E_1C_1 - 4{\cdot}2\, Q_1\, d\theta) - (E_2C_2 - 4{\cdot}2\, Q_2\, d\theta)}{4{\cdot}2\, (Q_1 - Q_2)\, d\theta},$$

from which J, or the number of joules per calorie $= 4{\cdot}2\, (1 \pm \delta)$. By substituting δ in either difference-equation, h can be obtained.

The value of J thus obtained will be the mean over the range $d\theta$ through which the water is heated, and apply to the mean temperature

$$\theta_0 + \tfrac{1}{2} (\theta_1 - \theta_0) = \text{T (mean)}.$$

If the variation of the value of J is not linear over this mean temperature, then for different values of θ_0 and θ_1 for the same value of T (mean), the value of J will be slightly different.

Application of the General Difference Equation to Test the Theory of the Method.—In order to test the accuracy of the assumptions made in regard to

(*a*) The dependence of the heat-loss on the rise of temperature,

(*b*) The dependence of the heat-loss on the flow, including the conduction correction,

we will consider the general difference equation. We have as before

$$4{\cdot}2\, Q\, (d\theta)\, \delta + (d\theta)\, h = EC - 4{\cdot}2\, Q\, (d\theta).$$

Dividing through by $d\theta$, the equation is expressed per degree rise, or

$$4{\cdot}2\, Q\, \delta + h = \frac{EC - 4{\cdot}2\, Q\, d\theta}{d\theta} = \Delta.$$

If h depends only on $d\theta$, then for different values of $d\theta$, for the same mean temperature and flow, we have

$$4{\cdot}2\,Q\,\delta + h = \Delta = \text{constant}.$$

This relation should hold provided the temperature coefficient of both δ and h is linear. A small variation from lineality can, however, be safely neglected.

If we vary the flow and keep the rise of temperature constant, then we have in the equation already given

$$4{\cdot}2\,Q\,\delta + h = \Delta.$$

The value of Δ for different values of Q will vary in proportion to $4{\cdot}2\,Q\,\delta$, but the variation will be a linear one, provided we are not neglecting any term on the left-hand side varying inversely as the flow. If $\delta = 0$, then

$$h = \frac{EC - JQ\,d\theta}{d\theta}$$

for any value of Q.

In Section 5 the experimental proof of these considerations is given, and it is shown that within wide limits of flow it holds with great accuracy. For very small values of Q the conduction becomes measurable, but the limits chosen in the present series of experiments are seen to hold for the higher temperatures as perfectly as for the lower.

Sec. 3.—*Measurement of Fundamental Constants.*

Owing to the importance attached to the measurement of the different constants in the general equation of the method, it is proposed to treat each one separately in this section, dividing them up under the two heads electrical and thermal. In the first we have the Clark cell, standard resistance and potential measurements, and in the second the measurement of temperature, weight and time.

The general plan of the electrical connections is given in fig. 3. A large 4-cell accumulator, of 200 ampere-hours each, supplied the steady heating current to the calorimeter through the resistance and rheostat. Potential terminals were taken from the calorimeter and resistance, and from two Clark cells in series, to the paraffin block, where they were placed in mercury cups cut in the solid paraffin. Wires leading from two holes, placed equi-distant from the other cups in the block, were carried to the potentiometer shown to the left, and included a galvanometer in the circuit. By interchanging two connections, the Clark cell, calorimeter or resistance could be connected through the galvanometer to the potentiometer. By altering the rheostat or connecting a smaller number of cells, the heating current could be adjusted for a change of water flow in the calorimeter, so as to produce the same rise of temperature.

If X_0 is the reading of the potentiometer for the balance point of the Clark cell,
X_1 potentiometer reading for difference of potential on calorimeter,
X_2 the same for resistance R,
e the E.M.F. of Clark cell,
R the value of the resistance,
then E, the potential across the calorimeter, is $X_1/X_0 \times 2e$, where the two Clark cells are used in series.

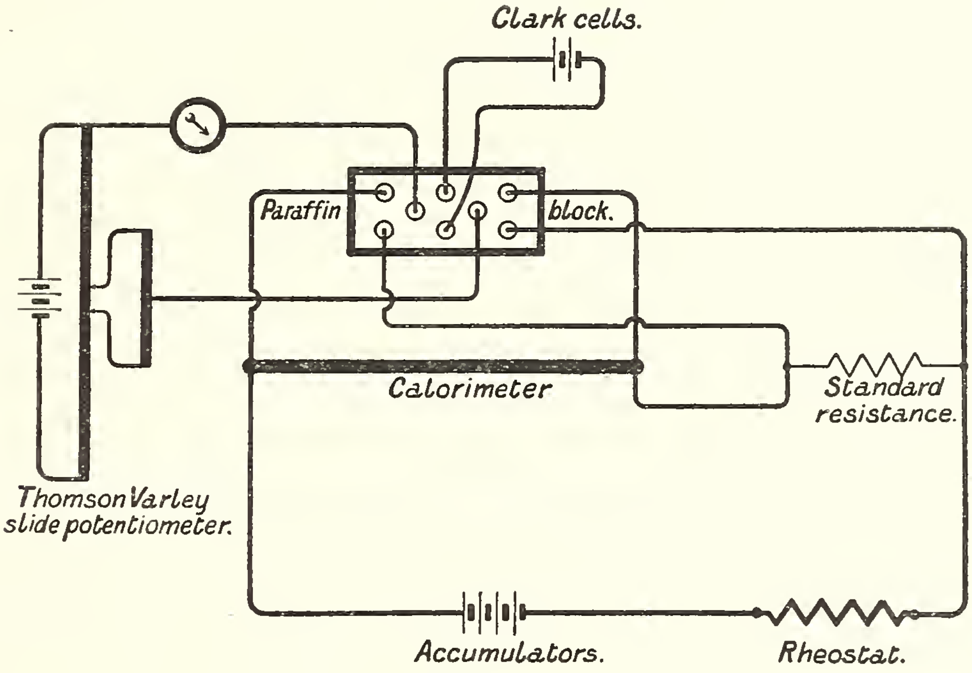

Fig. 3.

Also the current C in the circuit is $X_2/X_0 \times 2e/R$, from which we get the total watt energy per second supplied to the calorimeter, when the conditions have become steady, and used in heating the water,

$$EC = \frac{X_1 X_2 e^2 4}{X_0^2 R}.$$

The experimental error involved in the measurement of EC will depend on the accuracy of the measure of X_1, X_2, and X_0 and on the constancy of e and R.

Sec. 3*a*.—*Clark Cell.*

Some time previous to my undertaking the present series of experiments, I made a careful study of the Clark cell with Professor CALLENDAR in order to become more conversant with its behaviour, as well as to devise, if possible, a more reliable form of cell than the one in vogue at that time. The result of this work has already been published in full ('Proc. Roy. Soc.,' vol. 67, p. 117 (1897)), and in consequence may be passed over here with but a brief mention. A thorough study of the old form of cell recommended by the Board of Trade formed one of our chief objects, including measurements of the diffusion lag on a sudden and definite change of temperature. It was shown that for a change of 15° C. the time required for a B.O.T. cell to assume its true value was of the order of 14 days when left undisturbed, but only 2 days when shaken three times at different intervals. In cells where the saturated solution of zinc sulphate was replaced by moist zinc sulphate crystals, no such effect could be noticed, but the cells assumed their normal value on a sudden change in temperature in 10 or 15 minutes, or, in other words, in only such time as was required for the cell to assume the temperature of the surroundings.

These modified B.O.T. cells were studied in every detail, but more particularly as regards the formula governing the variation of the E.M.F. with temperature and their reproducibility. The remarkable constancy of these cells, their agreement amongst themselves, and the closeness with which they followed the temperature expression deduced, was a matter of much satisfaction. It was found that the temperature change of the E.M.F. depended on two conditions, a change of temperature and a change of strength of solution. These two changes were about equal and formed one-half of the total change. By keeping the strength of the solution constant and varying the temperature, the change was practically the same for all strengths, and equal to that found by Professor CARHART for the Carhart-Clark cell. If the temperature was kept constant and the strength of solution varied, then the E.M.F. followed the concentration in the linear relation in millivolts and grammes per cub. centim.,

$$dE = 42{\cdot}0 - 88{\cdot}0w.$$

The variation with temperature was followed for higher temperatures, and the transition point for the inversion of the heptahydrate (normal) crystals at 38·78° C. fixed. Various types of cells were devised which have been designated as the B.O.T. "crystal" cell, which is the modified Board of Trade form; the "sealed" cell, which is a form hermetically closed by glass fusion; and the "inverted" cell, which is a B.O.T. crystal cell reversed so as to place the negative electrode (zinc amalgam) at the bottom. These all have an identical temperature formula, which may be expressed in millivolts,

$$E_t = E_{15} - 1{\cdot}200\,(t - 15^\circ) - {\cdot}0062\,(t - 15^\circ)^2$$

between 0° and 30° for a mean temperature of 15°, or

$$E_t = E_{39} - 1{\cdot}635\,(t - 39^\circ) - {\cdot}0140\,(t - 39^\circ)^2$$

for a mean temperature of 39°.

For a cell about the mean temperature of 39°, with the hexahydrate crystals as solid phase, the formula

$$E_t = E_{39} - 1\cdot000\,(t - 39^\circ) - \cdot0070\,(t - 39^\circ)^2$$

was obtained. For temperatures above 30°, as the second formula shows, the values given by the first formula diverge from the observed values, due probably to a secondary change produced by the decomposition of the mercurous sulphate. If the first formula is corrected by the additional term

$$- \cdot00006\,(t - 15^\circ)^3,$$

the calculated values from 30° to 40° C. are brought into very close agreement with the observed values.

The Clark cells I have used in the present work are some of the original crystal cells described in the paper by Professor CALLENDAR and myself, "On the Variation of the Electromotive Force of the Clark Standard Cell," already referred to. These cells have been in the laboratory since 1895, and frequent comparisons made of their E.M.F. with newer cells constructed at different times, both by myself and the advanced electrical engineering students. As these cells are the originals from which the temperature formulæ already given were obtained, the constancy of the E.M.F. maintained to the present time is a matter of some surprise, considering the severe treatment they were subjected to during our earlier experiments. They were made in the generally accepted way in a test-tube, and sealed by means of a cork, on the top of which marine glue was melted. The life of such a cell is necessarily dependent on the speed with which the crystals commence to dry, and this fact has been raised against the use of moist crystals in place of a saturated solution. I have found however, that in point of usefulness our crystal cells have outlived several cells with saturated solution which were made at the same time. It appears that the crystals retain the moisture more tenaciously than the saturated solution does, so that whereas a solution may be reduced to one-third of its original bulk, with deposition of crystals, a mass of crystals retains its moisture without diminishing in bulk or uncovering the zinc rod. Owing to the dryness of the Montreal climate, the question of the slow evaporation of liquid from the cells is a serious one. Our cells have been re-sealed on one occasion by simply re-melting the marine glue, but apparently without harm except to one (X_3), which when left undisturbed for several months returned to its original normal condition, and is at present as good as the others.

Several sealed cells, inverted cells, and a number of new crystal cells have since been made in the laboratory, and have served to check the constancy of the original crystal cells. Independently several cadmium cells were made in 1897, in the inverted form, which proved to be quite satisfactory, and a comparison of the mean of these cells was made with the mean of the crystal cells. These cadmium cells

I have described in another place, and have shown that they cannot be relied on, as an accurate laboratory standard, to quite the same order of accuracy as a Clark cell, although as a commercial instrument they have distinct and unquestionable advantages over the Clark cell.

The method of keeping the Clark cells at a constant temperature has been already described in my earlier papers. Briefly it consists of a water thermostat with gas regulator, which is capable of maintaining the temperature constant to ·02° C. over extended periods. Whenever one of the experiments on the specific heat of water was performed, the bath was set to regulate as near 15° as possible, and throughout hardly ever varied more than ·01° or ·02°, unless some sudden change in the gas-pressure or water supply introduced a disturbance of too sudden a nature to be at once rectified by the regulator. The bath was supplied by a stream of water from a constant-level head through a spiral of copper tubing about 2 millims. diameter, and was heated by the gas flame, controlled by the regulator, as it passed through. During the winter, the water-supply in the laboratory was always between 8° and 10° C. at the place where the bath was located, so that there was no difficulty in maintaining the bath at 15°. During the summer, however, the water sometimes reached 18° or 20°, and it became impossible to keep the bath at 15° without running the inflowing water through an ice tank before it entered the bath. As this entailed considerable trouble, the bath was allowed simply to take the temperature of the inflowing tap water, and rose and fell in temperature slowly with it. There was no special object after all in keeping the cells at 15°, on account of the accuracy of the temperature coefficient, and the complete agreement of all the cells with one another at all the temperatures of comparison. The temperature of the bath was taken with a Geissler thermometer reading to ·01°. This thermometer was reduced to the nitrogen scale by comparisons, with a platinum thermometer, made both by Professor CALLENDAR and myself in 1896. It has seldom varied more than a few degrees either way from 15° since then, and as it was a somewhat old thermometer at the time of comparison with the platinum, it is unlikely that its readings have changed much since. Moreover, our later tests on the temperature coefficient made with this thermometer and thermometers calibrated by it, have agreed so well with the earlier measurements that there is no reason to doubt the correctness of its readings.

The comparison of the E.M.F. of the different cells was made on a specially constructed potentiometer, but as it has already been described it will be unnecessary to more than mention it here. Special attention was given to having the readings sufficiently sensitive to the order of accuracy we attempted, and defective insulation was amply guarded against. For differences in E.M.F. the potentiometer read directly in millivolts, at the rate of ·01 mv. for each millimetre of scale. A 6000-ohm galvanometer in the circuit was sensitive to a scale distance a little less than 1 millim.

In Table I. I have arranged the complete series of comparisons made on six of our

Table I.—Differences Expressed in Hundredths of a Millivolt from Mean.

	1898.										
	March.								April.		
	9.	10.	11.	14.	16.	23.	25.	31.	2.	12.	20.
X_1	− 5	− 6	− 4	− 4	− 5	− 4	− 4	− 4	− 5	− 4	− 4
X_2	+ 7	+ 8	+ 8	+ 7	+ 9	+ 7	+ 8	+ 8	+ 8	+ 8	+ 9
X_3	—	—	—	—	—	—	—	—	—	—	—
X_5	−17	−15	−13	−16	−16	−16	−14	−16	−17	−16	−16
X_{10}	+14	+12	+10	+15	+15	+15	+13	+14	+14	+14	+13
X_{11}	+ 1	+ 1	− 1	0	+ 1	0	+ 1	− 1	− 1	0	− 1
Temperature of comparison	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°	15°

	1898.										
	May.				June.		July.	Sept.	Oct.	December.	
	4.	5.	9.	28.	13.	17.	23.	10.	14.	14.	16.
X_1	− 4	− 3	− 4	− 3	− 5	− 4	− 6	− 2	− 4	− 8	− 8
X_2	+ 6	+ 6	+ 6	+ 7	+ 5	+ 5	+ 4	+14	+10	+15	+16
X_3	—	—	—	—	—	—	—	—	—	—	+ 1
X_5	−17	−17	−18	−18	−20	−20	−21	−15	−21	−20	−19
X_{10}	+15	+15	+16	+15	+17	+18	+18	+21	+16	+15	+15
X_{11}	− 1	− 1	− 1	− 2	0	0	+ 1	+ 4	− 2	− 5	− 3
Temperature of comparison	15°	15°	15°	15°	18°	18°	20°	19°	14°	15°	15°

	1898.		1899.					1900.		
	December.		Jan.	March.	May.	June.	Oct.	February.		March.
	19.	27.	17.	24.	6.	16.	25.	5.	12.	14.
X_1	− 8	− 8	− 9	−12	− 9	−10	−10	−17	−14	−15
X_2	+17	+15	+14	+11	+15	+15	+17	+17	+20	+14
X_3	+ 3	+ 1	+ 2	+16	—	—	—	+18	—	+17
X_5	−20	−19	−20	−23	−17	−18	−21	−23	−18	−24
X_{10}	+15	+15	+14	+12	+16	+18	+15	+11	+16	+12
X_{11}	− 5	− 3	− 3	− 6	− 2	− 2	− 2	− 8	− 3	− 7
Temperature of comparison	15°	15°	15°	15°	15°	16°	16°	15°	16°	15°

original cells from the date of the last comparison given in Table VII., Section 25, p. 151 (*loc. cit.*), to the close of the present series of experiments. Various other tables are given here in order for the other types of cells, and I have designated the different cells by capital letters indicating the type, and by a suffix to indicate the number of the particular cell. The crystal cells are given as X, the sealed cells by S, the inverted cells by XR, and the cadmium cells by Cd. In the original table of comparison already referred to, cells X_1, X_2, X_3, X_5, X_6, X_{10}, and X_{11} were given. Of these cells, all are at present in existence, with the exception of X_6, which was taken away from the laboratory and since broken. Table I. may be taken as a continuation of the older table. The relative differences in these cells, although somewhat larger than is usually obtained in constructing a number of cells from the same lot of materials, have been maintained so consistently that over extended periods a constancy of 1 in 100,000 can be easily assumed. Later results show that cells X_1 and X_5 have lowered somewhat, but even in these two cases the drop is less than ·1 mv., and takes place so gradually as to be easily corrected for. It is highly probable that all these cells will eventually become lower in value as they become older, on account of the drying up of the crystals.

During the winters of 1897–98 and 1898–99 a number of tests were made by some of the advanced students on cells prepared by themselves under my supervision. These cells were all subjected to a temperature cycle of 15° to 0°, to 15° to 30°, to 15°. The first batch of cells made during 1897–98 were in the inverted form, and were made in the usual way in a long test-tube for immersion in the water-bath. A 10 per cent. zinc amalgam was placed in the bottom of the test-tube and covered to the depth of about 2 centims with moist zinc sulphate crystals. The paste of mercurous sulphate and zinc sulphate crystals placed on top of the crystals was made in the usual way by mixing moist crystals with pure washed Hg_2SO_4. The positive electrode consisted of a platinum wire flattened at one end, amalgamated, and inserted in the paste. The wire was protected by a small glass tube and reached to the top of the test-tube, where the glass was melted around the wire to form a mercury cup. The negative electrode was a platinum wire protected in a similar way and thrust into the amalgam while still warm before the cell was filled with the other ingredients. The cell was sealed by shoving a cork down the test-tube, with the two electrodes passing through holes made for them, to within a few millims. of the ingredients. The cork was about 1 centim. thick, and was sealed by inserting particles of marine glue and melting them in place by carefully warming the glass over the cork. The crystals of zinc sulphate were prepared by re-crystallizing the ordinary pure heptahydrate salt after neutralization with zinc oxide, and treating with a small quantity of the washed Hg_2SO_4 when in solution in the usual way.

The cells made in 1898–99 were of the older type, with an amalgamated zinc rod with positive electrode at the bottom of the test-tube. They differed from the original crystal cells in having an amalgamated flattened platinum wire in place of the metallic mercury. In preparing the crystals for these cells it was deemed unnecessary to follow the old prescription, inasmuch as they were made from the purest anhydrous salt purchased from Merck. However, a few of the cells were made from crystals that had been treated when in solution with a small quantity of Hg_2SO_4, but filtered out before re-crystallizing.

In the table of comparison now given the inverted cells are expressed as difference from the mean of the five crystal cells X_1, X_2, X_5, X_{10}, and X_{11}. The temperature changes between 15° and 0°, and 15° and 30° are also given, as determined by the different students who made the cells.

TABLE II.—Comparison of Inverted Cells to Mean "Crystal" (1897–98).

Cell.	Difference from mean crystal in mvolts.	E.M.F. changes between	
		15°—0°.	15°—30°.
XR$_{11}$	+0·16	+16·67	−19·45
XR$_{12}$	+0·17	16·67	19·46
XR$_{13}$	+0·20	16·69	19·58
XR$_{16}$	+0·19	16·66	19·60
XR$_{17}$	+0·10	16·67	19·61
XR$_{18}$	+0·20	16·69	19·55
XR$_{19}$	+0·24	16·60	19·51
Means	0·166	16·67	19·54

These tests are sufficient to show that the inverted cell gives a value somewhat in excess of the older crystal cells. The temperature change between 15° and 0° is also somewhat larger than the value given by the crystal cells, which was + 16·62 mvolts. The reason for this may possibly be, as I have already pointed out in another place, that the sensitive electrode (negative) is at the bottom of the cell and deeply immersed in the bath, whereas in the crystal cells the negative electrode is a zinc rod at the top of the cell, and although immersed below the level of the liquid in the temperature bath, may yet conduct an appreciable amount of heat and be at a slightly different temperature to that of the cell.

I have used the term sensitive for the negative electrode because a small difference of temperature between it and the other parts of the cell influences the E.M.F. very considerably. This can be very forcibly shown in the case of an inverted cell by removing it from the 15° bath and standing it on a cold surface. This produces a larger change (increase) in the E.M.F. than if the complete cell were immersed at the cooler temperature; and in a similar way for a higher temperature, the negative electrode being warmer than the other parts of the cell, the E.M.F. decreases more than it would were all the cell at the same temperature. Hence, in the crystal cell, when immersed at a temperature above or below 15°, the possibility of the zinc rod being at a slightly different temperature to that of the cell is thinkable, and would act in such a way as to make the positive change between 15° and 0°, as well as the negative change between 15° and 30°, appear smaller than the true values.

Later on in the year, on September 10, a comparison was made of the old crystal cells with two of the original sealed cells, made in 1896, and at that time still in the possession of the laboratory, as well as three new sealed cells. This comparison is given in Table III. and gives the differences in millivolts between each sealed cell and the mean of the old crystal cells, the comparisons of which were given in Table I.

TABLE III.—Comparison of Sealed Cells with Old "Crystal" Cells.

Cell.	Difference from mean of old cells.	
S_1	+0·18 mv.	Mean +0·23 mv.
S_5	+0·34 ,,	
S_{11}	+0·20 ,,	
nS_{11}	+0·23 ,,	
S_{12}	+0·21 ,,	

The agreement of the new sealed cells with the old sealed cells is good, but both show that the mean of the old crystal cells is too low. This makes the mean of the sealed cells, on comparing Tables II. and III., agree with the mean of the inverted cells to ·06 mv.

A comparison of the six crystal cells X_1, X_2, X_3, X_5, X_{10}, and X_{11}, with six of the newer crystal cells made by the students in 1899, was made on March 14, 1900, when the last comparison of the old crystal cells given in Table I. was obtained. In Table IV. this comparison of the six new cells is given, and the differences expressed in millivolts from the mean. Cell X_2 is included, and differenced from, but not included, in the mean.

TABLE IV.—Comparison of New "Crystal" Cells, on March 14, 1900.

Cell.	Difference from mean.
X_{21}	−0·24 mv.
X_{23}	+0·05 ,,
X_{27}	−0·05 ,,
X_{29}	+0·05 ,,
X_{31}	+0·11 ,,
X_{33}	+0·08 ,,
X_2	−0·17 ,,

During the winter previous, when all these new cells were made, the tests on the temperature changes between 15° and 0°, and 15° and 30° gave the mean values + 16·60 and − 19·45 respectively, which agree very closely with the values given by the old cells, but are smaller than the values given by the inverted cells. X_2 in the above table is seen to be lower than the mean of the new crystal cells by − ·17. Under date March 14, in Table I., it is seen to be + ·14 mv. above the mean of the old crystal. This would make the mean old crystal lower than mean new crystal by ·31 mv. This excessively low value is influenced by cells X_5 and X_1 on the mean, which have apparently gone down since the earlier tests. If we reject these two cells from the mean, as being too low, the mean value of the four remaining cells is increased by ·10 mv. and the difference between mean old crystal and new crystal reduced to ·21 mv. In Table II. it was seen that the inverted cells in January, 1898, were ·17 mv. higher than the mean old crystal. If we reject cell X_5 from the mean of the old crystal cells, as being too low, then the difference between the two sets of cells is reduced to ·12 mv. Also in Table III. the mean of the old cells is seen to be ·23 mv. lower than the mean of the new and old sealed cells. If we reject X_5 as before from the mean, the difference is reduced to ·17 mv.

If now we can assume that the mean inverted and mean sealed was the same as the mean new crystal (which unfortunately could not be verified by a direct comparison), then we see that the old cells have lowered in value since January, 1898, by ·06 mv., or 4 parts in 100,000. Another indication that the cells have all lowered somewhat in value is afforded by a comparison as early as 1896 with six sealed cells, including S_1 and S_5 of Table III. The mean value of the sealed cells was ·08 mv. higher than the mean old crystal including cell X_5, which was more nearly in agreement with the mean at that time. (*See* Table VII., page 151, *loc. cit.*) It is evident that for some reason the old crystal cells, even from the first, are lower than what may be taken as the true Clark-cell value, if we may assume that the mean old sealed, mean new sealed, mean inverted, and mean new crystal are all within a few hundredths of a millivolt of each other, and of the true Clark-cell value.

In 1896 the old crystal cells were lower than the sealed cells by ·08 mv.; in 1898 lower than the inverted cells by ·12 mv., than the new sealed cells by ·17; and in 1900 lower than the new crystal cells by ·21 mv. This indicates that the mean value of the old crystal cells is ·14 mv. lower than the most probable value that we can assume, combining all our Clark cells, and this within the limits of error of perhaps ·02 mv.

We can now, from the table of comparisons, assign individual values for the two Clark cells which were used throughout in the present investigation. These cells were X_2 and X_{10} of the old crystal cells. From January to December, 1898, X_2 was ·08 mv. higher than the mean of the crystal cells, and X_{10} was at the same time ·15 mv. higher. If we neglect cell X_5 from the mean, as being too low, then this gives for cells X_2 and X_{10} in series the values +·03, +·10, or +·13 mv. above the mean. But as mean crystal, neglecting X_5, is ·14 mv. lower than what we have reason to believe is the true Clark-cell value, two mean crystal cells in series would be ·28 mv. lower. Therefore, cells X_2 and X_{10} in series are lower than the true value by ·15 mv. During 1899, cell X_2 was on an average ·15 mv. above the mean crystal cells. Neglecting X_5 but not X_1 this difference is reduced to ·10. X_{10} was also $+·15$ or, neglecting X_5, ·10. This gives for $X_2 + X_{10}$ the value $+·20$ mv., or different from the true Clark-cell value by $-·08$ mv. During the early part of 1900, cell X_1 commenced to go down more rapidly, partially through the introduction of cell X_3 again into the mean. If we take the comparisons on February 5th and March 24th, we find for X_2 the value $+·16$ mv., and for X_{10} $+·12$ mv. Neglecting X_1 as well as X_5 from the mean, the value of $X_2 + X_{10}$ becomes $+·06 + ·02$, or equal to $+·08$ mv., the difference from the true Clark-cell value being now $-·20$ mv. Summarizing we have, if e represents the true E.M.F. of the Clark cell in volts

$$\left.\begin{array}{llll}\text{In } 1898 & X_2 + X_{10} & 2 \times e & -·00015 \\ \text{In } 1899 & ,, & ,, & -·00008 \\ \text{In } 1900 & ,, & ,, & -·00020\end{array}\right\} \text{Mean value } -·00014.$$

This gives the mean error, if we assume from 1898 to 1900 the mean value $2 \times e - ·00014$ as representing the true E.M.F. of the two Clark cells used in these measurements, as in

$$1898, +4 \times 10^{-6};\ 1899, -2 \times 10^{-5};\ 1900, +2 \times 10^{-5};$$

all of which are less than 1 part in 10,000, and outside the possible limits of error of the other measurements.

Whenever the temperature of the Clark cell was other than 15° C., the E.M.F. was calculated, assuming a value at 15°, by the temperature formula obtained between 0° and 30° for a mean temperature of 15° which has already been given. As a matter of verification of this formula, which was deduced from the old crystal cells, I have summarized in Table V. the observations that have been made since, both by myself and the students under my supervision.

TABLE V.

Type of cell.		Change in millivolts between—	
		15° and 0°.	15° and 30°.
Old B.O.T. crystal	1896	+16·62	−19·48
Sealed	1896	+16·62	−19·58
Portable B.O.T. crystal	1897	+16·60	−19·40
Inverted	1898	+16·67	−19·54
Portable B.O.T. crystal	1899	+16·60	−19·45
Temperature formula	—	+16·60	−19·40
Values obtained by Dr. KAHLE	—	+16·40	−19·40

The values obtained by Dr. KAHLE at the Reichsanstalt are somewhat lower. They were obtained for the H-form of cell with negative electrode, zinc amalgam.

The portable crystal cell in Table V. refers to the case where the metallic mercury for positive electrode is replaced by a flattened platinum wire amalgamated. The portable cells in Table VII., original paper, p. 152, made by the students in 1897, and from which the tests (in 1897) in Table V. are taken, were compared with the old crystal cells rather too soon after setting up, to use in determining the true value of the E.M.F. of the old cells, as we have done for the latter cells and the sealed cells in 1896. The mean value of all these cells is very close to the crystal cells, but later tests showed that some of them gave too low a value at first.

Ratio of Clark to Cadmium Cells.—In 1897, to check the value of the Clark cells made by us in the laboratory, several Weston cadmium cells were constructed. These were made in the inverted form, and one was made in the H-form after type III. described by JAEGER and WACHSMUTH ('Wied. Ann.,' vol. 59, p. 580, 1896) in their paper on the cadmium cell. All the cells had a cadmium amalgam of 1 to 6 proportion, as recommended by JAEGER and WACHSMUTH, except two, which were made after the B.O.T. "crystal" cell type with cadmium stick. These two cells, however, as was expected, gave much too high an E.M.F. and were only made as a matter of interest. I have described these cells in another place ('Journ. Phys. Chem.,' vol. 4, 1900), with comparisons which were obtained in 1897.

The temperature coefficient obtained for these cells was a little in excess of that found by JAEGER and WACHSMUTH for their cells, but is more in agreement with the value found by DEARLOVE ('Electrician,' vol. 31, p. 645, 1893) and the original value given by WESTON. The expression is a linear one, and reads

$$E_t = E_{15} - {\cdot}086\,(t - 15^\circ),$$

and holds with great accuracy over the range 15° to 40° C. At 15° a change of state occurs in the cadmium sulphate, so that no formula can be made to hold below that point.

I made a determination of the ratio of these cadmium cells to the old crystal cells, by means of the cylinder potentiometer and 6000-ohm galvanometer which were used in the earlier comparisons of the Clark cell, given by Professor CALLENDAR and myself in our original paper (p. 121). The potentiometer was repeatedly calibrated by comparison with the Thomson-Varley slide potentiometer, described in another place.* The corrections for uniformity were somewhat large, but were exceedingly consistent, and were determined by myself, as well as by a large number of the students in the ordinary course of their work. The cells, both cadmium and Clark, were immersed at a constant temperature near 15° throughout the test. Table VI. contains the result of this test.

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* CALLENDAR, 'Phil. Trans.,' A, 1902, p. 63.

TABLE VI.—Comparison of Clark and Cadmium. March 6, 1897.

Cell.	Potentiometer reading corrected to 15°.	Corrected for uniformity.
X_1	68225	68290
Cd_3	48453	48575
Cd_4	48460	48582
Cd_5	48458	48580
Cd_H	48460	48582

Correcting reading of X_1 to mean of old crystal cells and reducing mean cadmium reading to 20° by the formula,

$$E_t = E_{15} - \cdot086\ (t - 15°),$$

the ratio of Clark to cadmium becomes

$$\frac{\text{Clark } 15°}{\text{cadmium } 20°} = \frac{68294}{48558} = 1\cdot40644.$$

The ratio obtained by KAHLE for the cells in the possession of the Reichsanstalt was ('Wied. Ann.,' vol. 67, p. 35, 1899),

$$\frac{\text{Clark } 15°}{\text{cadmium } 20°} = 1\cdot40663.$$

The value of our ratio is somewhat lower than the value given by KAHLE, which may be explained by either assuming the cadmium cells too high or the Clark cells too low. We have seen, however, that the mean of the old crystal cells is lower than the most probably true Clark-cell value obtained by comparison with later tests by ·14 mvt., or 1 part in 10,000.

Correcting the ratio by this amount, it becomes 1·40658, a value nearly identical with the value obtained by KAHLE.

The Absolute Value of e.—The assignment of the true value of *e* to the cells used in the present work is, at present, somewhat difficult. GLAZEBROOK and SKINNER found on standardizing the B.O.T. form of test-tube cell by means of the silver voltameter, and assuming the value ·001118 gram.-sec. for the electro-chemical equivalent of silver as determined by Lord RAYLEIGH and Mrs. SEDGWICK, that the value was 1·4342 international volt at 15° C. More recently we have the measurements made by Dr. KAHLE at the Reichsanstalt with the Helmholtz Electrodynamometer ('Wied. Ann.,' vol. 59, p. 532, 1896, and 'Zeit. für Instk.,' June, 1898), which give a result independent of the value assigned to the silver voltameter. We have also the value obtained recently by Professors CARHART and GUTHE, at Ann

Arbor, Michigan University ('Physical Review,' vol. 9, p. 288, 1899), with a type of dynamometer designed by themselves. The results of these measurements show a wide divergence. The values found are

Glazebrook and Skinner . . .	1·4342	volt at 15°.
Kahle	1·43285	,, ,, ,,
Carhart and Guthe	1·4333	,, ,, ,,

The large discrepancy in the value of the mechanical equivalent of heat obtained by the electrical methods used by Professor Griffiths and Professors Schuster and Gannon, as compared to the value given by the direct mechanical method, has so far hinged on the value to be assigned to the Clark cell. The older, and for so long a time accepted, value, 1·4342, there is every reason now to think is too high. The value given by Dr. Kahle, *i.e.*, 1·43285 volt, is at the same time probably a little too low. The value found by Carhart and Guthe depends on the mean of three determinations differing in the extreme by ·5 mvt. These three determinations were made for two Clark cells in series, one of which was afterwards compared to the Reichsanstalt cells and found to be in good agreement.

At present there is a grave uncertainty in the absolute value of this fundamental constant, which requires immediate attention. It has been pointed out that the value of the mechanical equivalent of heat found by Griffiths would be brought into harmony with the values found by Rowland by the direct mechanical method, by assuming the Clark cell 2 mv. lower than the value found by Glazebrook and Skinner. The value found by Schuster and Gannon requires a somewhat smaller correction in the same direction.

In the face of these uncertainties in the value to be assigned to *e*, I have adopted the older value, 1·4342 international volt, as the basis of my calculations of the absolute value of the mechanical equivalent, in order to bring my results into comparison with those of Griffiths and of Schuster and Gannon. On this basis I have had the temerity to combine the mean value of the mechanical equivalent obtained by integrating the curve of absolute values between 0° and 100° with the determination of the mean value obtained by Reynolds and Moorby, and have obtained by that way an absolute measure of the Clark cell in terms of the mechanical units, which is probably as accurate a value as has yet been obtained, provided the values assumed for my resistance standards are correct.

The discrepancy in the two values of the mean mechanical equivalent, the one obtained by integrating the variation curve, and the other obtained as a direct determination, is ·132 per cent. As I have used the value *e* of the Clark cell in my measurements squared, this reduces to ·066 per cent. on 1·43420, and shows that the value assumed for my cells is too high by this amount. The true value of the Clark cell I have assumed for calculation is 1·4342, which would give for the two cells $X_2 + X_{10}$ in series, the value 2·8684, provided they were equal to the true value. We have seen, however, that these two cells differ from the most probable true value of the Clark cells made in this laboratory by ·00014 volt, which would give for the true value of $X_2 + X_{10}$ 2·86826, or 1·43413 each. Reducing this value by ·066 per cent., we have, as the value of each of my Clark cells,

1·43318 int. volt,

and the most probable true Clark-cell value

1·43325 int. volt at 15° C.

which is in remarkable agreement with the absolute measurements of CARHART and GUTHE for their Clark cells.

From the ratio of the Clark to cadmium, the value of the cadmium cell is found to be

1·01895 int. volt at 20° C.

Sec. 3*b*.—*Measurement of Resistance.*

Next in importance to the value of *e* for the Clark cells, which we assume for the calculation of the absolute value of the mechanical equivalent of heat, is the value to be assigned to R for the resistance used in these experiments.

At the outset we were exceedingly fortunate in having the laboratory equipped with a large number of 1-ohm resistance standards certified by the Electrical Standards Committee of the British Association, which were obtained in 1893. The work, therefore, of standardizing the resistances which were made for the present series of experiments was reduced to a minimum by the facility with which they could be compared to these standards on a Nalder type of Carey-Foster commutator-bridge. This bridge was supplied with a set of ratio-coils and bridge-wires which could be interchanged at will, and selected to be comparable in size with the resistances compared. During the first experiments which we made on the specific heat of mercury and the early trial experiments with the water calorimeter, the electric heating current was passed through a 1-ohm manganin coil for standard, which was immersed in paraffin oil. The difference of potential across the terminals of this specially-constructed resistance was of the same order as that across the column of liquid in the fine flow-tube in the mercury-calorimeter, and also equal to that across the platinum heating-wire in the first water-calorimeter. This was arranged for convenience in balancing on the potentiometer.

The coil was made from two manganin wires, 1 millim. in diameter, connected in parallel and wound on an ebonite frame. Connections were made to the coil at the bottom of the frame, which was held vertical, by two heavy copper-wires, $\frac{1}{4}$ inch in diameter, so arranged as to have 3 or 4 inches immersed in the oil-bath with the coil.

The wires were bent into an inverted U and made to fit into mercury-cups, either on the commutator-bridge or in the main calorimeter circuit from which the potential terminals were taken to the potentiometer. For the later experiments with the water calorimeter it was found advisable to alter the resistance of the heating-wire to ·5 ohm, so that another manganin-resistance was made similar to the first one and connected in parallel with it in the calorimeter circuit. Our numerous comparisons of these ohms with the certified standards were far from satisfactory, but the cause was at first sight not apparent.

The resistance of both the coils was found to increase, after carrying currents of from 4 to 8 amperes in a series of experiments, of the order of 2 or 3 parts in 10,000 in two weeks. This was somewhat annoying, and necessitated repeated comparisons with the standards and numerous corrections. It was also a matter of doubt whether the resistance of the coils remained the same when the heavy currents were passing, seeing that they produced such a large permanent change in the resistance. We finally commenced to suspect the real cause of the trouble to be at the point where the manganin-wire was soldered on to the heavy copper-wire. In the face of this uncertainty it was decided to abandon these resistances altogether for others made of platinum-silver wire according to a different design. Both these new 1-ohm resistances have proved to be so reliable and constant since they were made, in May, 1898, that it is proposed to give a short description of them here. They were both made on an exactly similar design.

The frame-work consisted of two heavy plates of mica, 4″ × 2½″, placed side by side, and separated about ¾ of an inch by ebonite strips at each narrow end. Both ebonite strips were split from end to end, parallel to the mica plates and half-way between them. The strips were fastened to the mica plates by ebonite washers and small screws, shown in fig. 4, which gives a general view of a resistance. The plates were arranged so that they could be separated or put together quickly by removing two screws at either end, clamping the ebonite strips together. Two ¼-inch copper-wires were passed through holes bored for them through the splits in the ebonite strips at each end, in such a way that they were clamped in place by the ebonite. These heavy wires, when in place, connected the space between the mica plates with the outside of the frame-work. At each end the two wires were bent at right angles so as nearly to meet, and were inserted and soldered into holes made for them on the opposite faces of a small copper block. Heavy copper-wires (¼-inch) were soldered into holes in these copper blocks and bent into an inverted U for connecting to the commutator-bridge.

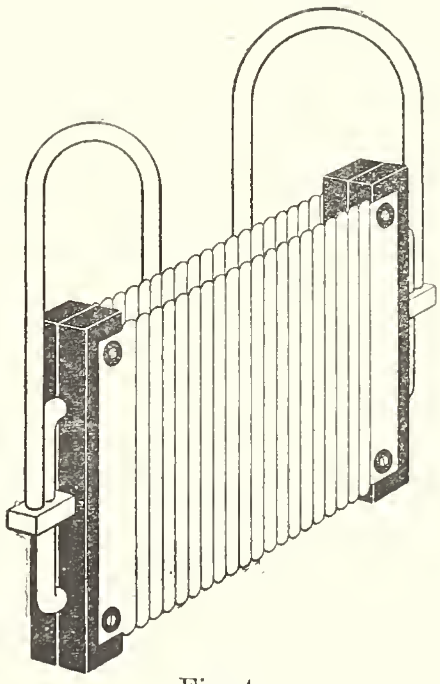

Fig. 4.

Each of the two mica plates was serrated on the two long edges and two bare platinum-silver wires, ·4 millim. in diameter, wound on side by side. After winding, the ends of the platinum-silver wire were fused to copper-wires of the same size in a blow-pipe flame. The wires on the frames were then annealed at a low red heat by passing a heavy electric current through them. After the two mica plates were clamped together so as to include the heavy copper-wires at both ends, the copper-wires that were fused to the platinum-silver wires were soldered to the end faces of the copper-wires protruding into the space between the mica plates. There being in all eight ends to be soldered and four heavy copper-wires to solder into, each large copper-wire was connected to two of the small copper-wires fused to the platinum-silver wire. Each 1-ohm consisted thus of four bare platinum-silver wires, 16 millims. in diameter, in parallel; direct solder joins of platinum-silver with copper were avoided, and the mica plates were arranged so as to give the best possible circulation when immersed in an oil-bath.

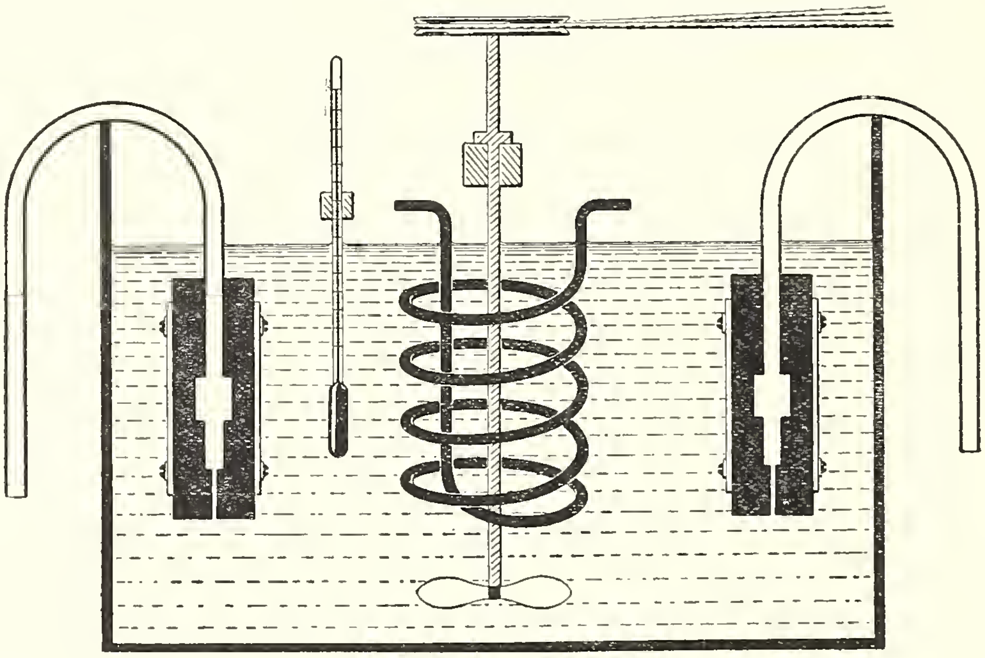

Fig. 5.

The paraffin oil-bath was made from a square ebonite box, and included, besides the two 1-ohm coils, a stirrer and coil of metal tube for a water circulation, fig. 5. The coils always remained fastened in the bath, and when it was necessary the bath, including the ohms, could be removed from the position assigned for it in the experiment where the ends of the two inverted U-shaped connections from the coils were immersed in mercury-cups in two heavy copper forgings in the calorimeter circuit. When a comparison was made on the commutator-bridge, the bath was conveyed to the place where the bridge was always kept. During a comparison, the stirrer was run by a small electric motor and the temperature of the oil taken by a thermometer immersed in the bath. For the determination of the temperature coefficient of the coils, water at different temperatures was run through the circulating tube so as to change the temperature of the oil.

Up to the time of writing, I have been unable to compare these ohms directly with official standards. It will, therefore, be necessary for me to describe a series of comparisons of these ohms with eleven certified ohms in the possession of this laboratory, together with a standard 1-ohm coil from the German Reichsanstalt, sent us for comparison by the Physical Department of the Massachusetts Institute of Technology. By means of these comparisons, we may possibly arrive at a result for the value of R somewhere near the truth.

Throughout the present work I have used only one of the certified standards (No. 4086) to check the constancy of the two platinum-silver ohms, as it was of a better and more convenient form to use on the bridge than the others and had a much smaller temperature coefficient.

Before describing the tests I will briefly review the method of comparing the ohms and the method of finding the value of the bridge-wire used on the Carey-Foster bridge throughout these tests. The 1-ohm pair of coils supplied by the makers of the bridge were used for the ratio coils, and a bridge-wire having a resistance of about ·002 ohm per centim. was used. The bridge-wire was just 10 centims. long, with a scale graduated into half centimetres and millimetres. A lens was also supplied for reading the position of the balance point. The galvanometer for obtaining the balance point was a very sensitive 9-ohm Thomson reflecting galvanometer, which was used for the thermometer work. It had a telescope and scale, and was sensitive to 50 scale-divisions for 1 millim. of bridge scale, which, of course, was far more sensitive than was required, or even quite convenient to work with. The current supplied to the coils was from one accumulator through 20 ohms external circuit. By simply lifting the commutator from the mercury cups on the bridge and revolving it through half a revolution, the connections could be made so as to reverse the position of the two resistances relative to the ratio coils. If P and Q are the ratio coils, R and S the resistances to be compared, then, when the current is reversed in R and S, but not in P and Q, we have, $R/S - S/R = \rho(d_1 - d_2)$, independent of P and Q.

Here d_1 and d_2 are the readings of the balance points on the bridge-wire, and ρ a constant to reduce to ohms.

Let $R/S = (1 + r)$, where r is a small quantity; then $S/R = (1 - r)$ and

$$R/S - S/R = 2r = \rho(d_1 - d_2).$$

To find ρ, S may be changed to S_1 by shunting with a known large resistance, say 100 ohms.

We have then, if $R/S_1 = 1 + r + dr$, $S_1/R = 1 - r - dr$, and reversing the current as before,

$$\mathrm{R}/\mathrm{S}_1 - \mathrm{S}_1/\mathrm{R} = 2\,(r + dr) = \rho\,(d_3 - d_4),$$

from which

$$\rho = \frac{2dr}{(d_3 - d_4) - (d_1 - d_2)},$$

therefore

$$r = \frac{dr\,(d_1 - d_2)}{(d_3 - d_4) - (d_1 - d_2)},$$

the value of dr being $\left(\mathrm{S} - \frac{\mathrm{S} \quad 100}{\mathrm{S} + 100}\right)$.

This gives for R the value $\mathrm{S}\,(1 + r)$, where S is the known standard. The value of ρ was obtained a number of times, both by myself and a number of the students. The values obtained since 1897 are in ohms—·001022, ·001015, ·001019, ·001011, ·001028, ·001028.

This gives a mean value of ·001020 ohm per division for bridge-wire C.

The following is a list of the standard 1-ohm coils used in the comparisons. Each coil had a certificate signed by the secretary of the Electrical Standards Committee, and dated either in 1892 or 1893.

LIST of Certified Standards.

PLATINUM-SILVER Wire Coils (embedded in Paraffin Wax).

No. 3565	certificate,	·99957	true ohm at	16°·4.
,, 3566	,,	·99960	,,	16·5.
,, 3567	,,	·99949	,,	16·4.
,, 3568	,,	·99961	,,	16·5.
,, 3569	,,	·99964	,,	16·5.
,, 3402	,,	·99971	,,	16·7.
,, 3403	,,	·99967	,,	16·5.
,, 3404	,,	·99970	,,	16·7.
,, 3405	,,	·99960	,,	16·3.
,, 3406	,,	·99960	,,	16·3.

MANGANIN Wire Coil (in Oil-bath).

No. 4086 certificate, ·99978 true ohm at 15°·9.

REICHSANSTALT Standard.

No. 1214 marked 1 true ohm at 20° C.

From 3565 to 3406 each ohm was of the older form, with the wire embedded in paraffin wax and made to insert in a water-bath, with long heavy wire connectors for the terminals of the Carey-Foster bridge. No. 4086 was the best form to use with the bridge, as the method of having the other coils always in paraffin wax is bad, and it is never possible to know exactly the true temperature of the coils. The German standard was evidently made of manganin wire on account of its very small temperature coefficient. Unfortunately coil 4086, to which all of my results were referred ('B.A. Report,' 1899), seems to be different to the others by as much as 6 parts in 10,000. It is difficult to see how it could have been injured in any way since it came into the possession of this laboratory, and, as will be seen presently, the comparisons of this ohm with both of the specially constructed platinum-silver ohms does not indicate any possible change since May, 1898. The cause that has been at work to alter its resistance has left it entirely unaffected during the last two years.

Two tables of comparisons are now given of all the 1-ohm coils. The first set in Table VII. was taken by myself and expresses all the ohms, except 3566 and 1214, in terms of 4086. For the second set in Table VIII. I am indebted to Mr. FRASER. For reducing the values of the ohms to one temperature, temperature coefficients were used which were obtained either by myself or Mr. FRASER in duplicate by special experiment, and verified repeatedly by the students. All the platinum-silver standard ohms were found to have the coefficient + ·000254 $t°$.

The manganin ohms 4086 and 1214 were found to have the coefficients + ·000018 and + ·000022 respectively.

The different columns of Table VII. are arranged so that the first gives the number of the ohm, the second the certified resistance at temperature given in the third column, and the fourth column gives the length of bridge-wire multiplied by ·001020 to reduce to ohms, which represents the difference in resistance between each ohm and No. 4086. In the fifth column is given the temperature of the different ohms during the comparison, and in the sixth the temperature of 4086. The seventh column contains the value of 4086 at the temperature of comparison found from the certified value by the temperature coefficient. As all the platinum-silver standard ohms were larger than 4086, the eighth column is obtained by adding columns 4 and 7. This gives the resistance of each ohm in terms of 4086. In the last column, for comparison, I give the value of each ohm in terms of its own certificate, and corrected to the temperature of comparison in column 5 by the temperature coefficient. The values in the eighth column in terms of 4086 are all systematically smaller than the values in the ninth column, whereas they should be equal. The observations differ amongst themselves somewhat, but they are as good as can be expected from the difficulty of knowing the true temperature of the coils embedded in the wax.

In all these tests the standard ohms were left for several hours near the place of test, so that they could assume, as nearly as possible, the temperature of the air.

TABLE VII.—Comparison of 1-ohm Standards in Terms of 4086.

Number of standard.	Resistance by certificate.	Temperature when certificate is correct.	Difference in ohm from 4086.	Temperature of standards during test.	Temperature of 4086 during test.	Resistance of 4086 by certificate.	Resistance of standards in terms of 4086.	Certified resistance corrected by temperature coefficient.	Difference involving error.
3565	·99957	16·4°	+ ·000370	21·4°	21·6°	·99988	1·00025	1·00089	·00064
3567	·99949	16·4	+ ·000565	22·0	21·8	·99989	1·00046	1·00091	·00045
3568	·99961	16·5	+ ·000483	21·4	21·7	·99989	1·00037	1·00085	·00048
3569	·99964	16·5	+ ·000657	21·8	21·8	·99989	1·00055	1·00099	·00044
3402	·99971	16·5	+ ·000545	21·7	21·8	·99989	1·00044	1·00103	·00059
3403	·99967	16·5	+ ·000616	21·6	21·8	·99989	1·00051	1·00096	·00045
3404	·99970	16·7	+ ·000555	21·7	21·8	·99989	1·00045	1·00098	·00053
3405	·99960	16·3	+ ·000482	21·6	21·7	·99989	1·00037	1·00095	·00058
3406	·99960	16·3	+ ·000565	21·7	21·8	·99989	1·00046	1·00097	·00051

TABLE VIII.—Comparison of 1-ohm Standards in Terms of 3569.

Number of standard.	Resistance by certificate.	Temperature when certificate is correct.	Difference in ohm from 3569.	Temperature of standards during test.	Temperature of 3569 during test.	Resistance of 3569 by certificate.	Resistance of standards in terms of 3569.	Certified resistance corrected to temperature of test.	Difference involving error.
3565	·99957	16·4°	− ·00015	13·3°	13·3°	·99883	·99868	·99878	− ·00010
3566	·99960	16·5	− ·00010	13·1	13·1	·99878	·99868	·99874	− ·00006
3567	·99949	16·4	− ·00026	13·1	13·1	·99878	·99852	·99865	− ·00013
3568	·99961	16·5	− ·00009	13·3	13·3	·99883	·99874	·99880	− ·00006
3402	·99971	16·7	− ·00009	13·0	13·0	·99875	·99866	·99877	− ·00011
3403	·99967	16·5	+ ·00008	13·3	13·3	·99883	·99891	·99886	+ ·00005
3404	·99970	16·7	− ·00010	13·3	13·3	·99883	·99873	·99884	− ·00011
3405	·99960	16·3	− ·00010	13·3	13·3	·99883	·99873	·99884	− ·00011
3406	·99960	16·3	− ·00005	13·2	13·2	·99880	·99875	·99881	− ·00006
4086	·99978	15·9	+ ·00145	14·8	13·6	·99890	1·00035	·99976	+ ·00059
1214	1·0000	20	+ ·00098	14·1	13·7	·99893	·99991	·99988	+ ·00003

A thermometer placed in the hole extending through the middle of the embedded coil was taken as the temperature of the coil. As No. 4086 was arranged with a stirrer, a thermometer could be placed in the oil in contact with the coil, and the true temperature obtained. The current used on the bridge was not sufficient to cause perceptible heating.

Table VIII. contains the comparisons of the ohms, at an entirely different temperature. These tests were made in the basement of the building, where the temperature was considerably lower than where the tests in Table VII. were made. In this case also the coils remained at least a day or two at the temperature of test, and did not vary to any extent from that. The table is arranged as in Table VII., only the comparisons were made in terms of No. 3569. This shows a very good agreement of all the platinum-silver standard ohms, including the Reichsanstalt ohm, 1214, but shows that by assuming the corrections of 3569, the value of 4086 is very much above that given in its certificate. This difference indicates an error of ·00059 ohm assuming 3569 as correct, or ·00065 referred to the mean of all the ohms. In Table VII. we saw that the platinum-silver ohms were all lower than their certified values when calculated assuming 4086 to be correct, the mean difference being ·00052. These differences are both in the same direction as regards the relationship of 4086 to the other ohms. The difference of 1 in 10,000, obtained by Mr. FRASER and myself between the two values, *i.e.*, ·00065 and ·00052, must be ascribed to the wide difference in temperature of our respective tests, as well as to the uncertainty of knowing accurately the true temperature of the paraffin-embedded coils.

We are forced now either to accept the certificate of 4086, and reject all the other 11 ohms as being in error, including the Reichsanstalt Standard, or to reject the certificate of 4086, and accept the certificates of all the others. The alternative of giving 4086 equal weight in the mean seems to be hardly justifiable considering the mass of evidence against it.

I have decided to reject the certificate of 4086, and I have accordingly corrected it in the following way: in terms of the platinum-silver standard ohms, 4086 is equal to its certified value +·00052 by the comparison made at 22° C. By the comparison made at 13° C. it becomes equal to its certificate +·00065. By comparing directly with 1214, the value of 4086 becomes equal to its certificate +·00056 in one test, and +·00061 in another test, or equal to +·000585 in the mean. This agrees very closely with the mean value of the two separate determinations with the other ohms, which comes out +·000585. We may, I think, then safely assume that the value of 4086 is equal to its certified value +·00058, which comes out ·99978 + ·00058 at 15°·9, or 1·00036 + ·000018 (20° − 15°·9), or equal to 1·00043 true ohms at 20° C.

A summary of the various comparisons made of the two new platinum-silver ohms is given in Table IX. in terms of 4086, assuming for convenience that it is exactly 1 ohm at 20° C. The resistance of each ohm is reduced to 20° C. in column 4 of each set by means of the temperature coefficient found from the tests given in Table X. Most of the comparisons up to September 10, 1898, were made by Mr. SHEFFIELD, and from that date on, by myself. The maximum variation from the mean is 5×10^{-5} ohm, and is within the limits of error for a series of comparisons such as these. As a rule the agreement is very much closer than this. Taking the value of 4086 as equal to 1·00045 true ohms at 20° C. in place of the value assumed for calculation in the table, we find Coil 1, $1·00132 + ·00043 = 1·00175$ true ohms at 20° C., and Coil 2, 1·00043 ohms. At any other temperature the coefficients +·000250 for Coil 1, and ·000246 for Coil 2, are used, which were obtained from the experiments detailed in Table X.

The value of the two 1-ohms in parallel is very easily determined on a small slide-rule, by assuming the ohms equal to $(1 + d_1)$ and $(1 + d_2)$ respectively, where d_1 and d_2 are equal to the small differences from unity, then

$$\frac{(1 + d_1)(1 + d_2)}{(1 + d_1) + (1 + d_2)} = ·5 + \frac{\frac{1}{2}(d_1 + d_2)}{2 + d_1 + d_2},$$

neglecting products and powers of d_1 and d_2.

At 20° C. the value of the fraction is

$$R = ·5 + \frac{·00109}{2·0021} = ·500544 \text{ ohm.}$$

At 10° C., when No. 1 is equal to (1 − ·00077), and No. 2 (1 − ·00205),

$$R = ·5 - \frac{·00141}{1·99718} = ·499294 \text{ ohm.}$$

We may accept then for calculation the most probable value of the two platinum-silver ohms in parallel to be

·500544 true ohm at 20° C., ·499294 true ohm at 10° C.,

where one true ohm = 1·01358 B.A., unit, as given in all the certificates of the standard ohms.

Current Heating.—It is a matter of importance to determine the true resistance of the two coils when the maximum current used in these experiments was passed through. For the largest flows of water, when the largest heating current was required, this amounted to 8 amperes. This current was divided between eight ·4-millim. platinum-silver wires immersed bare for their entire length, about 1 metre, in oil, which was vigorously stirred. Each wire was required to carry then only 1 ampere, or develop only 4 watt-seconds heat energy. It was impossible to imagine that the temperature of the wire could have been sufficiently different to that of the oil to appreciably affect the resistance. A difference of ·1° between the wire and oil

Table IX.—Comparison of Platinum-Silver ohms, with 4086 taken as 1 ohm at 20° C.

Date of comparison.	Coil 1.			Coil 2.			
	Temperature of comparison.	Resistance at temperature of comparison.	Resistance corrected to 20° C.	Temperature of comparison.	Resistance at temperature of comparison.	Resistance corrected to 20° C.	
1898.	°			°			
May 26th . . .	19·2	1·00113	1·00133	19·4	·99983	·99999	Observer, Sheffield.
,, 28th . . .	20·9	1·00158	1·00136	20·9	1·00017	·99995	
,, 31st . . .	20·8	1·00146	1·00127	20·9	1·00021	·99999	
June 11th . . .	16·9	1·00053	1·00131	18·1	·99956	1·00002	
,, 25th . . .	20·8	1·00147	1·00128	20·9	1·00023	1·00001	
September 10th .	19·1	1·00112	1·00133	19·2	·99981	1·00000	Observer, Barnes.
1899.							
February 22nd .	15·6	1·00022	1·00132	15·9	·99900	1·00000	
May 8th . . .	17·5	1·00071	1·00133	17·6	·99939	·99998	
August 9th . .	19·4	1·00118	1·00133	19·5	·99988	1·00000	
September 21st .	17·0	1·00059	1·00134	17·0	·99930	1·00003	
October 4th . .	15·2	1·00016	1·00135	15·3	·99889	1·00004	
1900							
May 26th . . .	16·9	1·00056	1·00133	16·8	·99926	1·00005	
Means	18·27	—	1·00132	18·46	—	1·00001	

Table X.—Temperature Coefficient of Platinum-Silver ohms.

Coil 1.			Coil 2.			
Temperature of Pt-Ag coil.	Difference from 4086 at 20° in ohms.	Calculated from curve.	Temperature of Pt-Ag coil.	Difference from 4086 at 20° in ohms.	Calculated from curve.	
°			°			
21·1	+ ·001590	+ ·001590	21·0	+ ·000258	+ ·000250	Observer, Barnes.
14·0	− ·000242	− ·000200	13·0	− ·001741	− ·001750	
6·5	− ·002027	− ·002055	6·9	− ·003170	− ·003220	
20·0	+ ·001337	+ ·001310	20·3	+ ·000070	+ ·000070	Observer, Sheffield.
19·9	+ ·001245	+ ·001290	19·3	− ·000190	− ·000190	
12·8	− ·000458	− ·000495	14·5	− ·001345	− ·001375	
8·7	− ·001346	− ·001520	11·4	− ·002130	− ·002130	
5·3	− ·002417	− ·002370	5·9	− ·003497	− ·003490	

would have produced an error less than ·00002 ohm, or less than 2 parts in 50,000, whereas it is probable the actual difference in temperature did not make an error one-tenth of this amount.

Sec. 3*c*.—*Measurement of Temperature.*

By far the most important factor that determines the character of the curve for the variation of the specific heat of water with temperature is the particular thermometric scale to which the results are referred. This was most forcibly brought out by ROWLAND in his memoir, and it was pointed out by him that without the greatest care in reducing his mercurial thermometers to the air scale, the value of the specific heat of water would have apparently remained constant in terms of the mercurial scale over the range of his experiments. The discovery of the rapid decrease in specific heat with increase of temperature from 0° to 30° C. was only made through this careful reduction.

In the present series of experiments there were no thermometric difficulties such as are to be met with in the use of a mercurial standard owing to the use of platinum thermometers. In working to the 10,000th part of a degree Centigrade, such corrections as a change of zero, pressure on the bulb, capillary and stem corrections, are so large in the case of the mercurial standard, that for large intervals of temperature the readings are far from reliable. With the platinum thermometer we still have to deal with the question of a change of zero and a stem correction, but these are so small that with sufficient care they may be eliminated altogether.

In speaking of these possible sources of error in connection with the measurement of temperature with the platinum thermometer, I am referring to a limit of accuracy seldom required in most determinations. The first source of error is already well known, and has often been subject of controversy over the reliability of the platinum thermometer, though chiefly, I am convinced, by those who are either prejudiced or who require more experience in this class of work. I have met with no difficulties of this nature that could not be attributed to my own carelessness, or could not be easily avoided with sufficient patience and care. In regard to the second source of error, I have never seen it referred to before in connection with this subject, and will therefore speak about it somewhat further on. We should, strictly speaking, include with the electrical measurements the subject of platinum thermometry. We shall, however, include it with the thermal constants and treat it entirely from that point of view.

The measurement of temperature by the change in resistance of a platinum wire has been carefully studied by Professor CALLENDAR, and his work is already too well known to make it necessary for me to dwell on the fundamental part of it. His introduction of the idea of a platinum temperature which depends on the term,

$$pt = \frac{R_t - R_0}{R_{100} - R_0} \times 100,$$

where R_0, R_{100} and R_t are the measures of the resistance of any one particular sample of platinum wire at 0°, 100°, or at a temperature t, has been now almost universally accepted.

The reduction of the platinum temperature to the air-scale was obtained from a series of comparisons with the nitrogen air thermometer at three fixed points 0°, 100° and 444°, which led to the well-known parabolic formula,

$$t - pt = \delta\left(\frac{t^2}{100^2} - \frac{t}{100}\right),$$

where t is the air temperature, and δ a constant depending on the purity of the platinum wire, the same for any particular purity of wire.

In selecting the wire for use in the present measurements, I was exceedingly fortunate in possessing a sample of the original wire standardized by Professor CALLENDAR and Mr. GRIFFITHS, who found its δ equal to 1·50.

The chief difficulty in selecting a form of thermometer for use in the calorimeter lay in choosing a size of bulb which would give a sufficiently large change in resistance for the rise of temperature produced in the water. On a rise of temperature of 10°, it was necessary to be sure of the measurement to ·001°, and to obtain the readings to ·0001° to have them comparable with the accuracy of the other measurements. At the same time it was impossible to have the bulbs too long, as it introduced increased possibilities of error in the outflow-tube of the calorimeter. For the size of wire used (·15 millim.), and the size of the units in the resistance-box for compensating the change in resistance, it was necessary to use about 4 metres of wire for each thermometer.

The first thermometers made were from some of the original sample of wire, which had been silk covered. Four metres of this wire were coiled up into a bulb, about 6 centims. long, and half a centim. in diameter, which served the purpose very well. Two sets of thermometers were made this way at different times, and will be described further on. The chief difficulty with this form was that, after bending into the coil, the wire could not be annealed well enough. Annealing for a length of time at 150° C. served to give fairly steady results. The difficulty, caused by the exciting current, of heating in the interior of the coiled wire, was also a serious question, which had to be carefully considered.

A pair of thermometers was made for the first tests with the water calorimeter, which were in the usual form of bare-wire wound on a mica frame. To keep the length of bulb within reasonable bounds, it was necessary to have these thermometers only one-half as sensitive as the others. However, this form was far preferable to the other, so that to produce the same sensitiveness as was required, with the most convenient length of bulb, a smaller wire was adopted than is usually employed for thermometric work. A thermometer was finally obtained which gave the required sensitiveness, and had a length and diameter of bulb quite suitable for the calorimeter. In point of steadiness and accuracy, the two thermometers forming the differential pair made in this way could hardly be surpassed.

I propose to describe the tests made on the various thermometers used during the course of this series of experiments. Before doing so, I must briefly describe the resistance boxes and method used for compensating the change in resistance in the wire due to a change of temperature.

The general plan of WHEATSTONE's bridge connections for the thermometer-circuit is already familiar. The wires leading to the bulb of the thermometer are compensated for a change in resistance due to a change in temperature by similar wires placed side by side with them, but connected to the opposite arms of the bridge circuit. The change in resistance in the thermometer is compensated by resistance coils on an opposite arm of the bridge, and a final adjustment made on a short bridge-wire, of which the coils are suitable multiples. A change in resistance is referred to a change in units of the box, rather than measured in ohms. It is evident that a change in the temperature of the resistance coils, while compensating a change in resistance in the thermometer, will produce an apparent change in the thermometer reading. This can be corrected for either by taking the temperature of the coils in air, or by immersing them in oil at a constant temperature. For very accurate work, however, it is better to introduce a different arrangement. If each resistance coil on the bridge is wound with another coil, which has the same temperature coefficient, but a different specific resistance, then if these second coils are connected with an opposite arm of the bridge system, any change in temperature of the bridge coils cannot affect the balance point on the bridge wire. This method, which was devised by Professor CALLENDAR, works exceedingly well.

Through the kindness of Professor CALLENDAR I have had the use of such a compensated resistance box throughout the greater part of my measurements. This box was exhibited to the Royal Society in June, 1893, by Professor CALLENDAR. Besides the compensated resistance coils, the special features of this box are the bridge-wire scale, which has a compensating device for a change in length due to a change in temperature, so that the galvanometer contact point always reads at the same point on the scale, and mercury cup contacts for each set of coils. The resistance coils were multiples of the bridge-wire, commencing from the smallest coil, which was equivalent to 10 centims. of bridge-wire, and doubling always as the coils became larger, *i.e.*, 10, 20, 40, 80, 160, &c., up to 2580. The resistance of the bridge-wire was ·0088 ohm per centim., so that the ten coil was rather less than ·1 ohm. The bridge-wire scale was of brass, very carefully divided to half-millims., and supplied with a vernier with lens reading to ·01 millim. The total length of bridge-wire was 40 centims., but it could be read only between 6 and 34 centims., leaving a margin of 6 centims. at each end.

Professor CALLENDAR was kind enough to allow me to make a resistance box after this design. This box I have used in my later determinations of the specific heat. It differs from Professor CALLENDAR's box in having a slightly greater unit, *i.e.*, 1 centim. of bridge-wire equal to ·0095 ohm, and the coils were made from bare wire wound on mica frames and annealed. Solder joins were avoided between the wire forming the resistance coils and the copper connecting wire, by fusing directly to the copper.

Each of the larger coils, before putting in place in the box, was tested for compensation in a specially constructed oil-bath, the temperature of which could be changed quickly at will in a way similar to the paraffin-bath used in the standard resistance determinations. Each coil was also made of either two or three wires in parallel, ·15 millim. in diameter, so as to avoid current heating. They were specially designed for immersion in oil when in place in the box, but this was not found necessary. It was not deemed necessary to test the small coils, from 10 to 40, for compensation, as the test of the larger coils showed that the calculation of the lengths of wire necessary was so nearly correct as to leave little room for error in the smaller coils over a wide range of temperature. The ratio coils in the box were made from ·15-millim. platinum-silver wire wound in parallel on a mica frame, and were adjusted to equality on the Thomson-Varley slide box. The resistance coils were connected to mercury cups and short-circuited when not in use by thick copper connectors.

The calibration of these boxes consists in determining the errors in the different box coils and the calibration of the bridge-wire and scale.

In determining the total change in resistance of the thermometers between 0° and 100°, which is termed the fundamental interval, or briefly F.I., the largest that it was necessary to use was coil 640. It is evident that, provided this coil is accurately compensated, it is the best one to which to refer the F.I. It is entirely unnecessary to know its absolute value in ohms provided we assume it equal to 640 even units, and refer the other coils, including the bridge-wire, to it.

From 640 down every coil differs from the sum of all the rest by very nearly 10 centims. of bridge-wire, or the size of the smallest coil. If we compare the lengths of bridge-wire obtained by differencing the coils in this way, we obtain the usual series of equations of the form

$$640 - \text{sum}_1 = a_1\,;\ 320 - \text{sum}_2 = a_2\,;\ 160 - \text{sum}_3 = a_3,\ \&\text{c.},$$

where a_1, a_2, and a_3 are very nearly 10 centims. and involve the coil errors.

If we eliminate the sum from any two equations, remembering that the next lowest sum differs from the one before by the lesser coil, then we have a series of the form

$$640 - 2 \times 320 = a_1 - a_2 ;\ 320 - 2 \times 160 = a_2 - a_3, \text{ \&c.},$$

which should equal 0 if $a_1 = a_2 = a_3$.

If we let the error in 640 be equal to 0, then the error in $320 = \frac{1}{2}(a_1 - a_2)$ in terms of 640 even units,

$$160 = \tfrac{1}{2}\{\tfrac{1}{2}(a_1 - a_2) - a_2 - a_3\},$$

and so on for all the coils.

The error in the bridge-wire, which we will call the bw. correction, is determined from the error in coil 10 obtained in terms of 640 even units. The calibration of the bridge-wire was done by inserting a small resistance, equal to about 3 centims. of bridge-wire, into the bridge circuit, so that by short-circuiting it by a heavy copper connector placed in mercury cups, the bridge-wire reading could be shifted the same amount at any part of the wire. The reading was found to vary ·0005 centim. per centimetre on either side of the middle point, 19, in such a way as to increase towards 30 and decrease towards 0. This showed that the wire was slightly smaller towards the zero end, and hence its resistance greater. As the equivalent length of 10 centims., obtained in the calibration of the box coils, never occurred at exactly the same spot on the bridge-wire, there is a small correction to be applied to the values of a_1, a_2, and a_3, due to their position. The correction is worked out so as to reduce the values to a length of bridge-wire extending over the middle point, between 14 and 24. The correction is very small, however, and would produce no appreciable error to the results if neglected altogether. In my own box the agreement of the equivalent length for the 10 coil above and below the middle point of the bridge-wire caused me to neglect this correction altogether.

In Table XII. I give a complete series of readings taken to determine the coil corrections in the first box. In Table XIII. a summary of tests is given extending over a period of a year.

Table XIV. contains the same obtained for my own box. The corrections in this latter case are somewhat larger. The reason being that it was more difficult to adjust the coils exactly when fused joins were used instead of solder, and at the same time preserve complete compensation. My aim was to be sure of having this latter condition fulfilled at the expense of the former, as the coil correction is always a definite and measurable quantity, and easy to apply.

The signs are affixed to the corrections in the way they should be applied to the reading. The bridge-wire correction is given per centimeter of length. In taking the readings the galvanometer was used which has already been referred to in connection with the comparison of the standard resistances. The sensitiveness was obtained so as to give from 40 to 50 scale divisions per millimetre of bridge-wire on reversing the current. For the small coils an external resistance of 350 ohms was

TABLE XII.—Set of Readings for determining Box Coil Corrections.

Coils.	640-sum.	320-sum.	160-sum.	80-sum.	40-sum.	20-sum.	10-sum.
Reading of bridge-wire . . {	24·979 14·950	21·970 12·096	20·645 10·631	19·711 9·815	25·113 15·135	27·640 17·624	28·787 18·911
Equivalent length	10·029	9·874	10·014	9·896	9·978	10·016	9·876
Correction to mean bridge-wire	0	+ ·002	+ ·003	+ ·004	– ·001	– ·002	– ·004
Corrected length	10·029	9·876	10·017	9·900	9·977	10·014	9·872
Differences, 640–2 × 320, &c. .	—	+ ·153	– ·141	+ ·117	– ·077	– ·037	+ ·142
Correction in terms of 640 coil	0	– ·077	+ ·032	– ·043	+ ·017	+ ·027	– ·057

TABLE XIII.—Box Coil Corrections in Terms of 640 even Units. Box 1.

Date.	320.	160.	80.	40.	20.	10.	Bridge-wire.
1898.							
May 6th . .	– ·087	+ ·027	– ·038	+ ·021	+ ·034	– ·050	+ ·008
„ 21st .	– ·072	+ ·028	– ·038	+ ·018	+ ·026	– ·055	+ ·007
„ 25th . .	– ·077	+ ·027	– ·036	+ ·017	+ ·028	– ·051	+ ·007
1899.							
January 7th .	– ·055	+ ·033	– ·044	+ ·019	+ ·030	– ·051	+ ·007
„ 9th .	– ·063	+ ·040	– ·042	+ ·020	+ ·030	– ·050	+ ·007
„ 12th .	– ·069	+ ·029	– ·045	+ ·019	+ ·024	– ·055	+ ·008
April 27th .	– ·077	+ ·032	– ·043	+ ·017	+ ·027	– ·057	+ ·007
Means . . .	– ·071	+ ·030	– ·040	+ ·019	+ ·029	– ·053	+ ·007

TABLE XIV.—Box Coil Corrections in Terms of 640 even Units. Box 2.

Date.	320.	160.	80.	40.	20.	10.	Bridge-wire.
1900.							
February 10th	– ·029	– ·054	+ ·210	+ ·144	– ·033	– ·074	+ ·0066
„ 13th	– ·025	– ·048	+ ·210	+ ·149	– ·030	– ·071	+ ·0061
„ 26th	– ·030	– ·053	+ ·208	+ ·149	– ·031	– ·072	+ ·0062
Means . . .	– ·028	– ·052	+ ·210	+ ·148	– ·032	– ·072	+ ·0064

required, which was reduced gradually to 150 ohms for the 640 coil in order to preserve the same sensitiveness throughout the test, with one accumulator. The galvanometer contact was arranged so that it could be held in contact with the bridge-wire. Therefore instead of obtaining an exact balance and reading the vernier, the contact was placed to the nearest millimetre or half-millimetre mark on the scale, with the help of the vernier, and the deflection of the galvanometer recorded. Accurate account was always kept, by repeated verification, of the sensitiveness of the galvanometer, which never altered as much as one scale division due to external disturbances.

For the sake of convenience, the diagram of the complete thermometer circuit is given in fig. 6. This shows the relative position of the resistance and compensating coils in the bridge system, the position of the ratio coils and bridge-wire. When differential thermometers are used we have them connected on opposite arms of the bridge, at P and C, and arranged so that the compensating leads for thermometer P are in series with thermometer C, and the compensating leads for C connected with P. Where P and C are at the same temperature, and of the same resistance, it is evident that the bridge system is in equilibrium with the galvanometer contact at the middle of the bridge-wire. For a change in the temperature of either P or C the bridge reading shifted either to the right or left, and when too great to be read on the wire, was compensated by the resistance coils. A change of temperature in C higher than P, however, could not be recorded beyond the bridge-wire. It was therefore necessary to arrange that P should always be used for measuring a change in temperature higher than C. The resistance coils were brought into the circuit by removing the heavy copper contacts from the mercury cups. When these contacts

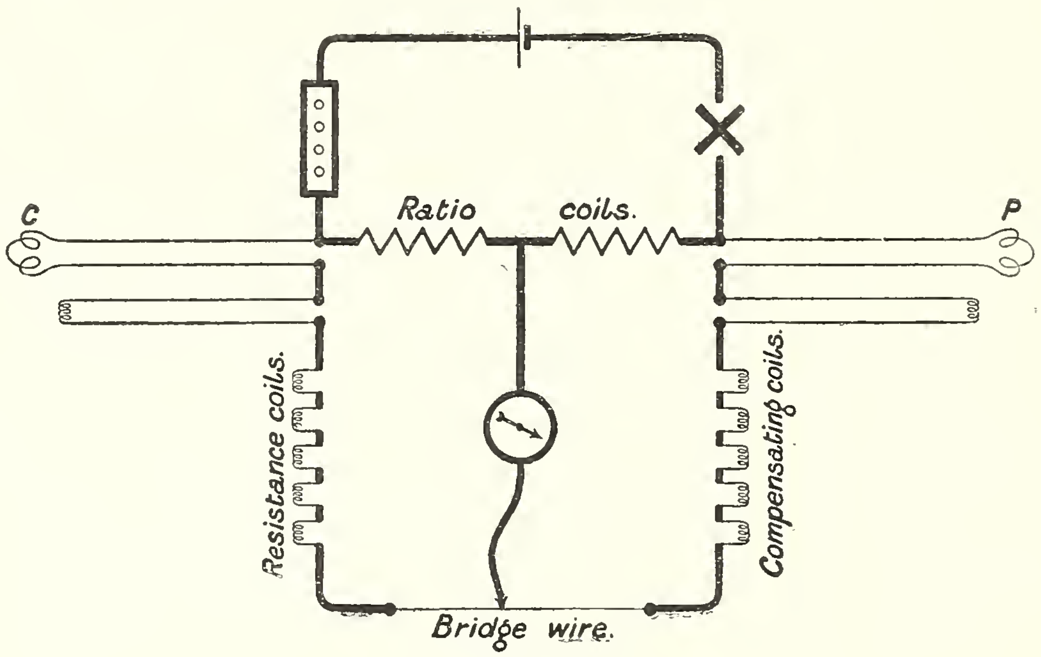

Fig. 6.

were removed, the contacts of each corresponding compensating coil were removed at the same time. To obtain the fundamental constant $(R_{100} - R_0)$ or interval, F.I., both C and P are balanced when immersed in melting ice, and then with C in ice and P in steam. To obtain the difference between the intervals of the two thermometers both are read when in steam. This gives the data required for converting into degrees a change of resistance in P relative to C.

During the progress of the present experiments, five pairs of differential thermometers were made and tested. In describing these, I shall letter them A, B, C, D, and E, respectively. The thermometers of pair A were made of the original silk-covered ·15-millim. platinum-wire, about 25 ohms resistance each. The bulb of each thermometer was about 6 centims. long and was fastened by solder joins to flexible copper leads placed side by side with compensating leads. The protecting tube was of glass, about 25 centims. long and a few millims. in diameter. The ends of the compensating leads near the bulb were connected by a small piece of platinum-wire about 4 centims. long. This was to correct any conduction error on the wire in the thermometers by heat conduction from the leads. This device was also used for all the other thermometers.

Thermometer B was made of 12½-ohms resistance, or one-half the sensitiveness of the other pair. Each thermometer of the pair was wound in the usual way on a mica frame, from the 6-millim. bare platinum-wire, and annealed at a low red heat. As these thermometers proved eventually to be too bulky for convenience in the calorimeter, they were soon discarded. It will, therefore, not be necessary to give them further mention.

Thermometer C was made from a pair of silk thermometers similar to A. The platinum-wire was fused to copper-wires, which in turn were soldered to copper leads. These thermometers proved satisfactory in many ways, although they finally gave trouble from defective insulation and had to be abandoned. These thermometers were used in our first preliminary measurements of J during the summer of 1898.

Thermometer D was the first pair made from ·10-millim. platinum-wire. This wire was some sent out to Mr. R. O. King by the Cambridge Scientific Instrument Company. Its δ was given as 1·50, which was subsequently verified by Mr. Tory in the course of his work. Each thermometer was about 20 ohms. in resistance, and was made by winding on a mica frame. The bulb was about 5 centims. long and between 6 and 7 millims. in diameter. Owing to the inconveniently small F.I. of this pair of thermometers (about 700 units of the box instead of 1000 for 100° C.), it was supplanted by pair E.

Thermometer E is by far the most important pair, as with it all the later measurements of the specific heat were obtained. The wire used in making each thermometer of the pair was drawn down to ·10 millim. from the original 6-millim. platinum-wire. The resistance of the thermometers was about 25 ohms each, and gave a F.I. about 970 units of the box. The bulbs were about 7 millims. in diameter and about

$6\frac{1}{2}$ centims. long, and were made, as in thermometer D, of the bare wire wound on a mica frame. The first arrangement was with the platinum-wire fused to about No. 18 copper-wire, which in turn was soldered to the copper leads about 6 centims. above the bulb. This was changed to having the wire fused to much longer copper-wires, which were soldered to the leads at a point considerably beyond the glass-tubes containing the bulbs. This avoided the changing of the temperature of the solder-joins in the glass-tube. The final arrangement was to have the wire gold-soldered to heavy platinum-wires, which in turn were fused to copper-wires about 6 centims. above the bulbs. These wires were then soldered to the main leads at a point sufficiently beyond the glass-tube so as to remain unaffected by a change in temperature in the interior of the glass-tube. All these changes were made to improve the thermometers, although the last one was not really necessary. A very considerable uncertainty was introduced with the first arrangement, which was removed on removing the solder-joins from the interior of the thermometer-tubes.

The ·10-millim. wire is exceedingly delicate to use for thermometric work, and great care had to be exercised in constructing the thermometers and in handling them. They gave, however, exceedingly consistent results. As a check, a sample of the wire was given to Mr. TORY, who very kindly determined its δ by comparing it with a piece of the original ·15-millim. wire. This came out 1·502, and showed that no change had been produced in the δ, due to its having been drawn from the larger size.

The fixed points 0° and 100° upon which the accuracy of the F.I. depends, were obtained as usual with a mixture of finely-cracked ice and water, and the usual form of hypsometer. In regard to the constancy of these points, the former depends on the percentage of ice or water present in the mixture, and its rate of melting, while the latter depends on the accuracy of reading of the barometer, accepting in both cases the purity of the ice or water. Great care was always taken with the freezing-point mixture, to have it compact and firmly placed in a copper vessel, heavily lagged, and in which water could be made to circulate through the ice around the thermometer bulbs. The thermometers were as far as possible placed side by side, separated only by a thin partition of ice.

After obtaining the balance-point with both thermometers in ice, one, P, was removed to the steam-jacket, leaving the other, C, still in ice. The change in resistance in P was compensated by the resistance-coils until the reading was brought on to the bridge-wire. When a sufficient time was allowed (about 15 minutes was generally sufficient) for the attainment of a steady temperature, as shown by the steadiness of the balance-point, the reading of the bridge-wire was recorded. Thermometer P was then returned to the ice-bath, and the first reading repeated, which gave a measure of any change of zero in P. The sensitiveness of the galvanometer changed slightly between the two points owing to the increase in resistance in the two arms of the bridge system, but this was determined always at both points.

In the tests to be described, an external resistance of at least 40 ohms was inserted in the battery circuit, which was supplied from one accumulator. The current was never as much as ·02 ampere in each thermometer, and current-heating could be safely neglected. In view, however, of a possible effect of current-heating on the differential readings, the F.I. of thermometer D was determined for different external resistances, but no effect could be measured. The current was left continuously running during a test, and was always the same as that used in the calorimetric experiments.

Three Fortin barometers, supplied by ELLIOTT BROS., of London, were used to obtain the steam-point. They were Nos. 571, 572, and 573. They had all been filled originally by ELLIOTT. During the preliminary part of the experiments, barometer 572 was used, but owing to an accident was replaced later by 571. Barometer 571 was, however, re-filled later as a check, by boiling out with mercury, and was compared with 573, to which most of the later steam readings were referred. As a check also the scale of barometer 572 was verified, and found correct to within ·1 millim. This was of sufficient accuracy for the determination of the F.I., as the mercury height could be measured accurately only to ·1 millim. with the vernier supplied with the scale. It was possible to estimate to ·02 millim. with a little care.

A comparison of 572 re-filled with 573, made on February 26, 1900, is given below.

No. 573, 75·415 centims., $t = 17·5$; No. 572, 75·410 centims., $t = 17·3$.

Second setting,

No. 573, 75·415 centims.; No. 572, 75·400 centims.

The temperature of the mercury column was taken from a thermometer embedded in the barometer case. I decided to adopt the readings of the highest barometer as likely to be most accurate. It is probable that barometer 573 was correct to ·01 centim. in its readings over different dates. An error of ·01 centim. in setting and reading the height of mercury would produce an error of about ·004° on the steam point, which is about the order of agreement given in the measurement of the F.I. from time to time. In repeating readings of the F.I., where it was not necessary to alter the setting of the barometer, much closer agreement than this was attained. The barometer readings were reduced to 0° C. and latitude 45°, and corrected for temperature by the formula

$$H_0 = H(1 - ·0001614t)(1 - ·000033) + ·0002t \text{ centim.}$$

The essential scheme followed for the determination of the F.I. has already been laid down. The following tables contain the results of the tests made on the different instruments used in these experiments. Owing to the importance attached to thermometer E, it is given first place. For this thermometer it will be necessary to divide the tests into four groups.

Group I. contains the results when the ·10-millim. platinum-wire is fused to short copper-wires, which in turn are soldered to the leads *inside* the glass-tubes of the thermometers, so that the solder-joins are subject to the temperature change 0° to 100°.

Group II. gives the tests when the solder-joins inside the glass-tubes were done away with.

Group III. contains the results in the case when the ·10-millim. wire was gold-soldered to heavy platinum-wire, which was fused to the copper leads.

Group IV. contains the determination of F.I. in terms of the second box. It comes smaller owing to the resistance of the unit being greater than in the first box.

In Group I. the variation from the mean value is somewhat larger than the errors of reading the barometer, amounting in the extreme case to ·007°. This was attributed to an uncertainty in the solder joins.

Group I.—Coils 640 + 320 + 10 = 969·876 units. Thermometer E.
10 units = 1° C. nearly. Box 1.

Date.	Bridge-wire corrected.	Total units.	Barometer corrected.	F.I. corrected to 76·00 centims.
February 24, 1899	+2·964	972·840	76·196	97·2141
,, 24 ,, ...	+4·597	974·473	76·630	97·2217
,, 27 ,, ...	−1·396	968·480	74·938	97·2260
,, 28 ,, ...	−2·022	967·854	74·789	97·2162
,, 28 ,, ...	−2·399	967·477	74·683	97·2160
Mean . . . . 97·2188				

Group II.—Coils 640 + 320 + 10 = 969·876 units. Thermometer E.
10 units = 1° C. nearly. Box 1.

Date.	Bridge-wire corrected.	Total units.	Barometer corrected.	F.I. corrected to 76·00 centims.
May 15, 1899.	+3·006	972·882	75·985	97·2935
,, 15 ,, ...	+2·495	972·371	75·844	97·2926
,, 18 ,, ...	+1·669	971·545	75·616	97·2916
August 10, 1899.	+1·302	971·178	75·492	97·2991
,, 10 ,, ...	+1·279	971·155	75·485	97·2993
September 11, 1899. . . .	+2·320	972·196	75·792	97·2939
,, 11 ,, ...	+2·211	972·087	75·760	97·2944
,, 21 ,, ...	+0·670	970·546	75·314	97·2993
Mean . . . . 97·2955				

In Group II. the agreement is much better, and it can hardly be said that the variations can be attributed to other causes than the setting of the barometer. For tests made on the same date, where the interval was repeated with but a small change in barometric reading, which could be followed by the vernier without other adjustments, the readings are as a rule exceedingly consistent.

The two tests in Group III. are given in full.

Group III. Date, September 26, 1899.

First determination.

Both in ice, reading of bridge-wire . . .	23·173. No coils.
C in ice ; P in steam	23·757 + coils, 640 + 320 + 10.

Second determination.

Both in ice, reading of bridge-wire . . .	23·175, 23·172. No coils.
C in ice ; P in steam	23·646 + coils, 640 + 320 + 10.
Both in steam	25·143. No coils.

Barometer in first determinations. Uncorrected, 75·073 centims. at temp. 18°·9 ; corrected, 74·851.

Barometer in second determinations. Uncorrected, 75·092 centims. at temp. 18°·8 ; corrected, 74·870.

	In first determination.	In second determination.
Bridge-wire	− 0·584	− 0·473
Bw. correction	4	3
	− 0·588	− 0·476
Coils	969·876	969·876
	969·288 in box units.	969·400 in box units.
Barometer correction .	+ ·4093°	+ ·4025°
F.I.	97·3381 in degrees.	97·3425 in degrees.

Mean value . . . . . 97·3403.

Group IV.—Coils 640 + 160 + 80 + 20 = 900·128 units.
9 units = 1° C nearly. Box 2.

Date.	Bridge-wire corrected.	Total units.	Barometer corrected.	F.I. corrected to 76·00 centims.
February 14, 1900	+4·143	904·271	75·778	90·5009
„ 14 „	+2·195	902·323	75·191	90·5006
„ 16 „	+4·307	904·435	75·816	90·5037
„ 16 „	+4·328	904·456	75·838	90·4994
„ 16 „	+4·361	904·489	75·846	90·5002

Summarizing we have the F.I.'s of thermometer E, as measured by the two boxes, as follows:—

Group I.—97·2188 measured with 1st box.
,, II.—97·2955 ,, ,, ,, ,,
,, III.—97·3403 ,, ,, ,, ,,
,, IV.—90·5009 ,, ,, 2nd ,,

This gives the corrections to be applied to the readings to make 100 10-units equal to 100° on the platinum scale:

Group I.—2·8610 per cent.
,, II.—2·7795 ,,
Group III.— 2·7324 per cent.
,, IV.—10·4962 ,,

The difference in the corrections, with the exception of Group IV., is due to the change in the lengths of the thermometer wire in changing the leads. No change was made to the thermometers themselves between Groups III. and IV.

The various tests on the other thermometers are given now as under. With thermometer D no difference could be noted in the F.I. measured with 80 ohms in the external circuit, or with 50 ohms. The tests with thermometer A are important as illustrating the results to be obtained from silk-covered wire thermometers, and also as they were the thermometers used in the mercury experiments.

THERMOMETER A. Box 1.

Date.	F.I. corrected.
May 22, 1897	99·9327
,, 24 ,, ...	99·9245

With thermometer C, also silk-covered thermometers, the tests are not so satisfactory.

THERMOMETER C.

Date.	F.I. corrected.	Date.	F.I. corrected.
April 30, 1898 . . .	101·4031	July 11, 1898 . . .	101·3908
May 2 ,, . . .	101·3931	August 8 ,, . . .	101·4006

THERMOMETER D. Box 1.

Coils 640 + 160 = 800·030 units.
8 units = 1° C., nearly.
With 80 ohms external circuit.

Date.	Bridge-wire corrected.	Total units.	Corrected barometer.	F.I. corrected to 76·00 centims.
July 21, 1898	−4·679	795·351	75·806	79·5924
,, ,, ...	−4·655	795·375	75·816	79·5913
,, ,, ...	−4·614	795·416	75·826	79·5925
With 50 ohms external circuit.				
,, ,, ...	−4·651	795·379	75·816	79·5917

All these fundamental intervals, of course, only apply to thermometer P of each pair, or the one which is used to determine the rise of temperature in the water.

No separate determinations are required when both the thermometers are at the same temperature over the scale between 0° and 100°. The correction is simply to thermometer P in its reading relative to thermometer C, when the water is heated through so many degrees in the outflow end of the calorimeter. The "cold" reading of the thermometers, when in place in the calorimeter, at any temperature of the water-jacket, will be the differential reading of the thermometers at the temperature indicated by the thermometer of the water-jacket. The effect of conduction from the ends of the calorimeter will appear as a slight change in this differential reading, but this is never more than ·01° or ·02°, and only comes in at the extremes of the range.

In regard to the errors referred to in the first of this section, to be met with in the practical employment of platinum thermometers for very accurate work, the first one, due to a change in zero, can always be avoided by sufficient annealing and offers no difficulty. The second one is by far the most important, and is caused by the conduction of heat away from the air around the bulbs through the metal leads. This is rendered worse rather than better by the presence of the compensating leads, because of the greater amount of good conducting material introduced into the thermometer tubes. The employment of a small length of wire to connect the compensating leads cannot rectify it, nor will the prevention of convection currents of air in the glass tubes render it harmless. It can be reduced to a negligible quantity only by immersing a sufficient length of the thermometer tube, and can always be measured by withdrawing the thermometer tube more or less from the vessel or steam-jacket in which it is immersed, and determining the drop in temperature indicated by the bulb. I took special care to reduce this correction, which could easily amount to ·01 or even more in the steam-jacket, to a negligible quantity, so that it could not have affected the F.I. as determined in my experiments to as much as ·001°, and probably much less. Convection currents in the stem of the thermometer enclosed in the glass-tube were avoided in all my thermometers by lagging the leads down to within a few centims. of the bulb with cotton-wool.

The insulation between the leads of the thermometers could be detected very quickly by a very simple adjustment in one of the box contacts, so that the battery in series with the galvanometer could be made to detect at once the smallest leak between the connecting and compensating leads.

In correcting the differential readings to the air scale two of the ordinary parabolic formulæ are combined.

If pt_1 and t_1 be the platinum and air temperatures for one thermometer of the differential pair and pt_2 and t_2 be the same for the other, then for one we have

$$t_1 - pt_1 = \delta\left(\frac{t_1^2}{100^2} - \frac{t_1}{100}\right),$$

and for the other

$$t_2 - pt_2 = \delta\left(\frac{t_2^2}{100^2} - \frac{t_2}{100}\right),$$

from which we have, for the differential reading,

$$(t_1 - pt_1) - (t_2 - pt_2) = \frac{\delta}{10{,}000}(t_1 - t_2)(t_1 + t_2 - 100).$$

The correction is always small, and amounts to ·1° in the extreme at the ends of the scale for a difference of 8°. It vanishes altogether at 50°, changing sign at that point.

In determining the correction pt_1 and pt_2 may be substituted in the right-hand side for a first approximation. A second approximation generally gives the correction with sufficient accuracy.

Sec. 3*d*.—*Measurement of Time.*

The method of measuring the average rate of flow over the time of any experiment was to divide the total weight of water by the time of flow. This total time of flow was generally of the order of 15 minutes, or 900 seconds. The interval was recorded on a chronograph, which marked seconds 1 centim. long, from a standardized clock. The drum of the chronograph revolved at the rate of one revolution per minute, and the record of each second was made by a lateral kick in a continuous line from a pen marking an attached sheet of paper. The pen was connected to a relay, which was excited by an electric current whenever the pendulum of the clock swung through a globule of mercury at the middle of each stroke. The stream of water from the calorimeter could be made to flow out of either one of two nozzles before it entered the tared flask for obtaining its weight. The switch-over device was made from a 3-way glass tap, and so arranged that when the tap was turned so as to change the flow from one tube to another, the time of closing one and opening into the other was recorded by the pen on the chronograph sheet. Between the opening and closing, the flow was shut off altogether, but as this only amounted to from two to three-tenths of a second, the expansion of the rubber tube connections in the water circuit prevented the flow of water through the calorimeter from being interrupted, and any sudden shock to the conditions was avoided.

Fig. 7 gives a general plan of the switch-over device. The handle of the glass tap was connected to a long arm, which could be moved between two stops, representing the position when either nozzle was open. At the time of switching over, two marks were recorded on the chronograph, the mean of which was taken in estimating the interval of any flow. These two marks could each be estimated to ·01 sec. very easily with a millimetre scale, and were probably in all cases accurate to ·02 sec. on 900 seconds.

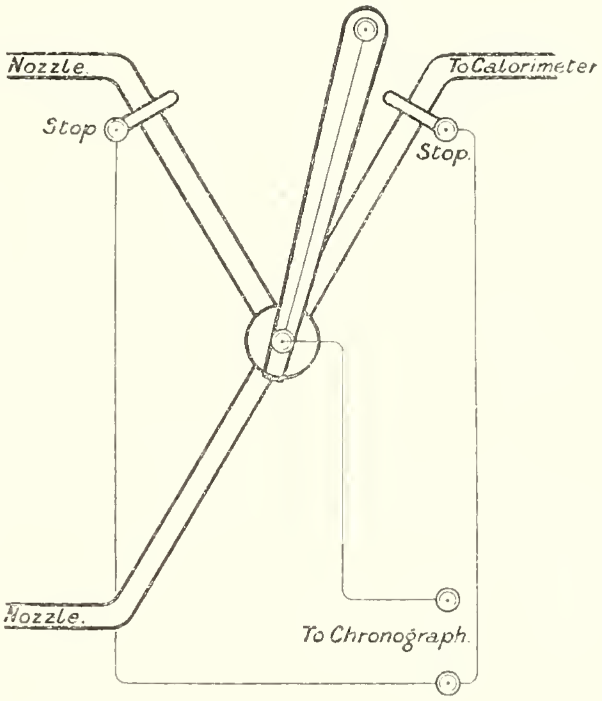

Fig. 7.

The standardization (indirectly to standard time) of the clock marking the seconds was done at frequent intervals during the course of the present series of experiments by comparison with a Frodsham and Keen ship's chronometer. The rate of this chronometer was determined not only by direct comparison with the standard clock at the University Observatory, but by repeated telephonic communication between an observer at the Observatory and myself in the Physics Building. This rate, which was a slight gain, was extraordinarily constant. The rate of the clock, a loss, varied considerably between winter and summer, although the variation was very consistent and regular. The rates during the corresponding months of a year agreed almost to 1 second a day.

TABLE XVI.—Clock Comparisons.

	1898.							1899.		
	May.	June.	July.	Aug.	Sept.	Oct.	Dec.	Jan.	Feb.	March.
	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.
1	—	28	35	35	—	38	—	—	—	—
2	—	27	32	36	—	—	—	24	—	—
3	—	27	—	36	—	—	—	24	—	—
4	—	27	33	33	—	—	—	—	—	18
5	—	28	33	—	—	—	—	25	—	—
6	—	28	35	35	—	—	—	25	—	—
7	—	—	33	—	—	—	—	25	20	—
8	—	—	33	35	—	—	—	—	—	18
9	—	—	36	37	—	—	—	24	—	—
10	—	—	—	35	—	—	—	24	—	—
11	—	—	33	35	—	—	—	23	—	—
12	—	—	35	36	—	—	—	24	—	—
13	—	—	—	35	—	—	—	23	22	—
14	—	—	33	—	36	—	29	—	—	—
15	—	—	34	—	—	—	28	—	—	—
16	—	—	34	—	37	—	29	23	—	—
17	—	—	—	—	—	—	28	—	—	—
18	—	—	33	—	—	—	—	—	—	—
19	—	—	34	—	—	—	28	23	—	—
20	—	—	32	—	—	—	27	23	—	—
21	—	—	34	—	39	—	26	23	—	—
22	—	22	32	—	—	—	25	—	18	—
23	—	24	35	—	37	—	26	22	—	—
24	—	30	—	—	—	—	25	—	—	19
25	—	32	34	—	—	—	23	—	—	—
26	—	—	34	—	—	—	24	—	—	—
27	—	32	34	—	—	—	25	—	—	—
28	25	32	35	—	—	—	25	—	—	—
29	26	33	35	—	—	—	25	—	—	—
30	26	33	34	—	—	—	26	21	—	—
31	27	—	—	—	—	—	25	—	—	—

TABLE XVI.—Clock Comparisons—*continued.*

1899.								1900.		
April.	May.	June.	July.	Sept.	Oct.	Nov.	Dec.	Feb.	March.	
seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	seconds.	
—	—	—	—	—	—	—	—	—	22	1
—	—	—	—	—	—	—	—	—	—	2
—	—	—	—	—	—	—	—	—	—	3
—	—	—	—	—	—	—	—	—	—	4
19	22	—	—	37	40	—	—	—	—	5
18	—	—	—	38	38	—	—	—	—	6
19	—	30	—	—	39	—	—	23	—	7
—	21	31	—	37	—	—	—	23	23	8
—	22	31	—	—	—	—	—	23	21	9
—	22	32	—	—	—	—	—	—	20	10
19	23	—	—	—	—	—	—	—	—	11
19	23	32	36	37	—	—	—	—	20	12
19	—	31	—	—	—	—	—	—	—	13
19	—	29	—	37	—	39	—	—	—	14
—	—	32	—	—	—	36	—	—	—	15
—	—	33	—	—	—	36	—	—	20	16
—	—	34	—	—	—	—	—	—	20	17
20	—	—	—	—	—	35	—	—	—	18
20	—	34	—	—	—	—	—	—	20	19
20	—	34	—	—	—	—	—	22	—	20
20	—	33	—	—	—	—	—	—	19	21
—	—	34	—	—	—	—	—	—	—	22
—	—	35	—	—	—	31	—	—	20	23
—	—	35	—	—	—	—	—	—	—	24
—	26	—	—	—	—	—	—	—	—	25
—	—	35	—	—	38	—	—	—	—	26
—	—	35	—	—	—	33	—	—	—	27
—	—	35	—	—	—	33	28	—	—	28
—	—	35	—	—	—	—	—	—	—	29
—	26	34	—	—	—	—	28	—	—	30
—	—	—	—	—	—	—	—	—	—	31

The following Table contains the results of the comparisons for the chronometer obtained by telephonic communication :—

TABLE XV.

Date.	Gain.	Date.	Gain.
Jan. 3 to Jan. 4, 1899	6·5 secs.	Jan. 11 to Jan. 14, 1899	19·5 secs.
,, 4 ,, ,, 5, ,,	6·5 ,,	,, 14 ,, ,, 16, ,,	12·0 ,,
,, 5 ,, ,, 6, ,,	7·0 ,,	,, 16 ,, ,, 23, ,,	48·5 ,,
,, 6 ,, ,, 7, ,,	6·5 ,,	,, 23 ,, ,, 30, ,,	49·0 ,,
,, 7 ,, ,, 9, ,,	12·5 ,,	,, 30 ,, Feb. 6, ,,	46·0 ,,
,, 9 ,, ,, 10, ,,	7·0 ,,	Feb. 6 ,, ,, 13, ,,	48·5 ,,
,, 10 ,, ,, 11, ,,	7·0 ,,	,, 13 ,, ,, 20, ,,	48·5 ,,
Mean gain . . . . 7·0 secs. in 24 hours.			

From March 20 to March 21 of the same year (1899) the gain was 7·0 secs. ; from February 9 to February 10, 1900, the gain was 7·0 secs. ; from February 10 to February 12 it was 15·0 secs.

In August, 1898, the chronometer was taken to the Observatory for two weeks, and daily comparisons were made with the standard clock. Its rate was found to vary between 6 and 9 seconds gain per day, which is a somewhat greater irregularity than I obtained, although the mean value agrees very well with the later comparisons. In rating the clock, I considered it safe to assume the rate of the chronometer constant to within a second from day to day, and equal to a gain of 7 secs.

In Table XVI., I give the comparison of the clock with the chronometer from May, 1898, to the close of the present work. The seconds represent the loss of the clock per day, and are not corrected for the rate of the chronometer.

In Table XVII., a summary of the previous Table is given, showing the greatest and least loss per month, with the mean loss corrected for the chronometer, which is obtained by subtracting 7 seconds. As far as possible, the rate of the clock was obtained over any day in which an experiment was obtained.

Table XVII.—Summary of Clock Comparisons.

Month.	Greatest loss in seconds.	Least loss in seconds.	Mean loss in seconds.	Mean loss corrected for rate of chronometer.
May, 1898 . . .	26	25	26	19
June, ,, . . .	33	27	30	23
July, ,, . . .	36	32	34	27
August, ,, . . .	37	33	35	28
September ,, . . .	39	36	38	31
December, ,, . . .	29	23	26	19
January, 1899 . . .	25	21	23	16
February, ,, . . .	22	18	20	13
March, ,, . . .	19	18	19	12
April, ,, . . .	20	18	19	12
May, ,, . . .	23	21	22	15
June, ,, . . .	35	29	32	25
September, ,, . . .	38	37	38	31
October, ,, . . .	40	38	39	32
November, ,, . . .	39	31	35	28
February, 1900 . . .	23	22	23	16
March, ,, . . .	23	19	21	14

The rate of loss diminishes in winter and just doubles during summer. This is probably due to the effect of the dry furnace heat in the building during winter on the wooden pendulum of the clock, in contrast to the more humid climate of the summer months. The furnace fires are started about the month of November and discontinue some time in April.

Sec. 3e.—*Measurement of Weight.*

In all the older methods of calorimetry, the question of evaporation of the water becomes a serious one for consideration. In the present experiments there were no such difficulties. The stream of water flowing from either one of the two nozzles on the outflow end of the calorimeter was caught in a weighed flask, which was fitted with a rubber stopper through which the nozzle passed. Through a second hole in the stopper a tube was fastened containing calcium chloride, so that the air in the flask, displaced by the inflowing water, passed through the calcium chloride. At no point between the calorimeter and the interior of the flask did the water come in contact with air.

In fig. 8 a drawing of the flask is given, showing the position of the calcium-chloride tube. The hole through which the nozzle of the calorimeter is thrust is closed, when the flask is removed, by a glass stopper. A similar stopper closes the end of the calcium-chloride tube and prevents the absorption of water vapour from the air.

The capacity of each of the two flasks, which were used in the experiments, was about 750 cub. centims., but the amount of water weighed in them was never more than 650 cub. centims., and usually varied from 350 to 600 grammes. The weight of the flasks was taken empty, just previous to a determination of the flow and after they had stood for some time unstoppered inside the balance case. The interior of the flasks was always wet on account of the water which had been weighed in them on a previous occasion.

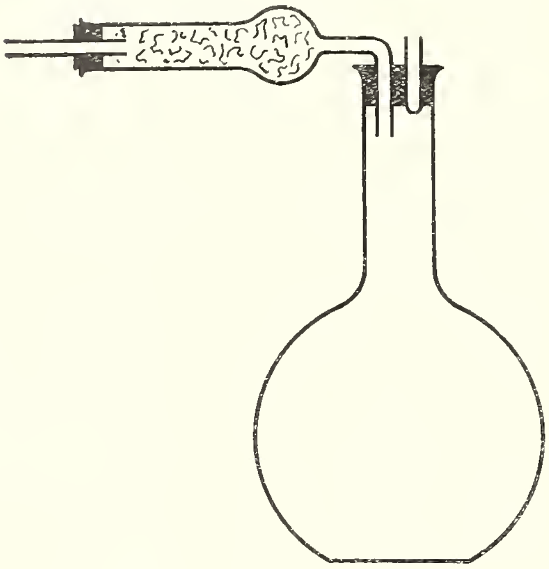

Fig. 8.

The weight was taken on a large Oertling balance, which proved to be most suitable for the purpose. It was sensitive to less than 1 milligramme with 500 grammes, which gave a measure of the weight to a sufficient accuracy. The weights used were brass, and were one of several sets supplied us by OERTLING. They were kept entirely for the present purpose. It is exceedingly unlikely that their errors would amount to as much as 1 milligramme, especially as the several sets sent us by OERTLING agreed much closer than that, and the different weights in the same set agreed very closely amongst themselves. Even if it could be imagined that the sum of the errors of the weights used in any given weighing could have amounted to 10 milligrammes, that would have produced an error in the estimation of the flow of only 1 part in 50,000, whereas it is most probable that the error was not so much as a tenth of this.

The correction to be applied to the weight for the ratio of the arms of the balance was found to be less than 1 in 100,000 for the weights used.

In the reduction of the weight of the water in the flask to weight in vacuum, it is necessary to correct for the presence of water-vapour in the displaced air. This water-vapour is retained in the calcium-chloride tube when the air is driven out and therefore appears not only in the weight of the flask empty, but when it contains the weight of water. It is consequently eliminated from the final weight. The actual weight of air displaced, however, is less than it otherwise would be, by the presence of the water-vapour. In applying this correction it may be assumed that the air inside the flask is completely saturated with water-vapour at the temperature of weighing.

Where brass weights are used the ratio of the weight in vacuum to the weight in air is given by the expression

$$\frac{\mathrm{W}\,vac.}{\mathrm{W}\,air} = \left(1 + \frac{\lambda_t}{\mathrm{S}} - \frac{\lambda_t}{8{\cdot}4}\right),$$

where for the calculation of λ_t we can use the formula

$$\lambda_t = \frac{\lambda_0}{(1 + {\cdot}00366t)}\,\frac{p - \rho}{\mathrm{P}}.$$

In this case $\lambda_0 = \cdot 001293$; $P = 760$; $p =$ the observed barometric pressure at the time of weighing; $\rho =$ the vapour-tension of water at the temperature of weighing.

This latter correction for the water-vapour is small and amounts to about 2 parts in 100,000 on the flow at the usual room temperature. In applying this correction, it was necessary to have the water enter the flasks at the temperature of the room, which was very nearly the temperature of the balance case. This was important, especially when the calorimeter was at a temperature very different to the room temperature. A cooler, consisting of a bath through which a constant stream of water could be made to flow, was arranged adjacent to the calorimeter, so that the outflowing water from the calorimeter was passed through a spiral of copper tube immersed in the water before passing through the switch-over device into the flasks. The temperature of the cooler was maintained near the temperature of the room by controlling the temperature of the stream of water by a gas flame. A stirrer was also fitted up for the bath.

A small change in temperature of the cooler, during the time of an experiment, required a small correction to the flow. This depended only on the readings of a thermometer in the cooler-water just previous to the switching over of the flow into the weighed flask, and just after it was turned off from the flask at the end of the interval. If dt represents the change in temperature obtained from the two readings, v the weight of water filling the copper-spiral in the cooler, and α the coefficient of expansion of water, then the correction to be applied to the flow is $\alpha v dt$. When dt is of the order of a degree, this correction is just negligible for the volume of the total length of copper-tube used, which contained about 22 grammes of water.

Sec. 4.—*Description of the Apparatus and Method of Making the Experiments.*

The Calorimeter.—A general plan of the calorimeter is shown in fig. 1 (p. 153). The first three calorimeters were made at Bonn, and sent out to the laboratory unexhausted. We exhausted the vacuum-chamber of two of these, but the third one was not used owing to the adoption in later experiments of a slightly different design. They all had the same dimensions, with a fine-bore flow-tube 2 millims. inside diameter and 50 centims. long, which was fused at both ends to larger tubes 25 centims. long and 1·8 centim. inside diameter. These larger tubes were sealed into the vacuum-jacket made from a glass-tube 4 centims. in diameter. The seal at each end was made at about the middle of the larger flow-tubes, at a point about 11 centims. from the end where the fine-bore tube was sealed on. Two side tubes were sealed into the larger tubes at each end, but were eventually done away with in the later design, with the exception of one on the inflow end. The vacuum-jacket was exhausted on a large five-fall Sprengel pump with a McLeod gauge for determining the vacuum, and connected to the pump by a side tube fused into the glass of the chamber. When exhausted sufficiently, to a vacuum of about ·002 millim. as shown by the gauge, the connecting tube was fused together on the pump so that the vacuum chamber was permanently and hermetically sealed. The jacket was carefully heated during exhaustion so as to drive off water-vapour and occluded gas from the glass.

Three other calorimeters have been made by EIMER and AMEND of New York, since September, 1898. The vacuum jackets of these were all exhausted by them while heating the calorimeter in an asbestos oven. These calorimeters were of a similar design to the earlier ones, except in having only one side tube at the inflow end, and in having fine-bore flow tubes of different sizes, ranging from 2 millims. to a little over 3 millims. One of the calorimeters was prepared with phosphorus pentoxide in the vacuum chamber, but this proved to be rather a drawback than otherwise, because of the greater capacity for heat of the calorimeter introduced by the P_2O_5. It was essential to have the jacket very perfectly exhausted to avoid the heat-loss due to convection currents of air, which acted in such a way as to make the radiation loss appear large and uncertain. Small losses, however, from conduction and convection in the residual vapours in the jacket produced no errors on account of the steady temperature conditions during an experiment. The radiation loss would depend on the state of the glass surface, but would apparently be increased at the lower temperatures, after the calorimeter had been maintained for several hours during an experiment at one of the higher points. It was impossible always to count on the constancy of the heat-loss from one experiment to another, even with one calorimeter at the same temperature, as it depended so much on the past history. The change in heat-loss occasioned by the driving-off of occluded gases and vapours from the glass when the calorimeter was at a high temperature took place so slowly that, during an experiment extending over several hours, no measurable alteration in it could be noticed. This same effect of a slight change in heat-loss from time to time was also noted in the calorimeter used for the mercury experiments.

In fig. 9 is given a cross-section of the calorimeter and interior fittings in place, in the water-jacket. The thermometer bulbs are shown included in their glass cases. These cases were about 9 millims. in diameter, and extended the full length and a little beyond the ends of the outflow and inflow tubes. The ends of the thermometer cases over the bulbs were enclosed in thin copper cylinders, gold-plated, about 10 centims. long. These copper cylinders served the double purpose of preventing generation of heat in the vicinity of the thermometer bulbs by the electric heating current, and of helping to equalize the temperature of the water around the bulbs. The heating current was conveyed to the copper cylinders by eight No. 12 copper wires at each end, which were soldered into slits cut for them in the ends. The cylinders were made with closed ends, in one of which a hole was made for soldering in the platinum heating wire, and in the other a special screw clutch for catching the wire after the cylinders were put in place in the calorimeter. Sections of the cylinders are given in fig. 10.

The central heating wire for the fine-bore tube was made in three ways; either a central solid platinum wire about ·4 millims. in diameter, or six strands made up of 6-millim. platinum wire in parallel, or a flat wire twisted into a spiral down the fine tube. Of these the first proved to be the most satisfactory and gave the steadiest results when held central in a tube by a silk-covered rubber cord wound around it in spirals of about 1 centim. The stranded heating-wire, although excellent, was more difficult to handle, especially in putting the fittings of the calorimeter together. The flat wire did not require to have the rubber band wound around it, and it was of the full width of the tube. It was very difficult indeed to arrange the interior of the calorimeter when using this form of twisted heating-wire, as a small strain on the wire was almost sure to tear it apart. Moreover, in all experiments such as these, where water is heated by an electric current conveyed in a wire, the temperature of the wire is always above that of the water, so that as this form of wire touched the sides of the glass-tube the heat-loss was increased by the heating of the glass-tube at the points where it was in contact with the wire. Still, this arrangement gave excellent results for two calorimeters in which it was tried, and served as a satisfactory check on the results obtained by the other heating-wires. The solid heating-wire was finally adopted as offering the least mechanical difficulties.

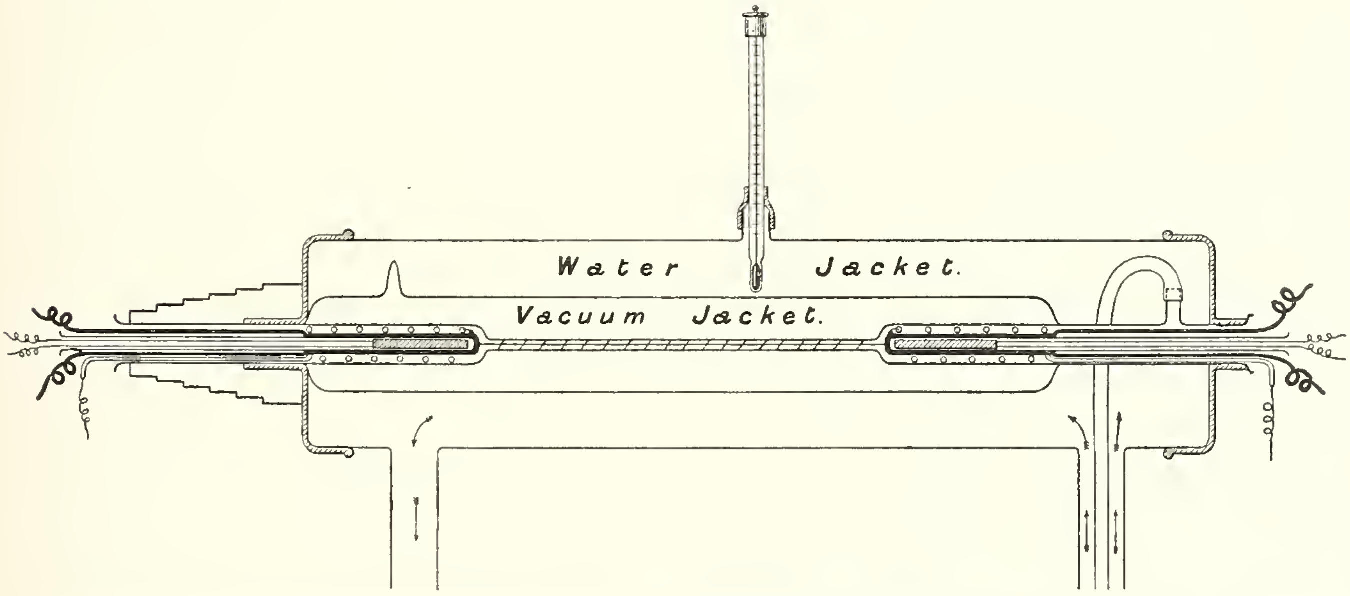

Fig. 9. Diagram of Continuous Flow Calorimeter.

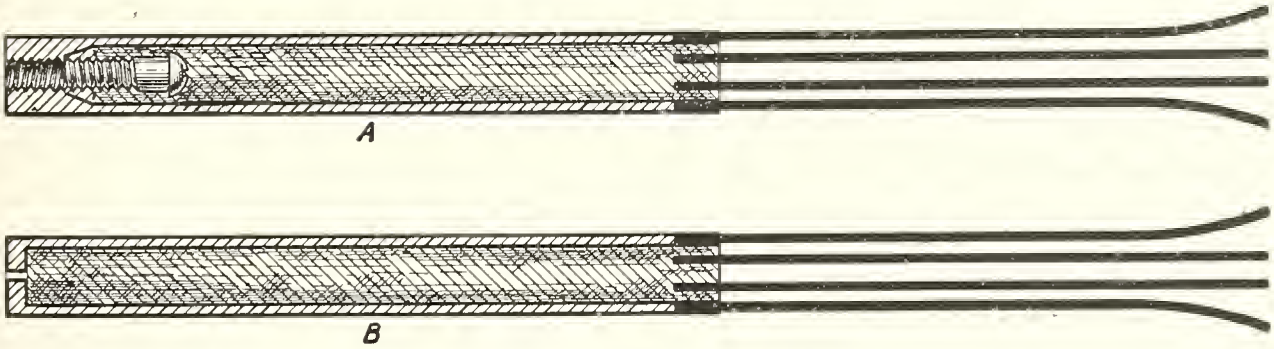

Fig. 10.

In fitting the copper cylinders into place, they were each wound with a small rubber tube, shown in section, in fig. 9. Through these rubber tubes on the two cylinders small copper wires were placed, and soldered to the ends near the heating-wire. These copper wires served both as potential terminals as well as a method of holding the rubber tubes in place on the copper cylinders. The rubber tube served three purposes; the holding of the cylinders central and firm, the stirring of the water as it flowed around the thermometer bulbs, and the insulation of the potential leads.

The platinum heating-wire was fused at one end to a copper wire of the same size, which was in turn soldered with pure tin into the hole in the end of cylinder B, fig. 10. The other end of the heating-wire was soldered with tin directly to three copper wires, which served to draw the platinum wire into place in the fine-bore tube.

When cylinder B, which was placed in the outflow end of the calorimeter, was shoved down into place as far as it would go, the heating-wire was about 3 centims. shorter than the fine tube at the further or inflow end. The three copper wires, which were attached to the heating-wire and protruded from the calorimeter tube, were pushed through slits cut for them between the copper screw and nut (shown in fig. 10) on cylinder A. These three wires could be drawn through readily with the screw only partly in place, and in this way by pulling the wires through, cylinder A was shoved down the calorimeter tube into its place in the inflow tube. When in place a screw-driver was inserted, and a jack to hold the cylinder from turning, and the copper screw turned into place. When it reached the part of the thread where the slits ended, the three wires were firmly gripped between the thread and screw. The copper screw was smoothed on the end so as not to cut through the wires, but simply to jamb them against the screw thread. When sufficiently firm a specially constructed cutter was introduced, and the wires cut off just at the head of the copper screw, this left the cylinder firmly attached to the heating-wire by the three copper wires. The glass-tubes for the differential thermometers were placed in the two ends of the calorimeter, and slid into the two cylinders prepared for them. The tubes were put in empty, as it was found better to introduce the thermometers themselves after the calorimeter was fitted up and in place in the water-jacket. The ends of the calorimeter were closed watertight by means of a rubber stopper placed on each glass thermometer tube near the end of the calorimeter tube. The eight copper wires at the ends were placed in slits prepared for them in the rubber stoppers together with the two rubber tubes containing the potential terminals. Rubber cement was then placed over the surface and allowed to dry. A strip of rubber sheet, also covered with rubber cement, was placed so as to surround each rubber stopper and a portion of the end of the calorimeter, and on being cemented together formed a sleeve. This rubber sleeve was then firmly wired in place around the rubber stopper and wires, and also around the calorimeter tube. The ingress for the water was by the glass side tube in the inflow end. The egress was by a glass-tube placed through a hole in the rubber stopper closing the outflow end.

The calorimeter was held in place in the water-jacket by heavy rubber caps specially made to withstand hot water. On the inflow end of the calorimeter the cap was placed at the end so as to include the whole length of tube in the water-jacket. On the outflow end the cap was drawn up to the vacuum-jacket. Side tubes, cemented into the rubber caps, served to hold them on the calorimeter. The calorimeter was shoved lengthwise through the water-jacket and the caps sprung into place over the ends.

The length of outflow tube protruding from the jacket was heavily lagged with flannel strips wound round it. As the outflowing water was made to flow the complete length of the outflow tube over the wires leading in the electric current, and as the tube itself was well protected from outside influences, the loss of heat from the water in the outflow tube was made as small as possible. This was shown very effectively by withdrawing the outflow thermometer, when the water was heated through about 8°, and determining the temperature at different points down the tube.

The glass-tube placed through the stopper closing the outflow end of the calorimeter was connected with a short rubber tube to the coil of tubing in the water cooler, which in turn was connected in a similar way to the switch-over device.

Water-jacket and Circulating System with Electro-thermal Regulator.—The water-jacket was an oval tube of $\frac{1}{32}$-inch copper, 2 ft. 9 in. long, with two lateral tubes 1 inch from each end on the under side. The jacket was 6 centims. wide and 8 centims. high. On the other narrow end of the oval two other lateral openings were made, one in the middle for a thermometer to obtain the temperature of the jacket water, and the other, which could be closed or opened at will, for an exit for accumulated air from the circulating water. The water in the jacket was circulated by means of a centrifugal pump run by a water-motor attached to the high-pressure mains in the laboratory. The water was drawn from the bottom of a large 10-gallon copper tank through the jacket to the pump, when it was thrown back again into the top of the tank. The whole system of circulating tubes formed a chain round which the water was constantly circulating. No water either left or entered the system, except that lost by evaporation, and that was exceedingly small except for the higher points. The circulating tubes were about 4 centims. in diameter, and the pumping was sufficient to supply a solid column of water from the tubes into the tank. The tank as well as the water-jacket and circulating tubes were all heavily lagged. For the higher temperatures a device was fixed to the tank to make up for the evaporation from the hot water, and to keep it always at the same level. This was most important, to prevent the exposure of part of the bulb of the thermo-regulator by the lowering of the water level in the tank.

In order to maintain the jacket at a constant temperature, a thermo-regulator was fitted up in the large tank, similar to the one described by GOUY ('Journ. de Physique,' vol. 6, p. 479, 1897). Fig. 11 contains a drawing of this regulator with its attachments. A bulb of glass A, containing about 300 cub. centims. of toluene resting on a mercury surface B, is connected to a fine heavy-walled tube about 1 millim. inside diameter, through which the mercury at B is made to pass by the expansion or contraction of the toluene. A three-way glass tap allows the mercury to pass either into the reservoir C, or up into the tube E. A platinum wire point is attached to a copper wire and drawn up and down about 4 millims. by a pivot on the wheel F, worked by a worm-wheel from the pulley C_1.

In this method, which is the distinctive feature of the Gouy regulator, the platinum point never sticks to the mercury surface, and consequently gives a sharper and more definite electrical connection between the thread of mercury in E and the wire. Connections were taken from this to a telegraphic relay, which was so arranged as to throw in and out a heating lamp placed in the tank. The arrangement is shown in fig. 12.

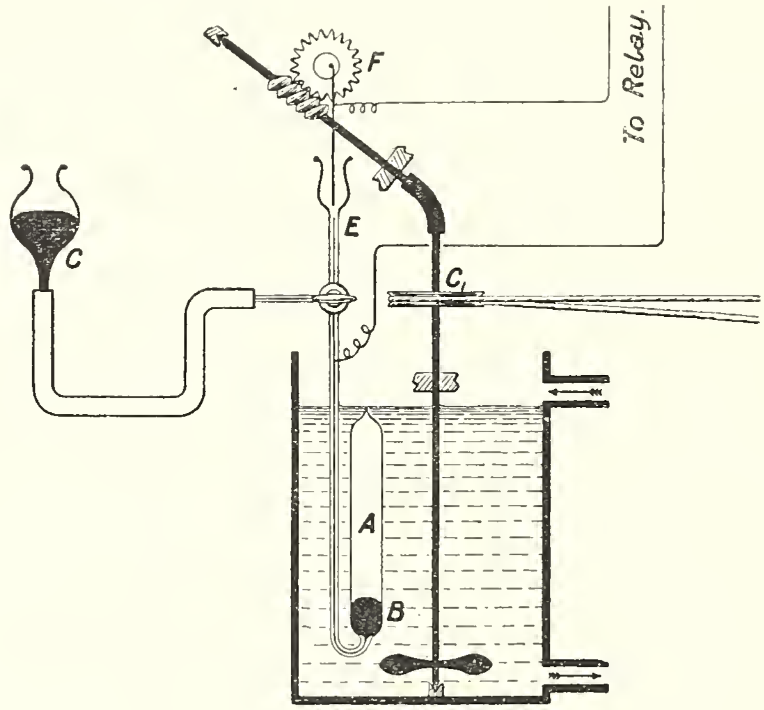

Fig. 11.

When the relay is inactive, the terminals of the lamp are short-circuited by the arm extending between the mercury cups *a* and *b*, and the full current is permitted to pass through the lamp B. When the relay is excited, the arm *ab* is raised and the circuit broken at *a*, so as to bring the lamps A and B in series. Lamp A was a 16-candle-power lamp of 200 ohms resistance, while B was either a 32-candle-power lamp of 100 ohms resistance, or a 50-candle-power lamp of about 60 ohms resistance. Either of the two heating lamps in series with lamp A was reduced in heating power over one-fourth of its full amount. The relay was made active by the closing of the connection between the wire and mercury column, and was supplied by either one or two accumulators. This form of regulator works exceedingly well, and is much to be recommended.

The electric heating lamp has practically no lag, so that the effect known as "hunting" was not apparent. The bulb of the regulator was long and narrow, and extended the whole height of the water in the tank. For high temperatures, lamp B could not supply enough heat to make up for the loss from the circulating system to the surrounding air, so that an auxiliary gas flame was necessary, which was placed under the centrifugal pump, and was supplied by a large constant-pressure gas regulator situated in the basement of the building. The final amount of heat necessary to keep the apparatus at the temperatures of the experiment required, was supplied by the lamp B, which thus acted as a fine adjustment over and above the heat supplied by the gas flame. For very high points it was necessary to maintain a second gas flame under the large copper tank, which was arranged on three brick supports for this purpose.

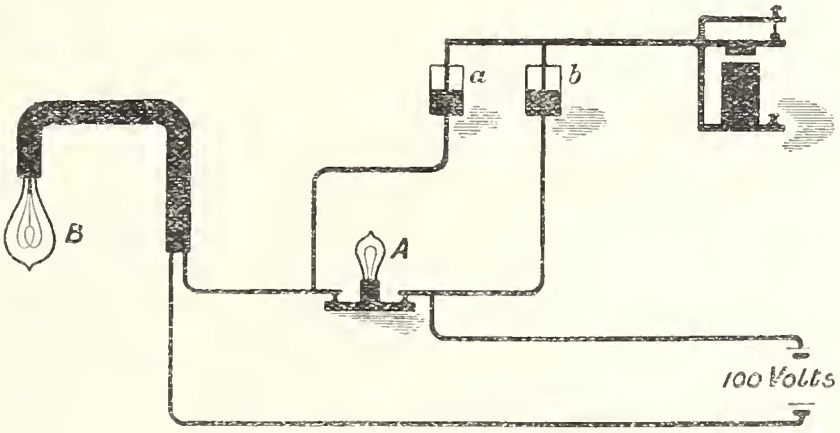

Fig. 12.

The water-motor which operated the pump in the circulating system ran at a very constant speed, on account of the very steady pressure of the water in the high-pressure mains. This aided very much in ensuring perfect regulation. Several stirrers in the apparatus were also operated by the water-motor from a pulley directly connected to it. One of the stirrers was placed in the tank and shown connected with the pulley C, in fig. 11. This helped to keep the water throughout the tank thoroughly mixed. It was connected to the pulley of the water-motor by a leather strap. Another cord was taken to the stirrer in the standardized resistance oil-bath, and a third to the stirrer in the cooler in the outflow end of the calorimeter shown in fig. 13. A general idea may be obtained of the arrangement of the apparatus by reference to fig. 13.

The accompanying photographs are added to give some idea of the appearance and arrangement of the apparatus. Fig. 14 is a side view, and fig. 15, a bird's-eye view, taken from the ceiling. Corresponding parts of the apparatus are indicated by the same letters in the two plates.

Fig. 14, is taken looking towards the slate slab along one side of the laboratory on which the greater part of the apparatus was arranged. The water-motor A, which supplied the driving power for the circulation and all the stirrers, is seen on the extreme right. B is the heater, containing a centrifugal pump driven direct from the motor, which delivers the water into the regulator tank C (fig. 14) through a large rubber hose. Behind the tank is the hypsometer T, which was employed for pre-heating the distilled water at the higher temperatures, and the water-bath P, containing the tube resistances for regulating the flow of the distilled water. The distilled water reservoirs were on the floor above. D is the ebonite box containing the standard resistances for current measurement immersed in oil with a stirrer driven by the central pulley (fig. 5). E is the copper water-jacket (fig. 11) containing the calorimeter, swathed in flannel, and connected by rubber hose on one side to the regulator tank C, and on the other to the circulating pump B. F is the switch-over tap (fig. 7) for delivering the flow into either of the two flasks G (fig. 8), and automatically recording the time of the switching over on the electric chronograph, the cylinder of which is marked Q in fig. 15. In the background of fig. 14, on the slate slab to the left are seen, H the Thomson-Varley slide-box, and K the 100,000-ohm galvanometer. Nearer the middle at M is the 20-ohm galvanometer for the platinum thermometers. These are all beyond the range of fig. 15. L is the zigzag platinoid rheostat for regulating the main current so as to obtain the desired rise of temperature in each case.

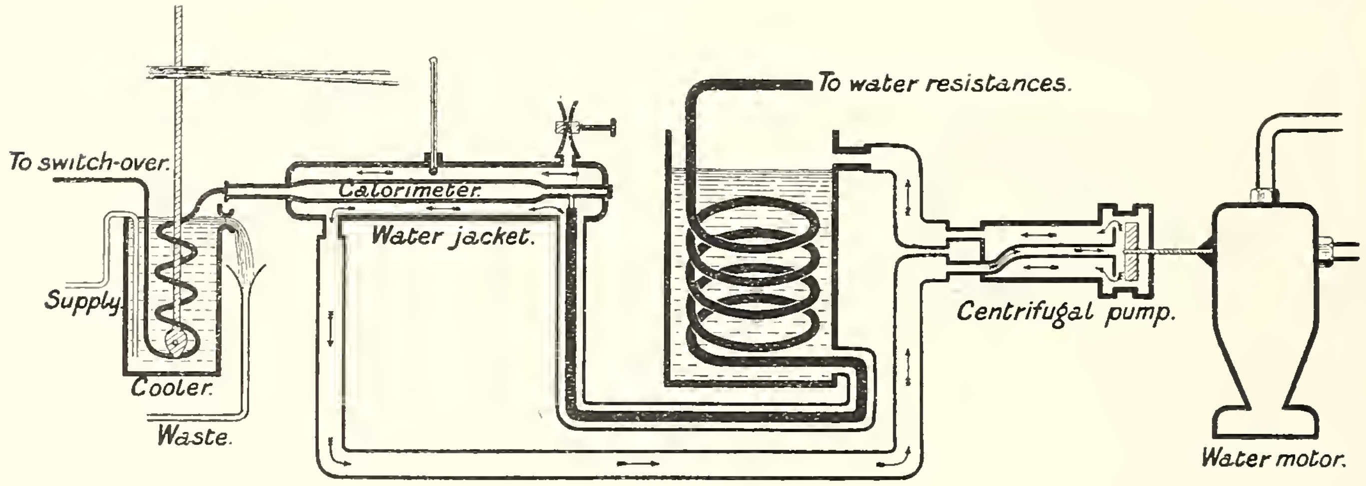

Fig. 13.

On the small table at the side in fig. 15 is seen the compensated resistance box R for the differential platinum thermometers, with small auxiliary boxes for current regulation. S is the rubber tube containing the leads to the heating lamp in the tank C. The relay, (fig. 14) worked by the regulator in the tank, and the shunt lamp are seen at Q in fig. 14, but are hidden by the jacket E in fig. 15. The Clark

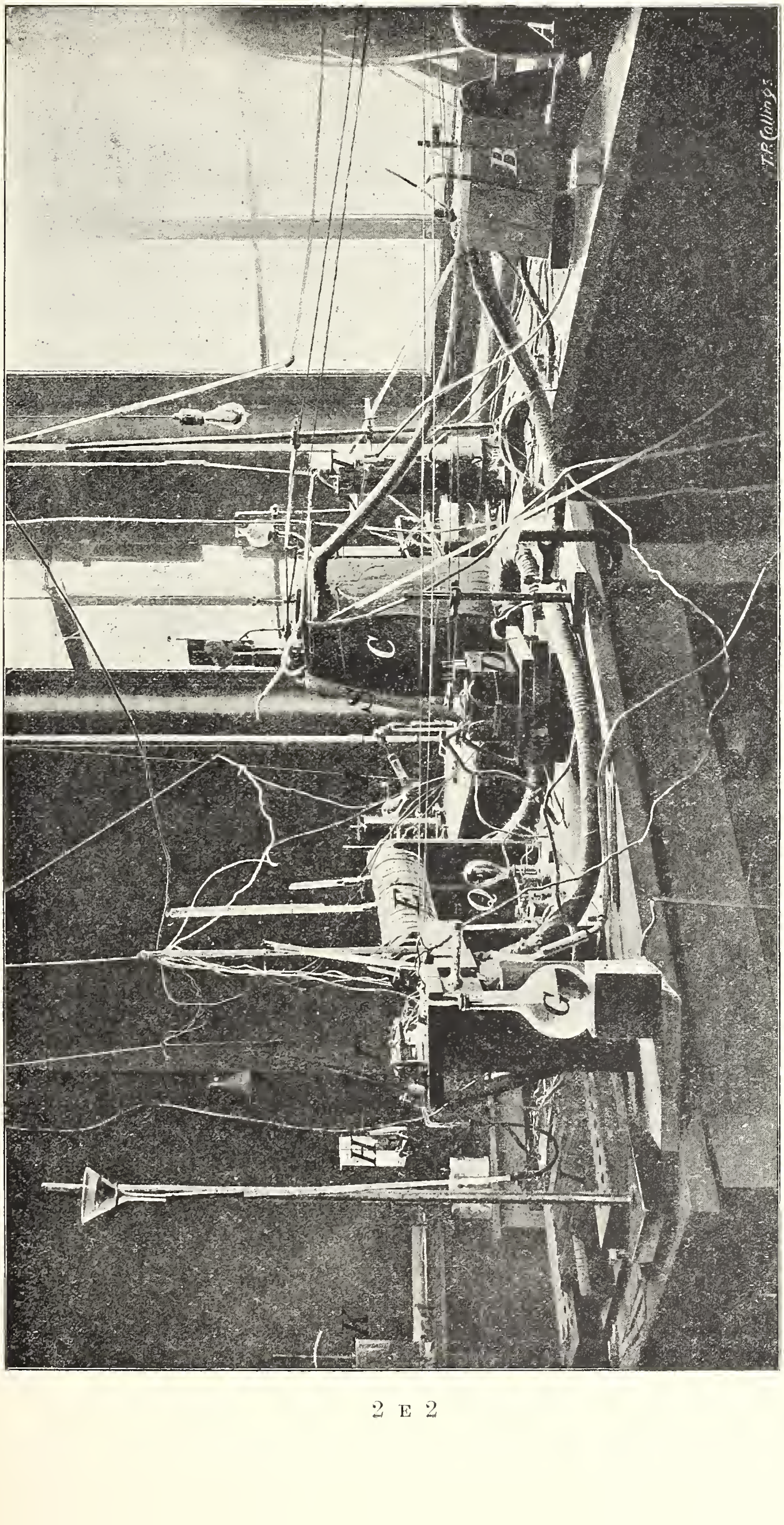

Fig. 14.

cell tanks and regulator are not shown in either view. They were at the other end of the laboratory.

Water Supply for Calorimeter.—The water supplied to the calorimeter passed through 40 feet of pure block-tin tube, $\frac{1}{4}$ inch in diameter, coiled up in the constant temperature tank. After passing through this and taking the temperature of the jacket water, it was passed from the tank to the water-jacket and into the calorimeter through a rubber tube placed inside the water circulating tube. By this means the water, after entering the tank, was entirely in the circulating system until it flowed out of the calorimeter. The head of water to maintain a steady flow was supplied from a reservoir placed on the floor above, and was connected to the apparatus by a glass-tube passed through a hole in the floor. In order to vary the supply, the water was passed through a series of fine tubes acting as resistances, which could be short-circuited by larger tubes connected across them. These larger tubes, offering no resistance, were thick-walled rubber tubes and connected to the ends of the fine tubes by T-pieces. When the water was to be passed through the fine tubes, the rubber tube was simply closed with a pinch-cock. The resistance tubes were two principal ones, 1 metre long and 1 millim. in section, and three lesser ones for fine adjustments. These were all immersed in a water-bath to keep them from changing in temperature suddenly, and thereby producing a change in the flow by changing the viscosity of the water.

No device was used to maintain a constant head, as a slight falling-off in the flow was rather an advantage than otherwise, as it tended to compensate for the slight falling-off in the electric current supplied to the calorimeter by the large accumulators. Two large bottles, holding about 4 gallons each, formed the head and were connected in parallel. A layer of heavy paraffin oil was put over the water to prevent absorption of air by the distilled water, which was always used for the experiments. This was supplied to the bottles in sufficient quantity for about two experiments, and was run in under the oil through a T-connection in the tube connecting the two bottles together and with the supply tube for the apparatus. The water was first boiled in a large copper tank, and while still boiling was siphoned over into the bottles. It was allowed to cool before being used for an experiment. This method of boiling the water was used for all the earlier experiments below 60° C.; but it was found impossible to obtain steady conditions of flow above this limit, owing to the liberation of air inside the calorimeter even from the boiled water. This was somewhat surprising and delayed the attainment of the final measurements at the high temperatures. It appears that to remove the last trace of air from boiled water, it is necessary to submit it to extreme agitation. Sufficient agitation was supplied to the water, as it ran through the fine-bore tube of the calorimeter, to set free some of the air retained by the boiling water when it was run into the bottles under the oil.

It was found necessary to devise some method of preparing absolutely air-free water before readings at the higher points could be obtained. To do this I found,

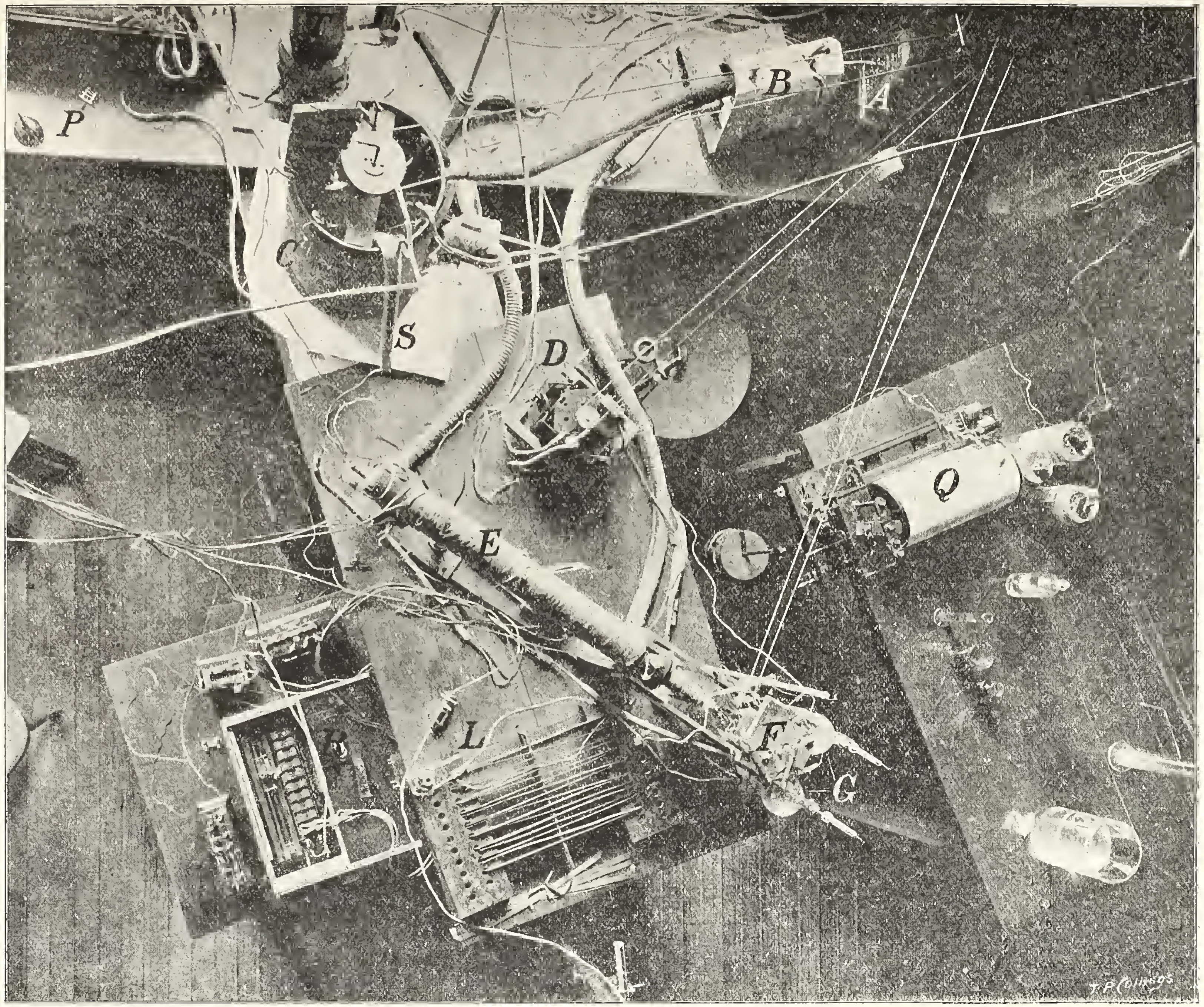

Fig. 15.

after repeated trials with other arrangements, that it was necessary, in order to separate the air from the water, to drive the latter into steam and condense it again in an air-free medium, and at the same time draw off the air before it had a chance to dissolve again. The method adopted finally was to exhaust the air over the oil in the two bottles by connecting with a water-pump while the boiling water from the copper tank was running in. In this way, by introducing a slight constriction in the siphon tube, such as a connection made from a small-bore rubber tube, the water in the tube separated into steam just past the constriction, and was condensed in the cold water already in the bottles from a previous filling. The air was at the same time sucked up through the oil and carried off by the pump. It was a matter of considerable surprise to see the amount of air thus drawn off.

After adopting this method of filling the bottles, there was no further trouble from air appearing inside the calorimeter, even as high as 90° C. When working at high temperatures, the distilled water, before it passed into the constant temperature tank, was passed through a spiral of tin tube in a steam-jacket. Instead of increasing the heat-loss of the circulating system by introducing cold water into the tank, a small quantity of heat was supplied by this means to the tank by the water flowing in from the steam-jacket. Moreover, the steam-jacket was a check on the state of the water, air bubbles being generated if the water was not perfectly air-free. The water which was run through the calorimeter was never used a second time, although it might just as well have been. Fresh distilled water was so easily prepared by means of a small water still in the laboratory that it was deemed unnecessary to use it twice.

A constant-level head was arranged near the apparatus to supply water for the cooler for the outflowing water; at the same time it also supplied the water circulation for the standardized resistance oil-bath, for the constant-level device of the tank, and for the condenser on the steam-jacket used at the higher temperatures.

Method of Making an Experiment.—Obviously various expedients were necessary in order to have the jacket maintained at a constant temperature at any point on the scale between 0° and 100° C. For the experiments near 0° C. the regulator was removed entirely from the tank, which was then filled with cracked ice and water. A wire sieve was placed over the stirrer in the bottom of the tank, so as not to have its action interfered with by the ice, as well as to prevent any ice from being drawn into the circulating tubes. Wonderfully steady conditions were produced in this way, and maintained without the variation of a hundredth of a degree for over an hour at a time. Between the measurements with each flow of water used, which lasted about an hour, the tank was replenished with ice. Not a great deal of ice was required for this replenishing, since only about one-quarter of the tank-full of ice was melted in the hour. From 50 to 60 lbs. of ice were melted during a complete experiment, although considerably more was used to cool the apparatus down to the ice-point before the experiment was started. From 100 to 150 lbs. of ice was generally required for a complete ice determination. It may be said, however, that these experiments were among the easiest to obtain.

At temperatures intermediate between the ice-point and room temperature, the regulator was used, and a stream of cold water run through a coil of metal tube placed in the tank. Water direct from the water mains usually sufficed for the cooler, but for lower temperatures the tap water was run first through a coil of tube immersed in a tank of ice. The desired temperature was attained through the equilibrium between the heat supplied by the lamp in the tank and the heat absorbed by the water flowing through the circulating tube. The tap water in the high-pressure mains varied, from about 5° in winter to about 18° in summer, in the laboratory where the apparatus was located. A temperature at least 2° lower than the desired temperature of regulation was required in the cooling water. The temperature of the laboratory varied from about 18° to 25° during the different seasons; but, in general, was steady to 1°, and often less during an experiment lasting 3 or 4 hours. When not using cooling water in the tank, the temperature of the apparatus had to be maintained a few degrees above the laboratory, so that the regulator could make up for the loss of heat to the surrounding air. Hence a temperature of about 26° or 27° in the tank was the most convenient point at which to work, which for an 8° rise in the calorimeter gave a mean temperature of about 30° C.

As the temperature of the jacket was increased more and more above the room temperature, more and more gas was required to aid the electric-heating lamp in maintaining a constant temperature. At a temperature of the jacket of about 90° C. two gas flames were required, and, in addition, the 50 c.-p. lamp. Even for the highest points the regulation proved to be most satisfactory, so long as the gas pressure did not vary. It was found that the high temperature experiments had to be taken at times when there was no other gas being used in the building, as even in using the large constant-pressure gas governor fluctuations in the gas pressure in the building caused perceptible alterations to the regulator. Where the fluctuations were small and regular, the jacket water seldom varied as much as ·01° during the time for obtaining the observations for each flow, even at the highest point attained. The wonderful efficiency of the regulator and circulating system, together with the preparation of air-free water, made it possible to obtain the observations at the higher temperatures with almost *the same degree of accuracy* as at the lower points.

At whatever temperature the jacket was maintained, and before the electric-heating current was turned on, the calorimeter water was allowed to flow through the apparatus for some time after the steady conditions were attained by the regulator. The balance-point so obtained for the differential thermometers we have already termed the "cold" readings, in contra-distinction to the readings obtained when the electric-heating current is turned on. The second balance-point, together with the requisite number of bridge resistance-coils required to compensate the rise in temperature in the water, we will term the "hot" reading. The conduction errors at the ends of the apparatus remained the same for both readings, except (as has already been pointed out) the conduction error due to the rise in temperature, $d\theta$, in the outflow end. It was therefore possible for any temperature over the scale between 0° and 100° to eliminate the conduction errors at the ends of the apparatus by the "cold" readings in a very simple manner, and reduce the only conduction error to be considered, *i.e.*, that due to the rise $d\theta$, to the *same amount all over the scale.* Unless this procedure had been followed, large errors would have been incurred, especially at the inflow end where the conduction effect was the largest.

The adjustment of the electric current to any given flow was made by varying the number of accumulators, or by inserting a number of platinoid strips, ·02 ohm, in series in the rheostat. While the conditions became steady in the calorimeter after turning on the electric current, requiring 10 to 15 minutes, the weights of the empty flasks were obtained as already described. One of these was then affixed to one of the nozzles on the calorimeter. The temperature of the cooler was then adjusted, and the preliminary readings of the potential difference across the standard resistance and calorimeter obtained. The chronograph being started, the accurate balance of the two Clark cells in series was obtained, together with the temperature of the Clark-cell bath. The other conditions remaining steady (including the thermo-regulator in the tank, the jacket circulation and the different water circulations to the resistance oil-bath, cooler, constant-level device and steam-jacket when used, as well as the thermo-regulation in the Clark-cell bath) the flow was switched over into the weighed flask at a given moment, which was recorded automatically on the chronograph. The complete set of observations then followed in order for 15 minutes. These, besides the temperature of the cooler at the beginning and end of the interval, were made every minute—first minute the deflection of the galvanometer at the nearest millimetre on the bridge-wire for the balance-point of the differential thermometers, then, in succession at every even minute, the potential balance of the standard resistance, the reading of the differential thermometers, potential across the calorimeter, reading of the thermometers, potential across standard resistance, and so on, including at the half-minutes the reading of temperature of standard-resistance oil-bath, jacket water, air temperature and temperature of thermometer resistance box, although this last was not really necessary.

At the end of the 15 minutes, to the nearest second by the watch used in starting the interval, the flow was switched over to the other nozzle, and the time automatically recorded. The balance-point of the Clark cells was then obtained, together with their temperature. On changing the full flask for a second empty one, a second set of readings for 15 minutes was obtained, without otherwise altering the conditions. The extreme steadiness of the potential balance for the Clark cells made it quite unnecessary to have it recorded oftener than just before and just after the 15-minute interval.

For each 15 minutes 8 readings in all were obtained of the differential thermometers, which were separated by 2 minutes each, the last one being taken just before switching over the flow, 3 readings of the potential across the calorimeter separated by 4 minutes, and 4 of the potential across the standard resistance also separated by 4 minutes. These readings were always corrected to the middle of the interval to correspond to the time of average flow. The thermometer readings sometimes increased and sometimes decreased during the interval, depending on the flow, but the change was never more than ·02° or ·03° over the 15 minutes, and generally much less. The question of the lag of the thermometers and of the thermal capacity of the calorimeter, which amount to such large corrections in all older calorimetric methods, was reduced therefore to a negligible quantity. The potential readings on the Thomson-Varley slide-box of the calorimeter and standard resistance generally fell off in a regular way throughout the interval, although quite often they remained steady altogether. The fall was seldom as much as 1 part in 1000 during the entire interval; hence a greater number of readings was unnecessary, since all the readings were taken at stated times, which were even minutes recorded from the seconds' hand of the watch used to start the flow over the interval.

In the earlier experiments, where two observers took the observations, simultaneous readings could be made of the temperature and potential difference every minute. This arrangement was of course preferable to the other, but where the conditions remained steady a large number of readings was really not necessary. When any sudden change in the conditions occurred, such as in the regulation, electric current or flow, so as to make the readings unsteady, these readings were either repeated during another interval where it was possible to restore the conditions in a short time, or they were abandoned altogether until such other time as the complete experiment could be repeated. My aim was, as far as possible, to produce a series of measurements, over the entire range of temperature between 0° and 100°, under as steady and uniform conditions as possible.

The number of flows usually taken in a complete experiment was two, but sometimes three. Other flows were tried to test the theory of the method beyond the limits of flow chosen for the actual experiments. In all the flows two intervals of 15 minutes were taken, which, when worked out, gave a complete check on the steadiness of the conditions and the accuracy of the observations.

None of these measurements depend very much on the absolute readings of mercury thermometers except the Clark cell. The temperature of the standard-resistance was always taken with the thermometer used in its calibration with the standard ohm, which in turn had such a small temperature coefficient that it made it of very little importance whether the thermometer used to obtain its temperature was in error by as much as ·5°. As a matter of fact, by direct comparison, all the thermometers used agreed with our standard thermometer to within ·1°. The thermometer used to obtain the temperature of the jacket-water between 0° and 50° C., was a new Müller graduated to ·1° and reading to $\frac{1}{100}$ths. Its error was determined by comparison with the standard thermometer, and its readings were found to be ·03° too large. The standard thermometer was a Geissler reading to $\frac{1}{100}$th between $-2°$ and 50° C., which has been in the possession of the laboratory for several years, as before stated. In 1896 both Professor CALLENDAR and I separately determined its error, and reduced its readings to the nitrogen scale over the entire range by comparison with a platinum thermometer. The error was very consistent, and showed its readings too high by ·11° to ·12° from 0° to 50°. This thermometer was used in the Clark-cell bath and has already been referred to in that section. For jacket-temperatures between 50° and 90° C., a second Müller thermometer, reading between 50° and 150°, was used, which was graduated to $\frac{1}{5}$th of a degree.

Specimen Tables of Observations.

[*Added April 20th*, 1901.—H.T.B. Owing to the necessity of condensing the tables since the communication of this paper, I have considered that it would be of advantage to give specimen tables of observations as recorded during a complete experiment. I have therefore included here two sets, made as typical as possible, which illustrate more clearly the remarkable steadiness of the conditions. The experiments selected are those given under date October 27, 1899, and March 10, 1900. They include two calorimeters and different-sized flow-tubes (Calorimeters C and E), as well as flat and round heating wires. One of the sets includes the observations taken for the measurement at the highest point of the range. In the first set box 1 was used, on the second set box 2. The order in which the readings were obtained has been described in Section 4. In all cases the time of taking the readings was as closely as possible on the even minute. The time for the start and finish of an interval, during which the flow was measured, is of course given, as recorded on the chronograph, to ·01 second. The reading of the contact point on the bridge-wire (b.-w.) is given in centims. (10 centims. = 1° C.), and the deflections of the galvanometer noted, it being accurately set to the nearest millimetre by means of the vernier reading to hundredths of a millimetre. The sensitiveness of the galvanometer remained very constant, but was repeatedly checked during a set of observations. The balance-point on the bridge-wire was calculated by interpolation from the observations of the deflection. In the electrical readings of the potential, S stands for the balance-point for the difference of potential across the standardized resistance, and P for the same across the calorimeter heating-wire. These readings are of course uncorrected for the errors in the Thomson-Varley slide coils. The temperature of S is that of the oil in which the standardized resistance was immersed, and the temperature of the Clark cells is here uncorrected for the thermometer error. The inflow temperature is the same as the temperature of the jacket. In some cases the air temperature was recorded just at the calorimeter, as well as the temperature of the balance case, but in general these never differed much from the temperature of the air as recorded on the barometer case, which was always taken with the reading of the barometer. The weights are given here in grammes, just as recorded during the experiment. The Abridged Tables sent in with the paper give the summary of these observations, together with the necessary corrections.]

[*Added May 28th*, 1902.—H.T.B. The comparative failure of my attempts to obtain consistent results in the experiments carried out previous to my discovery of the effect of stream-line motion on the distribution of heat in the fine bore flow-tube, appears to me to have been largely due to the fact that the stranded conductor was in nearly all cases annealed before being inserted in the calorimeter. This caused the different strands to lie together more in the nature of a solid conductor. It is probable that better results would have been obtained in these early experiments had the wires been stiffer, the flow-tube smaller, and had it been possible to distribute the strands more thoroughly in the water column, and at the same time to prevent them from changing their relative position in the tube between the experiments.]

SPECIMEN Table of Observations XXXVI. October 27, 1899. Calorimeter E (3 millims.). Flat Heating Wire. Mean Temperature, 29°·92.

Large flow.

Cold readings.

Time.	B.-W.	Deflec.
2·33	23 600	11 c.p.
34	,,	11 c.p.
35	23·700	25 s.a.
36	,,	24 s.a.
37	,,	24 s.a.
38	23 600	12 c.p.
39	,,	10 c.p.
40	23·700	25 s.a.
41	,,	25 s.a.
42	,,	26 s.a.
43	23·600	11 c.p.

Weights.

	First interval.	Second interval.
Flask (1) . .	99·379	—
,, (2) . .	—	120·793
,, (1) full	659·755	—
,, (2) ,,	—	680·500

Barometer . . 76·57
Temperature . 18·2

Temperature balance case not taken.

4·4 Electric heating current on.

3·04·00·42 Start. Pot. bal. C.C. 63004. Box coil 80.

05	22·100	11 s.a.					
06			Pot. bal.	S.	70251	Temp. C.C.	. 16·14
07	,,	15 s.a.				,, inflow	25·74
08			,,	P.	76282		
09	,,	19 s.a.				,, air	. 18·8
10			,,	S.	70246		
11	,,	19 s.a.				,, S. .	. 14·0
12			,,	P.	76277		
13	,,	21 s.a.					
14			,,	S.	70241		
15	,,	21 s.a.					
16			,,	P.	76274		
17	,,	23 s.a.				,, S. .	. 14·0
18			,,	S.	70238		
18·30	,,	30 s.a.					

3·19·00·12 Flow switched over.

3·22·00·29 Start. Pot. bal. C.C. 63004. Second interval.

23	22·000	Bal.					
24			Pot. bal.	S.	70230	Temp. C.C.	. 16·13
25	,,	1 s.a.				,, inflow	25·75
26			,,	P.	76263		
27	,,	5 s.a.				,, air	. 19·0
28			,,	S.	70227		
29	,,	8 s.a.				,, S. .	. 14·0
30			,,	P.	76262		
31	,,	9 s.a.					
32			,,	S.	70224		
33	,,	14 s.a.					
34			,,	P.	76257		
35	,,	22 s.a.				,, S. .	. 14·0
36			,,	S.	70219		
36·30	,,	29 s.a.					

3·37 00·16 Flow switched over.
Pot. bal. C.C. 63003 Temp. C.C. . 16·13

Small flow.

Cold readings.

Time.	B.-W.	Deflec.
3·55	23·600	8 c.p.
56	,,	8 c.p.
57	,,	8 c.p.
58	23·700	29 s.a.
59	23·600	8 c.p.
4·00	,,	8 c.p.
01	,,	8 c.p.

Weights.

	First interval.	Second interval.
Flask (1) . .	99 162	—
,, (2) . .	—	120·255
,, (1) full	444·392	—
,, (2) ,,	—	464·695

Barometer . . 76·57
Temperature . 18·2

Temperature balance case not taken.

4·02 Electric heating current on.

4·19·00·62 Start. Pot. bal. C.C. 62998. Box coil 80.

20	22·000	2 s.a.					
21			Pot. bal.	S.	55596	Temp. C.C.	. 16·14
22	,,	3 c.p.				,, inflow	25·75
23			,,	P.	60235		
24	,,	4 c.p.				,, air	. 18·8
25			,,	S.	55591		
26	,,	6 c.p.				,, S. .	. 13·5
27			,,	P.	60231		
28	,,	5 c.p.					
29			,,	S.	55589		
30	,,	4 c.p.					
31			,,	P.	60227		
32	,,	4 c.p.				,, S. .	. 13·5
33			,,	S.	55586		
33·30	,,	3 c.p.					

4·34·00·12 Flow switched over.

4·59·01·05 Start. Pot. bal. C.C. 62997. Second interval.

5·00	21·900	4 c.p.					
01			Pot. bal.	S.	55571	Temp. C.C.	. 16·14
02	,,	Bal.				,, inflow	25·75
03			,,	P.	60211		
04	,,	1 c.p.				,, air	. 19·3
05			,,	S.	55570		
06	,,	2 s.a.				,, S. .	. 13·5
07			,,	P.	60208		
08	,,	2 s.a.					
09			,,	S.	55567		
10	,,	5 s.a.					
11			,,	P.	60206		
12	,,	9 s.a.					
13			,,	S.	55567		
13·30	,,	13 s.a.					

5·14·00·59 Flow switched over.
Pot. bal. C.C. 62996 Temp. C.C. . 16·13

SPECIMEN Table of Observations LIII. March 10, 1900. Calorimeter C. Solid Heating Wire. Mean Temperature 91°·55.

Large flow.

Cold readings.

Time.	B.-W.	Deflec.
3·08	22·600	2 c.p.
09	,,	7 c.p.
10	,,	7 c.p.
11	22·700	29 s.a.
12	,,	28 s.a.
13	22·600	7 c.p.

Weights.

	First interval.	Second interval.
Flask (1) . .	97·683	—
,, (2) . .	—	121·207
,, (1) full	678·004	—
,, (2) ,,	—	699·584

Barometer . . 75·77
Temperature . 22·0

Temperature of balance case taken as that of air.

3·14 Electric heating current on.

3·38·00·30 Start. Pot. bal. C.C. 63562. Box coil 80.

39	29·200	Bal.					
40			Pot. bal.	S.	74004	Temp. C.C.	. 15·27
41	,,	20 s.a.				,,	inflow 87·42
42			,,	P.	76674		
43	,,	8 s.a.				,,	S. . . 7·0
44			,,	S.	73990		
45	,,	9 s.a.					
46			,,	P.	76658		
47	,,	20 s.a.					
48			,,	S.	73976		
49	,,	Bal.					
50			,,	P.	76647		
51	,,	24 s.a.				,,	S. . . 7·0
52			,,	S.	73965		
52·30	,,	25 s.a.					

3·53·00·69 Flow switched over.

3·56·00·82 Start. Pot. bal. C.C. 63562. Second interval.

57	29·100	3 s.a.					
58			Pot. bal.	S.	73949	Temp. C.C.	. —
59	,,	10 s.a.				,,	inflow 87·41
4·00			,,	P.	76621		
01	,,	21 s.a.				,,	S. . . 7·0
02			,,	S.	73939		
03	29·000	10 c.p.					
04			,,	P.	76613		
05	,,	1 s.a.					
06			,,	S.	73930		
07	,,	8 c.p.					
08			,,	P.	76605		
09	,,	Bal.				,,	S. . . 7·0
10			,,	S.	73921		
10·30	,,	5 s.a.					

4·11·01 30 Flow switched over.
Pot. bal. C.C. 63561 Temp. C C. . 15·24

Small flow.

Cold readings.

Time.	B.-W.	Deflec.
5·23	22·400	10 c.p.
24	,,	12 s.a.
25	,,	44 s.a.
26	,,	40 s.a.
27	,,	38 s.a.
28	22·300	5 c.p.
29	,,	3 s.a.
30	,,	9 s.a.
31	,,	6 s.a.
32	,,	5 c.p.
33	,,	2 c.p.
34	,,	Bal.
35	,,	1 s.a.
36	,,	4 s.a.
37	,,	5 c.p.

Weights.

	First interval.	Second interval.
Flask (1) . .	97·538	—
,, (2) . .	—	121·034
,, (1) full	459·847	—
,, (2) ,,	—	481·545

Barometer . . 75·77
Temperature . 22·0

5·38 Electric heating current on.

6·09·00 45 Start. Pot. bal. C.C. 63557. Box coil 80.

10	28·600	16 c.p.					
11			Pot. bal.	S.	59290	Temp. C.C.	. 15·24
12	,,	10 s.a.				,,	inflow 87·43
13			,,	P.	61350		
14	,,	12 s.a.				,,	S. . . 6·6
15			,,	S.	59287		
16	,,	29 s.a.					
17			,,	P.	61347		
18	28·500	11 s.a.					
19			,,	S.	59283		
20	,,	13 s.a.					
21			,,	P.	61343		
22	28·400	15 s.a.				,,	S. . . 6·6
23			,,	S.	59281		
23·30	,,	46 s.a.					

6·24·00·40 Flow switched over.

6·27·00·42 Start. Pot. bal. C.C. 63557. Second interval.

28	28·200	7 c.p.					
29			Pot. bal.	S.	59277	Temp. C.C.	. 15·22
30	28·100	14 c.p.				,,	inflow 87·43
31			,,	P.	61338		
32	,,	14 c.p.				,,	S. . . 6·6
33			,,	S.	59274		
34	,,	21 c.p.					
35			,,	P.	61336		
36	,,	11 c.p.					
37			,,	S.	59272		
38	,,	6 c.p.					
39			,,	P.	61334		
40	,,	10 s.a.				,,	S. . . 6·6
41			,,	S.	59270		
41·30	,,	22 s.a.					

6·42·01·12 Flow switched over.
Pot. bal. C.C. 63557 Temp. C.C. . 15·20

Abridged Tables Showing Method of Correction.

To illustrate the method of correction and calculation of results, we here append the corresponding Abridged Tables giving the correction and reduction of the means of the observations taken during each interval for the two specimen tables of observations already given. As it would have been impracticable to place on record the complete observations for the whole work, the abridged tables only were sent in with the paper. The greater part of these tables consisting of small corrections of no intrinsic interest, it was felt to be unnecessary to reproduce them in full. They have been preserved in the Archives so as to be available for reference and verification if required. The samples here given will sufficiently illustrate the nature of the information they contain.

Abridged Table XXXVI., Series 5. Inflow Temperature, 25°·75. Mean Temperature, 29°·92. October 27th, 1899.

Calorimeter E.

ELECTRICAL.	First interval.	Second interval.
Potentiometer reading corrected—		
Clark cell	63000	63000
Resistance S.	70241	70222
Calorimeter P.	76275	76259
Temperature of C.C.	16·02	16·01
Temperature of S.	13·9	13·9
Value of C.C.	1·43291	1·43292
Value of S.	·49977	·49977
Jac. temperature	25·74	25·75

RISE OF TEMPERATURE.	First interval.	Second interval.
"Cold" read	23·630	—
"Hot" read	22·046	21·970
B.W. in 10-units	+ ·1584	+ ·1660
B.W. correction	+ 11	+ 11
Box coils	80	80
Coil correction	− 40	− 40
Correction to F.I.	+ ·2228	+ ·2231
Correction to air thermometer	− 502	− 502
Rise of temperature	8·3281	8·3360

WEIGHT.	First interval.	Second interval.
Weight in air	560·376	559·707
Weight in vacuum	560·959	560·290
Cooler correction	—	—
TIME.		
Interval on chronograph	899·70	899·87
Corrected for rate of clock	900·00	900·17
Flow per second	·623288	·622427

ELECTRICAL.	First interval.	Second interval.
Potentiometer reading corrected—		
Clark cell	62994	62993
Resistance S.	55585	55564
Calorimeter P.	60226	60203
Temperature of C.C.	16·02	16·02
Temperature of S.	13·4	13·4
Value of C.C.	1·43291	1·43291
Value of S.	·49971	·49971
Jac. temperature	25·75	25·75

RISE OF TEMPERATURE.	First interval.	Second interval.
"Cold" read	23·622	—
"Hot" read	22·011	21·889
B.W. in 10-units	+ ·1611	+ ·1733
B.W. correction	+ 11	+ 12
Box coils	80	80
Coil correction	− 40	− 40
Correction to F.I.	+ ·2230	+ ·2233
Correction to air thermometer	− 502	− 502
Rise of temperature	8·3310	8·3436

WEIGHT.	First interval.	Second interval.
Weight in air	345·230	344·440
Weight in vacuum	345·589	344·798
Cooler correction	—	—
TIME.		
Interval on chronograph	899·50	899·54
Corrected for rate of clock	899·80	899·84
Flow per second	·384073	·383177

	EC	4·2 Q$d\theta$	Diff.	$\frac{\text{Diff.}}{d\theta}$	
LARGE FLOW	22·1831	21·8013	·3818	·04584	d = − ·00542
	22·1727	21·7919	·3806	·04566	h = + ·05994
SMALL FLOW	13·8652	13·4387	·4265	·05119	
	13·8551	13·4377	·4274	·05122	J = 4·1772

Abridged Table LIII., Series 8. Inflow Temperature, 87°·42. Mean Temperature, 91°·55. March 10, 1900.
Calorimeter C.

Electrical.	First interval.	Second interval.
Potentiometer reading corrected—		
Clark cell	63558	63558
Resistance S.	73982	73932
Calorimeter P.	76658	76610
Temperature of C.C.	15·15	15·12
Temperature of S.	6·9	6·9
Value of C.C.	1·43395	1·43399
Value of S.	·49890	·49890
Jac. temperature	87·42	87·41

Rise of Temperature.	First interval.	Second interval.
"Cold" read	22·620	---
"Hot" read	29·163	29·029
B.W. in 10-units	– ·6543	– ·6409
B.W. correction	– 39	– 38
Box coils	80	80
Coil correction	+210	+210
Correction to F.I.	+ ·7708	+ ·7722
Correction to air thermometer	+1025	+1028
Rise of temperature	8·2361	8·2513

Weight.	First interval.	Second interval.
Weight in air	580·321	578·377
Weight in vacuum	580·924	578·977
Cooler correction	—	—
Time.		
Interval on chronograph	900·39	900·48
Corrected for rate of clock	900·55	900·64
Flow per second	·645077	·642851

Electrical.	First interval.	Second interval.
Potentiometer reading corrected—		
Clark cell	63553	63553
Resistance S.	59280	59268
Calorimeter P.	61342	61331
Temperature of C.C.	15·11	15·09
Temperature of S.	6·5	6·5
Value of C.C.	1·43400	1·43402
Value of S.	·49885	·49885
Jac. temperature	87·43	87·43

Rise of Temperature.	First interval.	Second interval.
"Cold" read	22·300	—
"Hot" read	28·482	28·127
B.W. in 10-units	– ·6182	– ·5827
B.W. correction	– 37	– 35
Box coils	80	80
Coil correction	+210	+210
Correction to F.I.	+ ·7746	+ ·7783
Correction to air thermometer	+1031	+1037
Rise of temperature	8·2768	8·3168

Weight.	First interval.	Second interval.
Weight in air	362·309	360·811
Weight in vacuum	362·685	361·186
Cooler correction	—	—
Time.		
Interval on chronograph	899·95	900·70
Corrected for rate of clock	900·11	900·86
Flow per second	·402934	·400935

Large Flow	EC	23·1450	4·2 $Qd\theta$	22·3142	Diff.	·8308	Diff. $d\theta$	·10088	d =	+ ·00042
		23·1161		22·2783		·8378		·10155	h =	+ ·10011
Small Flow		14·8450		14·0069		·8381		·10130	J =	4·2017
		14·8398		14·0049		·8349		·10030		

Sec. 5.—*Experimental Proof of the Theory of the Method.*

In Section 2 it was shown that the conditions to be studied in the general difference equation of the method were the relations of the heat-loss to the rise of temperature and to the flow. In the present section I wish to summarize the different experiments which have a more particular bearing on the theory of the method. In the first place in regard to the question, which arises in all experiments where a quantity of water is heated by an electric current conveyed in a wire, of the excess temperature of the wire over the water, it may be said that in the present method the measurement of the electrical energy is completely independent of any value to be assumed for the resistance of the heating-wire, and not only that, but owing to the steady temperature conditions inside the apparatus, no uncertainty of a change in resistance in the wire with a change in temperature is introduced. When the temperature inside the calorimeter has arrived at a steady state, only such energy is used in warming the water as is supplied to the calorimeter by the electric-heating current. The fact that the results were completely independent of the resistance of the heating-wire was shown by using heat-wires of very different resistances.

In regard to the insulation of the platinum heating-wire and of polarization and similar effects, it was considered that these played no part in the results. The resistance of the water column through which the heating-wire passed was enormously high and equal to a column of water 50 centims. long and 2 millims. in diameter, hence in comparison with the resistance of the central heating-wire, which varied from ·4 to ·8 ohm, was quite negligible. This is true even if it is admitted that the conveyance of the electric current by the water itself could have produced any error on the final result.

Polarization by the naked wire in the water, I am satisfied, did not take place. Not the slightest trace of gas was ever generated in the calorimeter which could not be referred to the liberation of air in the water, and this was verified by watching the column of water in the fine tube when the calorimeter was removed from the water-jacket and a large electric current passed through. The effect of reversing the electric current in the apparatus, and making it flow either with or against the water flow, was tried in some of the earlier experiments, but it was found to produce no effect on the heat-loss as measured by the difference between the electrical and thermal measurements. The effect, if any, on the electrical readings was entirely negligible.

The first experiments which were tried to test the method, were on the relation of the heat-loss to the flow, and were made by varying the flow over a wide range and at the same time keeping the inflow temperature and rise of temperature constant.

The following list of calorimeters, used in the present work, will aid in describing these and subsequent experiments :—

Calorimeter A.—The first one of the set of three obtained from Germany, with the fine-bore tube 2 millims. in diameter. This was the first one tried in the trial experiments in 1897.

Calorimeter B.—Second of the same set, with same dimensions, and used in the preliminary measurements of the mechanical equivalent.

Calorimeter C.—This was the first one made by EIMER and AMEND, after the later design. It had a 2 millims.-bore tube, and has been used for the greater number of the later experiments.

Calorimeter D.—The second E and A calorimeter, with the fine-bore tube 2·8 millims inside diameter and P_2O_5 in the vacuum chamber.

Calorimeter E.—The third from E and A, with the fine-bore tube 3 millims. inside diameter.

The results of the experiments made to determine the relation of the heat-loss to the flow, are now given. They have been taken from the experiments detailed in Tables I., II., III., and IV. in Section 8. The results are taken from the observations on two calorimeters with fine-bore flow-tubes of different sizes, the heating wire in the two cases being made up of either the six strands of ·15-millim. platinum wire or the solid wire, and held central by the silk-covered rubber elastic wound round it. The water was therefore completely stirred in its passage through both the tubes, and stream-line motion avoided.

For convenience in showing the relationship I have expressed the difference between the electrical and heat watts by using the value of J obtained from the experiment for two flows in place of 4·2 joules. In this case the value of the heat-loss per degree rise should come constant for all of the flows as long as the conduction effect is negligible.

The first set comprises observations made with Calorimeter D at a mean temperature of 28° C. The flow was varied from ·67 gramme per second to ·25, and the rise of temperature was kept approximately the same by adjusting the electric heating current.

CALORIMETER D.—Mean Temperature, 28°·01 C. February 15, 1899.
$\delta = -\cdot 00485.$ $J = 4\cdot 1797.$

$d\theta$.	Q.	$(EC - JQ\,d\theta)/d\theta$.	Difference from mean, ·07128.
7·5234	·674106	·07122	− ·00006
7·8882	·496655	·07147	+ ·00019
7·7745	·399290	·07130	+ ·00002
7·9463	·390196	.07113	− ·00015
8 0033	·248234	·07197	+ ·00069

It will be seen that over the range of flow from ·67 gramme to ·39, the value of the heat-loss remains constant to within the limits of error of the different measurements, and gives a mean value of ·07128 in watt-seconds per degree rise. The largest variation from the mean is for a flow of ·49 gramme per second, and amounts to ·00019 watt on a total supply of 2·1 watts per degree, which is less than 1 in 10,000. For the small flow, the difference from the mean of the other flows amounts to ·00069 watt on 1·1 watts. This shows an increase in the heat-loss of nearly 7 parts in 10,000, and is *much too large* to be included within the limits of error. It is evident, then, that for flows below ·3 gramme per second, the conduction effect commences to be measurable, and cannot be eliminated by the method of "cold" readings.

For Calorimeter C, the measurements for the different flows are given under date February 20, 1899. These are for double intervals of 15 minutes each, and include the same limits of flow as for Calorimeter D. I have taken $\delta = \cdot00490$, instead of $- \cdot00469$ as given from these measurements, so as to give results comparable with the other sets of observations made at about this time.

CALORIMETER C.—Mean Temperature, 29°·09 C. February 20, 1899.
$\delta = \cdot00490$. $J = 4\cdot1794$.

$d\theta$.	Q.	$(EC - JQ\,d\theta)/d\theta$.	Difference from mean, ·04997.
8·2608	·398498	·04972	− ·00025
8·2560	·398540	·04988	− ·00009
8·2199	·501957	·05016	+ ·00019
8·2301	·501026	·04998	+ ·00001
7·9646	·666042	·05009	+ ·00012
7·9775	·664388	·04999	+ ·00002
8·2281	·258114	·05057	+ ·00060
8·2284	·257947	·05070	+ ·00073

The largest variation from the mean value of the heat-loss is −·00025 watt, and amounts to a little more than 1 in 10,000. For the small flow, the divergence from the mean of the other flows amount to ·00067 watt, and shows that the heat-loss has been increased, which agrees very closely with the result obtained for Calorimeter D. The agreement of the results for the two calorimeters, the one with a 3-millim. bore tube and the other with a 2-millim., seems to prove fairly conclusively that the increase in the heat-loss taking place below a certain limit of flow, cannot be attributed to a change in the radiation loss from the fine bore tube, but can only be referred to conduction from the outflow tube, which was the same size in both calorimeters.

The observations under February 22 and March 2 were taken with Calorimeter C, using the limits of flow which I have since adopted for the present measurements.

CALORIMETER C.—Mean Temperature, 29°·11 C. February 22, 1899.
δ = ·00490. J = 4·1794.

$d\theta$.	Q.	$(EC - JQ\,d\theta)/d\theta$.	Difference from mean, ·04938.
8·2680	·392606	·04939	+ ·00001
8·2635	·392663	·04937	− ·00001
8·1938	·496708	·04928	− ·00010
8·1844	·496591	·04946	+ ·00008
7·9031	·660865	·04945	+ ·00007
7·9083	·658741	·04932	− ·00006

CALORIMETER C.—Mean Temperature, 29°·21 C. March 2, 1899.
δ = − ·00499. J = 4·1790.

$d\theta$.	Q.	$(EC - JQ\,d\theta)/d\theta$.	Difference from mean, ·04968.
8·4310	·375154	·04963	− ·00005
8·4304	·375076	·04967	− ·00001
8·3979	·472489	·04967	− ·00001
8·4060	·471670	·04986	+ ·00018
8·3390	·590477	·04960	− ·00008
8·3439	·589356	·04969	+ ·00001

The agreement of the heat-loss is very satisfactory, and the variations from the mean value are easily within the limits of error of all the measurements, and are all less than 1 part in 10,000.

The three sets of readings for Calorimeter C show a small difference between the values of the mean heat-loss. This shows, as has been pointed out, that the absolute value of the radiation loss for one calorimeter cannot be relied on from time to time, but will vary, for many reasons. However, this never produced any error in the measurements of the specific heat of the water, on account of the method adopted of always eliminating the heat-loss from at least two different flows taken within a short time of each other, between which the temperature of the calorimeter never varied.

In selecting the limits of flow to be used in all the measurements, the accuracy of the limits was tested for two other temperatures by recording observations for three different flows at 13° and at 60° C. In these cases the theory of the method was given a severe test.

I have tabulated here the two sets, one for a mean temperature of 13° C. and the other for a temperature of 60° C. I have taken the values of δ for each set from the variation curve.

Calorimeter C.—Mean Temperature, 13°·79 C. March 9, 1899.
$\delta = - \cdot 00208$. $J = 4\cdot 1913$.
Temperature of surrounding air, 19° C.

$d\theta$.	Q.	$(EC - 4\cdot 2\, Q\, d\theta)/d\theta$.	Difference from mean, ·03940.
8·5768	·372746	·03946	+ ·00006
8·5803	·372262	·03947	– ·00007
8·5586	·459149	·03923	– ·00017
8·5683	·458194	·03930	– ·00010
8·5499	·573318	·03953	+ ·00013
8·5616	·571920	·03940	·00000

Calorimeter C.—Mean Temperature, 59°·80 C. June 17, 1899.
$\delta = - \cdot 00360$. $J = 4\cdot 1849$.
Temperature of surrounding air, 22° C.

$d\theta$.	Q.	$(EC - JQ\, d\theta)/d\theta$.	Difference from mean, ·07254.
8·3805	·612400	·07277	+ ·00023
8·3835	·611227	·07263	+ ·00009
8·3158	·462971	·07236	– ·00018
8·3395	·461364	·07240	– ·00014
8·3534	·388491	·07261	+ ·00007
8·3674	·387534	·07242	– ·00012

The variation from the mean value in both sets is less than 1 part in 10,000. It is a matter of interest to compare the balance points on the bridge-wire for the "cold" readings of the differential thermometers, when in place in the calorimeter, for the different flows at different parts of the scale.

The three "cold" readings at 60° are, for the largest flow 23·681, for the next 23·582, and for the lowest 23·544. A decrease in the bridge-wire reading means that the inflow thermometer is at a lower temperature than the outflow. The heat conduction at the inflow end, through the copper wires leading in the electric current, which depends only on the difference existing between the temperature of the calorimeter water and the temperature of the laboratory, can affect the temperature of the inflowing water less for the largest flow than for the smallest flow, and therefore explains the difference in the "cold" readings for the different flows. For the flows used in the present work, the effect of the conduction at the outflow end on the temperature, as indicated by the outflow thermometer, must have been very small indeed, even at the highest points of the range. All of the "cold" readings at the high points are slightly less than the interpolated reading from the differential ice and steam-points. For the "cold" readings at the ice-point, the effect was, as might be expected, reversed, and conduction of heat into the calorimeter from the laboratory took place.

The readings given in Table XLIV., on November 18, 1899, are—

For a flow of ·59 gramme	23·330
,, ,, ·39 ,, ...	23·392

on November 22, 1899, Table XLV.—

For a flow of ·62 gramme	23·329
,, ,, ·37 ,, ...	23·398

The peculiar exception to this seems to be in the experiment made at the ice-point on March 24, 1899 (Table XV.), when the "cold" reading for the small flow was lower than for the high. I have not an exact record of the conditions under which this experiment was taken, but it is possible that the outflow end may not have been properly lagged, which would produce the effect indicated by the readings. As the observations, when reduced, give such a consistent measurement of the specific heat, even in the face of this apparent exception, additional evidence is given of the necessity of the "cold" readings to render the results independent of extraneous conditions. The "cold" readings for experiments with the jacket water at the temperature of the laboratory were, as a rule, all at the same point on the bridge-wire, and identical with the interpolated reading from the differential ice and steam-points.

The radiation loss increases only very slightly as the temperatures of the calorimeter and jacket are raised, and this is of course on account of the temperature of the calorimeter flow-tube being always the same amount above the jacket water at all points of the scale (when the water is heated by the electric current). The increase is from the temperature coefficient of the radiation, and appears to be almost exactly linear over the range 0° to 100°.

To show the relation between the heat-loss and the rise of temperature, I have summarized the observations in Tables XXXIII., XXXIV., XXXV., for rises of 8°, 5°, and 2° respectively. These were made with Calorimeter C, but the flat heating-wire was used in place of the central heating conductor with rubber elastic.

RELATION of heat-loss to rise of temperature.

Calorimeter C.—Mean Temperature, 28°·6 C. October 14, 18, and 19, 1899.

$d\theta$.	Q.	$(EC - 4{\cdot}2Q\,d\theta)/d\theta$.	Difference from mean value, ·04535.
		Large flow.	
8·3069	·626436	·04521	− ·00014
8·3212	·625128	·04533	− ·00002
5·1009	·636545	·04518	− ·00017
5·1086	·635186	·04573	+ ·00038
2·2054	·620890	·04544	+ ·00009
2·2096	·619353	·04525	− ·00010
		Small flow.	Mean value, ·05047
8·2446	·381577	·05044	− ·00003
8·2446	·381454	·05021	− ·00026
5·0887	·388460	·05058	+ ·00011
5·0894	·388232	·05066	+ ·00019
2·2417	·376414	·04951	− ·00096
2·2433	·375879	·04992	− ·00055

The observations were taken for different inflow temperatures so as to give approximately the same mean temperature for the different values of $d\theta$, in consequence of which I have used the value 4·2 joules in obtaining the heat watts, the value of δ being the same for the different values of $d\theta$. For the large flows, the agreement of the values of the heat-loss is good, and much better than might be expected, having obtained the values from experiments made on different dates, although they were within a day or two of each other, and the calorimeter did not vary more than a few degrees between each experiment.

The values for the small flow do not agree so well for the 2° rise, but the values for the 5° and 8° show that the lower value given by the former must be exceptional. Here is an error of nearly 1 part in 1000, to be accounted for by assuming either that for the small flows the heat-loss is not proportional to the rise in temperature, in which case the value of the heat-loss per degree rise increases with rise of temperature, and the value for the 8° rise or the value for the 5° rise must be regarded as exceptional, or that the error in question was due to some uncertainty at that time in the experimental conditions. The latter must be regarded as the most probable on account of the greater difficulty of measuring so small a rise of temperature to the same order of accuracy. Moreover, the second 15-minute interval shows a decided increase, and would possibly have attained the correct value given by the mean of the other readings if the experiment had been further continued. An error of only ·001° on the 2° rise would account for the error in the second interval.

Besides the observations I have just given, which were selected from a series of trial experiments on the flat heating-wire, a large number of the other experiments were taken with rises of temperature ranging from 1° to 12°. These are detailed in the tables to be given later, and include results with the central heating-wire as well. It was a matter of convenience only that governed my choice of a rise of temperature for any experiment, and it sometimes happened that it was more convenient to change the mean temperature of an experiment by changing the rise of temperature in the water rather than by altering the inflow temperature—for example, in obtaining a measure of the specific heat in the neighbourhood of the zero point, where it was impossible to maintain the inflowing water at a temperature lower than 0° C.

Heat Capacity of the Calorimeter.

Although nearly always negligible in the calculation of results, the thermal capacity of the calorimeter is of value in showing the size of error introduced by a change in temperature in the calorimeter water. To determine this, the electrical supply was suddenly cut off from the calorimeter at a given moment and the rate of fall in temperature recorded. This was done for both the limits of flow used in the present work. The lag, on breaking the circuit of the thermometer before it commenced to fall, was in both cases not more than 2 or 3 seconds. If θ be the temperature indicated by the outflow thermometer above that of the inflow thermometer, then at any time after shutting off the heat supply, the value of θ will be approximately $\theta = ke^{-at}$, from which

$$d\theta/dt = kae^{-at} = a\theta.$$

But $\mathrm{C}\, d\theta/dt = d\mathrm{H}/dt$, where C is the thermal capacity of the calorimeter, and H is the total quantity of heat carried off by the water.

Writing $\mathrm{JQ}\theta$ for $d\mathrm{H}/dt$, $\mathrm{C}a\theta = \mathrm{JQ}\theta$, and $\mathrm{C} = \mathrm{JQ}/a$.

The following set of observations was obtained for Calorimeter C :—

Flow, ·598 gramme per second.

Time in seconds, after breaking electric current.	Temperature of outflow thermometer.
0	8·375
35	3·968
54	1·721
73	0·574
101	0·237
159	0·008
187·5	0·002
202·5	0·000
$a = \cdot 0386$	C = 50·5 joules.

Flow, ·392 gramme per second.

Time in seconds, after breaking electric current.	Temperature of outflow thermometer.
0	8·068
48	3·646
77	1·400
114	0·264
152	0·142
179	0·032
228	0·010
266	0·005
299	0·003
320	0·000
$a = \cdot 0311$	C = 54 joules.

The logarithmic relation can of course hardly be said to hold with accuracy, or to be even approximately true for the relation between the fall in temperature and time, as given by the above series of readings, on account of the sudden descent of the temperature during the first two minutes. For changes in temperature in the outflowing water, occasioned by a change in the electrical supply or flow, greater than ·02° during the 15-minute intervals, the thermal capacity as calculated by the above relation is of sufficient accuracy for the application of a small correction. It was seldom that the variation in temperature of the outflowing water amounted to more than ·02° during a set of readings, and was nearly always less than ·01° for the small flows.

Sec. 6.—*Effect of Stream-line Motion on the Distribution of Heat in the Fine-flow Tube.*

In Section 2 we discussed two conditions possibly existing in the fine-flow tube of the calorimeter, and explained generally the effect of these conditions on the temperature gradient of the glass surface and its influence on the heat-loss. In the present section I shall give briefly the experimental sequel to the theoretical considerations. In the light of the recent experiments of Professor HELE-SHAW,* so beautifully illustrating stream-line motion for water flowing at velocities under the critical velocity, and of Mr. T. E. STANTON† on 'The Passage of Heat between Metal Surfaces and Liquids in Contact with them,' the results might have been anticipated which I am about to describe. I do not think, however, that the effect of stream-line motion in fine tubes has been at all sufficiently appreciated.

As the critical velocity at which the stream-line motion breaks down is so great (of the order of 10 feet per second) for tubes of from 2 to 3 millims. in diameter, the effect is inseparably connected with all experiments having to do with tubes of this size. More especially does the flow tend to become linear, and to divide up into distinct and parallel lines, when a change of viscosity is introduced with a change of temperature.

I must, in treating this part of the subject, apologise for the present incompleteness of my experiments, but I feel that I must give such as I have at present, not only to justify myself for the time and trouble I have taken to completely eliminate the effect of stream-line motion from my calorimetric measurements, but also as a beginning to some experiments on the distribution of heat from a metal conductor in water flowing at different velocities through fine tubes, which I hope to continue in the near future, and which I hope may at the same time throw some light on the difference in the rate of flow from the centre to the sides of the tube.

My earlier experiments in 1898 were made with Calorimeter B, with a 2-millim. bore tube and central heating conductor, but with no special device for preventing stream-line motion.‡ The measurement which we obtained of the mechanical equivalent at that time, as I have already pointed out, is affected to a certain extent by this, which was at once apparent when I came to use Calorimeter D, with a 3-millim. bore tube. I undertook two sets of observations with Calorimeter D under two conditions, one with the heating wire, which was made of six strands of 6-millim. platinum wire, resting all along the edge of the tube, the other by drawing the wire, as best I could, straight through the centre of the tube.

The results are as follows :—

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* 'Proc. Inst. Naval Arch.' (1897), (1898); 'Proc. Royal Inst.' (1899); 'Proc. Liverpool Eng. Soc.', 20, 37, (1898).

† 'Phil. Trans.,' A, vol. 190, 67 (1897).

‡ See note p. 219, *supra*.

First Set.—Heating wire resting on sides of fine-bore tube.
Mean Temperature, 26°·1 C. November 4, 1898.

$d\theta$.	Q.	4·2 Q $d\theta$.	EC.	Difference.	Diff./$d\theta$.
		Large flow.			
8·2666	·600605	20·8528	21·6696	·8158	·09870
8·2759	·599645	20·8429	21·6624	·8195	·09902
		Small flow.			
8·3056	·276991	9·6624	10·3699	·7075	·08518
8·3043	·276888	9·6573	10·3668	·7095	·08544

Second Set.—Heating wire drawn straight through fine-bore tube.
Mean Temperature, 27° C. November 21, 1898.

$d\theta$.	Q.	4·2 Q $d\theta$.	EC.	Difference.	Diff./$d\theta$.
		Large flow.			
8·4676	·600527	21·3571	21·6677	·3106	.03668
8·4861	·599570	21·3696	21·6695	·2999	·03534
		Small flow.			
8·8111	·271465	10·0460	10·6749	·6289	·07138
8·8144	·271088	10·0358	10·6724	·6366	·07223

The mean temperature in the two sets is so nearly the same that in comparing the two we can for the moment neglect the temperature coefficient of the radiation loss from the glass surface. Without otherwise disturbing the experimental conditions, the heat-loss for a flow of ·60 gramme per second has been reduced exactly one-third by simply drawing the heating-wire central. The temperature of the outflowing water being the same in the two cases, the difference in the heat-loss between the two sets gives a measure of the space represented by the diagram in fig. 2 (p. 154), between the lines drawn for condition 1 and condition 2.

The value of the heat-loss for the same calorimeter and same flow, but introducing the device for eliminating stream-line motion, is very nearly ·06 watt per degree rise, which lies midway between ·09 and ·03 watt as given here respectively. For the small flow, as might be expected, the heat-loss is more nearly the same in the two cases, on account of the greater opportunity for conduction throughout the water column ; but the effect is still shown. It is of interest also to calculate the actual temperature of the same heating wire in the two cases.

Flow per second.	Resistance of heating wire.	Corrected to a mean temperature of 26°·1.
	First set.	
·60	·52427 ohm.	·5243
·28	·51740 „	·5174
	Second set.	
·60	·53460 ohm.	·5331
·27	·52383 „	·5225

Correcting to the same mean temperature by the temperature coefficient of the platinum, the results show that, as might be expected, the wire held central is hotter than when in contact with the glass. This means that the central wire is surrounded by a cloak of hot water moving parallel with it, and the more completely prevented from diffusing the greater the velocity of the flow. This is shown conclusively by comparing the temperature of the wire, as indicated by its resistance, with the temperature of the same wire measured "cold" and reduced to the same mean temperature. A measurement of this for a current through the wire, not sufficient to cause a rise in temperature of more than ·1° in the outflowing water, gave the value ·5100 ohm.

For the case where the wire is held central in the largest flow and the conditions are most perfect for the formation of a moving cloak, the mean temperature of the wire, as given by its increment of resistance, over and above the mean temperature of the water column in the flow-tube, is of the order of 12° C. This shows that, at the very most, only one-quarter of the total quantity of water flowing through the 3-millim. flow-tube per second was receiving heat from the wire.

In the case where the wire touches the sides of the tube for its full length, a greater area of water is heated by conduction and diffusion throughout the layers along the sides of the tube, which do not move at such a high rate of velocity as in the centre. The increment of resistance for the large flow given in the first set of readings for this case shows that the wire was of the order of 7° hotter than the mean temperature of the water, and indicates that about one-half of the total flow was employed in carrying off the heat from the wire. When the water is thoroughly stirred around the heating wire, and in particular where the flat heating wire, twisted into spirals down the flow-tube, is employed, the mean temperature of the wire is much more nearly the same for the two flows and more nearly equal to that of the water column, the differences being of the order of 1° C. only.

Sec. 7.—*Preliminary Measurements of the Mechanical Equivalent.*

Our first measurements of the mechanical equivalent in the summer of 1898 were made with Thermometer C and Calorimeter B. This had a flow-tube slightly less than 2 millims., and, with the exception of the device for eliminating stream-line motion, was fitted up in a similar way to the later calorimeters. It is a matter of interest to determine the way in which the heat-loss varies with rise of temperature for this case. I have summarized the observations which we made at that time to determine this, and expressed them here in terms of the same values for the units as the later measurements. The results are corrected to the same value of Q, and were all obtained approximately at a mean temperature of 30° C.

Relation of Heat-loss to Rise of Temperature.

Large flow. Q = ·54000 gramme per second.		Small flow. Q = ·27300 gramme per second.	
$d\theta$.	$(EC - 4 \cdot 2\, Q\, d\theta)/d\theta$.	$d\theta$.	$(EC - 4 \cdot 2\, Q\, d\theta)/d\theta$.
3°·0462	·04445	2°·9717	·04941
5·9427	·04403	5·8891	·04904
8·9131	·04298	9·0285	·04982
12·2129	·04070	11·9785	·04809

The readings for the large flow are very consistent, as shown by the plot in fig. 14. For the small flow the variations in the observations are far from satisfactory, but they show a similar decrease in the value of the heat-loss with rise of temperature as for the large flow. The decided bend in the curves shows that, as the temperature of the out-flowing water is decreased, the temperature gradient down the fine-bore tube approaches more nearly a straight line (*cf.* fig. 2, p. 154.) The decrease in the heat-loss with increase of temperature points to the more perfect confinement of the heated water around the wire in its passage through the tube, which is occasioned by its greater difference in density.

The small flow allows of the more perfect distribution of heat throughout the water column in the flow-tube, and the curve approaches a limiting value, as the temperature is lowered, much sooner than in the case of the large flow. If we may assume the two limiting values of the heat-loss per degree rise in the calorimeter for the two flows by extrapolating for a value of $d\theta = 0$ in the two cases, and accept these values as being true for any rise where the temperature distribution is uniform throughout the water column and stream-line motion avoided, then the value of d may be calculated. The two values of the heat-loss per degree rise so obtained were for a flow of

·54000 gramme per sec., ·04445 watt. ·27300 gramme per sec., ·04965 watt.

The latter value has not to be corrected for the small conduction effect for the small flow on account of the method of treatment. Hence the value of d comes out $-$ ·00464, from which

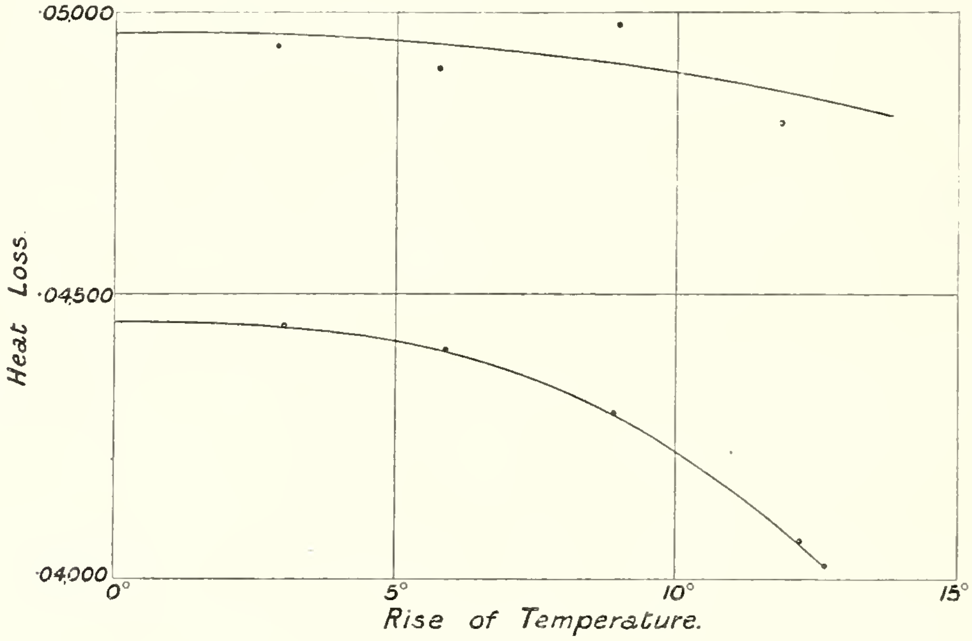

Fig. 16.

$$J = 4{\cdot}2\,(1 - 00464) = 4{\cdot}1805 \text{ joules, at } 30^\circ \text{ C.}$$

The value of J at the same temperature, obtained with the other calorimeters for any rise of temperature when using the various devices for obviating stream-line motion, is 4·1780 joules, which agrees to 1 part in 2000 with this value. This is quite as good an agreement as can be expected from the manner of treating the observations, and the want of agreement in the observations themselves for the small flow, which is no doubt occasioned by the uncertainty introduced by the stream-lines.

Sec. 8.—*Experiments between 0° and 100° C.*

As soon as it became clear that the main cause of error had been removed in eliminating the effect of stream-line motion in the calorimeter, I commenced a series of experiments to extend over the entire range of temperature. These experiments are summarized in the following table from I. to LV., and include upwards of 46 complete experiments. They extended over a period of just a year, and divide themselves naturally into 8 separate series.*

Series 1. Nos. I. to XV.

This series includes experiments with Calorimeter C, between 4° and 35° C., and Calorimeter D, at 28°. Both calorimeters were fitted with a stranded platinum heating-wire with the silk-covered rubber cord wound round. The distilled water supplied to the calorimeter was boiled before running under the oil, in bottles forming the head, but no special care was taken to keep it hot while running in. A large quantity of the air was driven off in the process of boiling, but subsequent results have shown that the water in the head must still have contained a considerable quantity of dissolved air. Several of the experiments include other flows, besides the flows used throughout the entire series of experiments. These have been already summarized in Section 5. The correction for Thermometer E is that given under Group I., Section 3, *c*.

Series 2. Nos. XVI. to XXVII.

Between Series 1 and 2 several alterations were made to the apparatus, one of the chief being the introduction of 40 feet of tin tubing into the constant temperature tank to replace a similar amount of copper tubing used previously. This was found necessary owing to the gradual formation of copper rust in the tube. This rust was carried into the small rubber tube conveying water from the tank to the calorimeter, and gradually reduced the flow. The experiments were extended from 22° up as far as 60° C., where they had to be discontinued in order to further refine the regulating attachments. The calorimeter was fitted with a solid platinum heating-wire, with silk-covered rubber cord. The agreement of the results at the lower points between 22° and 35° with those in Series 1 is very satisfactory. Above 45° the results are not so consistent, probably on account of the fluctuations in gas-pressure supplying the main heat to the circulating system. The experiment at 60° was taken, however, when no other gas was being used in the building, and the conditions were unusually steady. Rises of temperature of 11° and 5° were tried as a check on the measurements. The correction for Thermometer E is that obtained in the test in Group II., Section 3, *c*.

Series 3. Nos. XXVIII. to XXXII.

This series includes another attempt to obtain the high temperatures, but nearly all the experiments were spoiled by the liberation of air inside the calorimeter. The experiment at 67° is given as an illustration of the effect produced by the appearance of air. In this series the air bubbles were found in the calorimeter water after the experiment, in spite of the fact that the distilled water was kept continuously boiling as it was supplied to the head bottles, and was cooled from 100° C. only by the cold

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* In the following d is used instead of the δ of Sec. 2.

water already in the bottles. The correction to the fundamental interval of Thermometer E is the same as for the last series.

Series 4. Nos. XXXIII. to XXXV.

This series includes experiments with Calorimeter C, using the flattened platinum strip for heating wire, instead of the central wire conductor and elastic strip. These observations are summarized in Section 5. The use of the flat wire was found to produce more irregularity in the heat-loss between the different flows, especially apparent on the small flows, and no doubt occasioned by the fact that the wire touched the sides of the tube. The correction for the fundamental interval of Thermometer E is that given under Group III., in Section 3, *c*.

The agreement of the value of J with the other measurements is very satisfactory, and the more so because the heating conductor was changed not only in form but in resistance.

Series 5. Nos. XXXVI. and XXXVII.

Experiments with Calorimeter E with flat heating strip. The fine-bore tube was slightly over 3 millims. in diameter, and was the largest tried in these experiments. The first experiments with this calorimeter were made with the central wire conductor and large rubber cord, but were neither satisfactory nor consistent. The effect of the stream-line motion apparently began to come in, with the helical motion in the water, probably from the size of the flow-tube compared to the size of the heating-wire. The thermometer was the same in every respect to that used in Series 4.

Series 6. Nos. XXXVIII. to XLVIII.

In this series, Calorimeter C was refitted with central solid platinum heating-wire with silk-covered rubber cord. Thermometer E, Group III., was still used. Measurements from 20° to 0° were made, and the values obtained under Series 1 and 2 completely verified. The observations were extended below 4°, and the lowest point obtained was for a rise of temperature of 1° above 0°. In this experiment only one flow was obtained, but the value of *d* may be calculated with some degree of approximation by assuming the value of the heat-loss for the two other determinations with inflow-water at 0°, and correcting for the temperature coefficient of the radiation. This experiment was done principally to test the rapid increase of the specific heat at the freezing-point. An attempt was also made to obtain the high points, but with no more success than in the previous attempts.

Series 7. Nos. XLIX and L.

Between Series 6 and the present series, various devices were tried to obviate the effect of dissolved air in the boiled water. The plan was finally adopted of preparing absolutely air-free water, as described in Section 5, and from this time on the work at the higher points progressed more favourably. In this series observations were obtained at 30° and 86°, but the latter unfortunately with only one flow. The second flow could not be taken on account of the rapid evaporation of water from the tank, the constant-level device not being used at that time. Here again, extrapolation for the heat-loss from the value at 30° can be made, but the procedure can hardly be justified with a greater accuracy than 1 in 1000. The agreement with the later results is, however, extraordinarily good.

Series 8. Nos. LI. to LV.

This series was made with box 2 and Thermometer E, involving the F.I. correction in Group IV. It extends from 32° C. to 92° C., and in many respects is the most important series of the whole. The Calorimeter C was refitted throughout so as to give an entirely new set of observations. The complete agreement of the measurement of the specific heat at 32° C. with the other measurements with box 1, eliminates any possible error due to the box and its connections. The four sets of observations at the higher points are exceedingly consistent, and distinctly show that the previous trouble to obtain the measurements in this region was due to the effect of the air in the water. Not the slightest trouble was experienced with air making its appearance in the calorimeter in these experiments. The order in which these observations were taken was as follows: 32°, 74°, 92°, 80° and 68°, between which the calorimeter cooled down to the temperature of the laboratory, and had to be heated up to the desired point each time. The measurement at 86° in Series 7 is in very good agreement with these. The beautiful consistency of this last series of measurements might make it desirable to repeat the observations between 50° and 60° C. with air-free water. I did not consider this was necessary, however, as the continuity of the observations at the two ends of the range is so good, and the divergence in the results obtained between 50° and 60° C. is so clearly explained by unforeseen and extraneous causes.

The calculation of the results in the tables just given for the determination of the value of the electrical and heat energy has been very much facilitated by the use of the Brunsviga calculating machine, which is very much to be recommended for this class of work. For the application of the small correction factors, and for the final estimation of the values of *d* and *h*, the Fuller cylinderical slide-rule has been constantly used. The values of the electrical and heat watts given in the summary at the foot of each table may therefore be in error by 2 or perhaps 3 in the fourth decimal place, but no more, but I feel confident that in the estimation of the mean value, upon which the value of *d* depends, this error tends to disappear, and that the value of *d* given by the measurements in any of the tables, represents the observations to an accuracy of 1 part in 100,000.

Summary of Results of Observations.

The following table contains a summary of the observations arranged and abstracted by Professor CALLENDAR. The original tables (abridged), giving details of corrections and calculations, are preserved for reference in the Archives of the Royal Society.

The first column gives the number and date of the corresponding Abridged Table preserved in the Archives. The second column gives the temperature of the jacket water or inflow, taken by means of a mercury thermometer, and corrected to the nearest hundredth of a degree. The third column gives the mean difference of temperature, $d\theta$, between the inflow and outflow, observed to the ten-thousandth of a degree by means of a pair of differential platinum thermometers, and reduced by the parabolic difference formula, assuming the boiling-point of sulphur to be 444·53° C. The fourth column gives the flow of water, Q, through the calorimeter, in grammes per second, reduced to vacuum. The fifth column gives the value of the product, $4{\cdot}2\,\mathrm{Q}\,d\theta$, for comparison with the power, EC in watts, given in the next column. The seventh column gives the difference, $\mathrm{EC} - 4{\cdot}2\,\mathrm{Q}\,d\theta$, of the numbers in the two previous columns divided by $d\theta$. This quotient is denoted by D, and is used in calculating the results given in the last column, by means of the difference equation

$$\mathrm{EC}/d\theta - 4{\cdot}2\,\mathrm{Q} = \mathrm{D} = 4{\cdot}2\,\mathrm{Q}\,d + h,$$

in which d expresses the fractional variation of the specific heat of water in terms of an arbitrary unit 4·200 joules, as defined by the relation $\mathrm{J} = 4{\cdot}200\,(1 + d)$, and the symbol h denotes the rate of heat-loss in watts per degree rise of temperature. The value of d is found by combining the observations for the two different flows Q' and Q'', which give the relation

$$d = (\mathrm{D}' - \mathrm{D}'')/4{\cdot}2\,(\mathrm{Q}' - \mathrm{Q}'').$$

The values of h and J follow immediately from that of d. The values of EC and J are calculated assuming the E.M.F. of the Clark cell at 15° C. to be 1·4342 volts, but this does not affect the relative values.

In cases where more than two different flows were taken at the same temperature, the values of d and h are calculated from the largest and smallest flow. These values of d and h are then assumed to calculate a value of D for the intermediate flow for comparison with the value of D deduced from the observations.

TABLE XVIII.—Summary of Results of Observations.

Number and date.	Jacket. Temp. °C.	Temp. rise. $d\theta$, ° C.	Flow Q. gm./sec.	Product. 4·2 Q $d\theta$.	Watts. EC.	Diff./$d\theta$. D.	Results. *d*, *h*, J.
	Series I. Calorimeter D. Stranded Conductor. Thermometer E, I.						
I.	24°·03	7°·5234	·674106	21·3006	21·7331	·05749	*d* = − ·00485,
Feb. 15,	(Not repeated)						*h* = + ·07122,
1899.	24·04	7·7745	·399290	13·0379	13·5290	·06317	J = 4·1796,
	24·02	7·9463	·390196	13·0225	13·5245	·06318	at 28°·01 C.
II.	24·00	7·8882	·496655	16·4544	16·9383	·06135	*d* = − ·00533,
Feb. 15,	(Not repeated)						*h* = + ·07247,
1899.	24·01	8·0033	·248234	8·3447	8·8802	·06691	J = 4·1776,
	(Not repeated)						at 28°·01 C.
	Calorimeter C. Stranded Conductor. Thermometer E, I.						
III.	25°·03	7°·9646	·666042	22·2800	22·5697	·03637	*d* = − ·00469,
Feb. 20,	25·03	7·9775	·664388	22·2607	22·5504	·03632	*h* = + ·04944,
1899.	25·06	8·2608	·398498	13·8260	14·1689	·04151	J = 4·1803,
	25·06	8·2560	·398540	13·8194	14·1634	·04167	at 29°·10 C.
IV.	25·03	8·2281	·258114	8·9199	9·2922	·04525	*d* = − ·00546,
Feb. 20,	25·03	8·2284	·257947	8·9144	9·2879	·04539	*h* = + ·05123,
1899.	25·06	8·2199	·501957	17·3294	17·6567	·03982	J = 4·1771,
	25·06	8·2301	·501026	17·3186	17·6450	·03966	at 29°·09 C.
V.	25·07	7·9031	·660813	21·9361	22·2194	·03585	*d* = − ·00489,
Feb. 22,	25·07	7·9083	·658690	21·8800	22·1628	·03576	*h* = + ·04937,
1899.	25·07	8·2680	·392575	13·6334	13·9749	·04131	J = 4·1795,
	25·07	8·2635	·392362	13·6280	13·9692	·04129	at 29°·11 C.
VI.	25·07	8·1938	·496670	17·0937	17·4137	·03906	D calc.
Feb. 22.	25·07	8·1844	·496553	17·0700	17·3911	·03924	= ·03917.
VII.	25·01	8·3390	·590477	20·6807	20·9912	·03723	*d* = − ·00499,
Mar. 2,	25·01	8·3439	·589356	20·6536	20·9653	·03734	*h* = + ·04965,
1899.	25·01	8·4310	·375154	13·2841	13·6363	·04177	J = 4·1790,
	25·01	8·4304	·375076	13·2807	13·6362	·04181	at 29°·21 C.
VIII.	25·01	8·3979	·472489	16·6652	16·9992	·03977	D calc.
Mar. 2.	25·01	8·4060	·471670	16.6524	16·9885	·03998	= ·03975.
IX.	9·51	8·5768	·372746	13·4272	13·7377	·03620	*d* = − ·00208,
Mar. 9,	9·51	8·5803	·372262	13·4153	13·7261	·03622	*h* = + ·03946,
1899.	9·51	8·5499	·573318	20·5876	20·8827	·03452	J = 4·1913,
	9·51	8·5616	·571920	20·5654	20·8595	·03439	at 13°·79 C.
X.	9·51	8·5586	·459149	16·5046	16·8060	·03522	D. calc.
Mar. 9.	9·51	8·5683	·458194	16·4889	16·7912	·03529	= ·03546.
XII.	13·30	8·7411	·357638	13·1298	13·4508	·03673	*d* = − ·00309,
Mar. 11,	13·30	8·7241	·358131	13·1222	13·4428	·03675	*h* = + ·04139,
1899.	13·31	8·9195	·566221	21·2117	21·5153	·03404	J = 4·1870,
	(Second interval, regulator failed)						at 17°·69 C.

Table XVIII.—Summary of Results of Observations—*continued.*

Number and date.	Jacket. Temp. °C.	Temp. rise. $d\theta$, °C.	Flow Q. gm./sec.	Product. 4·2 Q $d\theta$.	Watts. EC.	Diff./$d\theta$. D.	Results. d, h, J.
Series I. Calorimeter C. Stranded Conductor. Thermometer E, I.—continued.							
XIII.	19°·95	8°·4978	·373778	13·3404	13·6769	·03960	$d = -\cdot00446$,
Mar. 16,	19·95	8·5149	·372934	13·3371	13·6734	·03950	$h = +\cdot04655$,
1899.	19·95	8·4695	·587077	20·8834	21·1846	·03556	J = 4·1813,
	19·95	8·4963	·584879	20·8686	21·1708	·03557	at 24°·20 C.
XIV.	30·15	8·6230	·358452	12·9819	13·3758	·04568	$d = -\cdot00561$,
Mar. 17,	30·16	8·6154	·358388	12·9682	13·3639	·04593	$h = +\cdot05424$,
1899.	30·16	8·6037	·567099	20·4924	20·8450	·04099	J = 4·1765.
	30·17	8·6283	·565123	20·4794	20·8314	·04080	at 34°·47 C.
XV.	0·13	8·3170	·559701	19·5511	19·9014	·04212	$d = +\cdot00330$,
Mar. 24,	0·13	8·3407	·557801	19·5402	19·8913	·04210	$h = +\cdot03437$,
1899.	0·13	8·2833	·361401	12·5730	12·8992	·03938	J = 4·2138.
	0·13	8·2883	·360873	12·5622	12·8898	·03953	at 4°·28 C.
Series II. Calorimeter C. Solid Conductor. Thermometer E, II.							
XVI.	18°·17	7°·9225	·404339	13·4542	13·7653	·03927	$d = -\cdot00413$,
June 6,	18·16	7·9999	·633704	21·2922	21·5737	·03519	$h = +\cdot04619$,
1899.	18·17	7·9672	·401420	13·4324	13·7441	·03913	J = 4·1827,
							at 22°·16 C.
XVII.	27·29	8·2190	·618698	21·3573	21·6793	·03918	$d = -\cdot00542$,
June 8,	27·30	8·2310	·617503	21·3472	21·6712	·03936	$h = +\cdot05334$,
1899.	27·30	8·1357	·394624	13·4843	13·8447	·04430	J = 4·1773,
	27·30	8·1545	·393530	13·4780	13·8404	·04444	at 31°·40 C.
XVIII.	27·97	8·4281	·602990	21·3447	21·6740	·03908	$d = -\cdot00536$,
June 9,	27·97	8·4467	·601265	21·3305	21·6632	·03939	$h = +\cdot05282$,
1899.	27·97	8·3590	·383786	13·64739	13·8410	·04392	J = 4·1775,
	27·97	8·3803	·382529	13·4640	13·8360	·04439	at 32°·17 C.
XIX.	36·82	8·3641	·636775	22·3694	22·7438	·04476	$d = -\cdot00540$,
June 12,	36·82	8·3726	·635489	22·3469	22·7246	·04511	$h = +\cdot05939$,
1899.	36·83	8·3746	·381973	13·4352	13·8606	·05068	J = 4·1773,
	36·84	8·3717	·381800	13·4245	13·8493	·05074	at 41°·02 C.
XX.	41·30	8·3720	·632463	22·2389	22·6538	·04956	$d = -\cdot00514$,
June 12,	41·30	8·3892	·630617	22·2195	22·6331	·04931	$h = +\cdot06306$,
1899.	41·30	8·4063	·397132	14·0213	14·4785	·05439	J = 4·1784,
	41·30	8·4068	·396628	14·0043	14·4633	·05460	at 45°·49 C.
XXI.	45·70	7·9687	·666393	22·3033	22·7174	·05197	$d = -\cdot00531$,
June 14,	45·70	7·9689	·665414	22·2705	22·6825	·05171	$h = +\cdot06669$,
1899.	45·69	7·9639	·419567	14·0339	14·4908	·05737	J = 4·1777,
	45·70	7·9648	·418914	14·0136	14·4700	·05730	at 49°·68 C.
XXII.	50·52	8·2051	·631248	21·7537	22·2358	·05876	$d = -\cdot00372$,
June 14,	50·52	8·2065	·630085	21·7173	22·2001	·05884	$h = +\cdot06867$,
1899.	50·50	8·1496	·401674	13·7486	14·2543	·06206	J = 4·1844,
	50·53	8·1528	·400859	13·7261	14·2374	·06272	at 54°·61 C.

TABLE XVIII.—Summary of Results of Observations—*continued.*

Number and date.	Jacket. Temp. ° C.	Temp. rise. $d\theta$, ° C.	Flow Q. gm./sec.	Product. 4·2 Q $d\theta$.	Watts. EC.	Diff./$d\theta$. D.	Results. d, h, J.
Series II. Calorimeter C. Solid Conductor. Thermometer E, II.—continued.							
XXIII.	55°·64	8°·3805	·612400	21·5553	22·0876	·06351	$d = -$ ·00341,
June 17,	55·64	8·3835	·611227	21·5217	22·0532	·06339	$h = +$ ·07220,
1899.	55·61	8·3534	·388491	13·6299	14·1874	·06674	J = 4·1849,
	55·61	8·3674	·387534	13·6191	14·1760	·06656	at 59°·80 C.
XXIV.	55·61	8·3158	·462971	16·1699	16·7134	·06536	D calc.
June 17.	55·61	8·3395	·461364	16·1595	16·7052	·06542	= ·06559.
XXV.	27·15	11·3447	·642348	30·6064	31·0604	·04002	$d = -$ ·00528,
June 20,	27·15	11·3383	·641338	30·5410	30·9955	·04008	$h = +$ ·05429,
1899.	27·17	11·3324	·402771	19·1703	19·6835	·04529	J = 4·1778,
	27·17	11·3428	·402108	19·1562	19·6715	·04542	at 32°·81 C.
XXVI.	27·16	11·2504	·489797	23·1437	23·6345	·04363	D. calc.
June 20.	27·17	11·2418	·488845	23·0811	23·5726	·04372	= ·04345.
XXVII.	27·98	5·1297	·610593	13·1551	13·3565	·03926	$d = -$ ·00555,
June 22.	27·98	5·1365	·608831	13·1344	13·3379	·03962	$h = +$ ·05364,
	27·99	5·1579	·383538	8·3086	8·5392	·04471	J = 4·1767,
	27·99	5·1613	·382650	8·2948	8·5256	·04472	at 30°·54 C.
Series III. Calorimeter C. Thermometer E, II. Solid Conductor.							
XXVIII.	25°·44	8°·0202	·634819	21·3838	21·7067	·04026	$d = -$ ·00496,
Sept. 4,	25·44	8·0343	·632988	21·3596	21·6841	·04039	$h = +$ ·05352,
1899.	25·45	8·0981	·384855	13·0896	13·4580	·04549	J = 4·1792,
	25·45	8·1079	·384098	13·0797	13·4487	·04552	at 29°·47 C.
XXIX.	27·14	8·0488	·630942	21·3290	21·6566	·04070	$d = -$ ·00544,
Sept. 6,	27·14	8·0548	·630005	21·3131	21·6420	·04083	$h = +$ ·05518,
1899.	27·14	8·1703	·380614	13·0608	13·4412	·04656	J = 4·1771,
	27·14	8·1808	·379886	13·0526	13·4340	·04662	at 31°·22 C.
XXX.	34·60	8·3187	·394336	13·7775	14·2055	·05145	$d = -$ ·00530,
Sept. 12,	34·60	8·3139	·394088	13·7609	14·1916	·05180	$h = +$ ·06041,
1899.	34·60	8·3018	·626817	21·8555	22·2412	·04647	J = 4·1777,
	34·60	8·3159	·625193	21·8360	22·2225	·04648	at 38°·76 C.
XXXI.	63·33	8·3443	·390990	13·7027	14·3302	·07520	$d = -$ ·00395,
Sept. 14,	63·33	8·3517	·390431	13·6952	14·3256	·07547	$h = +$ ·08182,
1899.	63·33	8·3782	·627514	22·0812	22·6775	·07117	J = 4·1834,
	63·33	8·4042	·625068	22·0633	22·6657	·07168	at 67°·52 C.
XXXII.	50·41	8·2923	·393061	13·6893	14·2326	·06552	$d = -$ ·00473,
Sept. 18,	50·42	8·2990	·392595	13·6841	14·2267	·06538	$h = +$ ·07325,
1899.	50·43	8·2824	·626272	21·7855	22·2875	·06061	J = 4·1801,
	50·43	8·2965	·624643	21·7658	22·2722	·06104	at 54°·57 C.

TABLE XVIII.—Summary of Results of Observations—*continued.*

Number and date.	Jacket. Temp. ° C.	Temp. rise. $d\theta$, ° C.	Flow Q. gm./sec.	Product. 4·2 Q $d\theta$.	Watts. EC.	Diff./$d\theta$. D.	Results. d, h, J.
Series IV. Calorimeter C. Spiral strip, no rubber cord. Thermometer E, III.							
XXXIII.	24°·64	8°·3069	·626436	21·8557	22·2313	·04521	$d = -\cdot00493$,
Oct. 14,	24·64	8·3212	·625128	21·8476	22·2248	·04533	$h = +\cdot05826$,
1899.	24·65	8·2446	·381577	13·2130	13·6288	·05044	J = 4·1793,
	24·65	8·2446	·381454	13·2087	13·6226	·05021	at 28°·77 C.
XXXIV.	25·97	5·1009	·636545	13·6372	13·8676	·04518	$d = -\cdot00497$,
Oct. 18,	25·97	5·1086	·635186	13·6286	13·8622	·04573	$h = +\cdot05870$,
1899.	25·98	5·0887	·388460	8·3024	8·5598	·05058	J = 4·1791,
	25·98	5·0894	·388232	8·2987	8·5565	·05065	at 28°·52 C.
XXXV.	27·38	2·2053	·620890	5·7508	5·8510	·04544	$d = -\cdot00427$,
Oct. 19,	27·38	2·2095	·619353	5·7475	5·8475	·04525	$h = +\cdot05645$,
1899.	27·38	2·2416	·376414	3·5437	3·6547	·04951	J = 4·1821,
	27·38	2·2432	·375879	3·5412	3·6532	·04992	at 28°·49 C.
Series V. Calorimeter E (3 millims.), spiral strip. Thermometer E, III.							
XXXVI.	25°·74	8°·3281	·623288	21·8013	22·1831	·04584	$d = -\cdot00542$,
Oct. 27,	25·75	8·3360	·622427	21·7919	22·1727	·04566	$h = +\cdot05994$,
1899.	25·74	8·3310	·384073	13·4387	13·8652	·05119	J = 4·1772,
	25·75	8·3436	·383177	13·4377	13·8551	·05122	at 29°·92 C.
XXXVII.	17·02	7·7440	·689271	22·4184	22·7443	·04208	$d = -\cdot00404$,
Nov. 1.	17·02	7·7488	·687919	22·3883	22·7199	·04280	$h = +\cdot05414$,
	17·08	7·7804	·485563	15·8671	16·2241	·04589	J = 4·1830,
	(Flow not repeated)						at 20°·92 C.
Series VI. Solid Conductor. Thermometer E, III. Calorimeter C.							
XXXVIII.	16°·01	8°·2408	·603561	20·8901	21·1857	·03587	$d = -\cdot00384$,
Nov. 3,	16·01	8·2549	·602250	20·8804	21·1744	·03598	$h = +\cdot04567$,
1899.	16·01	8·2575	·375191	13·0122	13·3381	·03947	J = 4·1838,
	16·01	8·2554	·375065	13·0043	13·3325	·03976	at 20°·18 C.
XXXIX.	16·00	2·1866	·576497	5·2944	5·3737	·03627	$d = -\cdot00310$,
Nov. 4,	16·00	2·1878	·575717	5·2901	5·3699	·03647	$h = +\cdot04387$,
1899.	16·00	2·1855	·357957	3·2857	3·3713	·03917	J = 4·1870,
	16·00	2·1866	·357600	3·2841	3·3699	·03924	at 17°·09 C.
XL.	17·57	5·0878	·606172	12·9531	13·1370	·03615	$d = -\cdot00397$,
Nov. 6,	17·57	5·0992	·604361	12·9433	13·1274	·03611	$h = +\cdot04622$,
1899.	17·59	5·1071	·377173	8·0903	8·2943	·03995	J = 4·1833,
	17·60	5·1142	·376515	8·0874	8·2916	·03993	at 20°·13 C.
XLI.	16·34	8·1889	·608476	20·9275	21·2381	·03793	$d = -\cdot00420$,
Nov. 14,	16·34	8·2003	·607098	20·9093	21·2208	·03799	$h = +\cdot04867$,
1899.	16·36	8·2198	·383107	13·2261	13·5703	·04188	J = 4·1824,
	16·38	8·2261	·382518	13·2159	13·5613	·04199	at 20°·45 C.

TABLE XVIII.—Summary of Results of Observations—*continued.*

Number and date.	Jacket. Temp. ° C.	Temp. rise. $d\theta$, ° C.	Flow Q. gm./sec.	Product. 4·2 Q $d\theta$.	Watts. EC.	Diff./$d\theta$. D.	Results. d, h, J.
Series VI. Solid Conductor. Thermometer E, III. Calorimeter C.—continued.							
XLII.	14°·65	2°·1581	·581584	5·2715	5·3533	·03790	d = − ·00254,
Nov. 16,	14·65	2·1614	·579646	5·2620	5·3464	·03905	h = + ·04467,
1899.	14·63	2·1391	·363655	3·2672	3·3543	·04072	J = 4·1893,
	14·63	2·1420	·362870	3·2646	3·3521	·04085	at 15°·71 C.
XLIII.	7·50	2·1065	·587245	5·1955	5·2791	·03969	d = + ·00022,
Nov. 17,	7·57	2·1050	·586733	5·1873	5·2720	·04024	h = + ·03943,
1899.	7·67	2·0664	·372448	3·2325	3·3141	·03949	J = 4·2009,
	7·70	2·0577	·372092	3·2158	3·2982	·04044	at 8°·66 C.
XLIV.	0·15	2·1993	·592582	5·4737	5·5842	·05024	d = + ·00512,
Nov. 18,	0·15	2·1982	·591463	5·4606	5·5714	·05041	h = + ·03759,
1899.	0·15	2·1909	·389629	3·5853	3·6861	·04601	J = 4·2215,
	0·15	2·1916	·389077	3·5813	3·6820	·04594	at 1°·35 C.
XLV.	0·15	5·0561	·616583	13·0935	13·3381	·04838	d = + ·00370,
Nov. 22,	0·15	5·0694	·614942	13·0929	13·3344	·04764	h = + ·03842,
1899.	0·15	5·0738	·369790	7·8802	8·1040	·04410	J = 4·2155,
	0·15	5·0772	·369335	7·8758	8·1007	·04429	at 2°·68 C.
XLVI.	0·15	1·0483	·598234	2·6339	2·6880	·05160	d = + ·00597,
Nov. 22.	0·15	1·0493	·597057	2·6313	2·6863	·05241	h = + ·0370.
XLVII.	25·22	8·4686	·601120	21·3807	21·7224	·04035	d = − ·00497,
Nov. 27,	25·22	8·4910	·599162	21·3675	21·7149	·04093	h = + ·05316,
1899.	25·21	8·4064	·377559	13·3304	13·7105	·04522	J = 4·1791,
	25·21	8·4159	·376851	13·3205	13·7023	·04537	at 29°·43 C.
XLVIII.	46·77	8·5495	·592608	21·2822	21·7592	·05579	d = − ·00513,
Nov. 29,	46·78	8·5767	·590139	21·2580	21·7367	·05582	h = + ·06855,
1899.	46·79	8·4380	·370080	13·1155	13·6267	·06058	J = 4·1785,
	(Not repeated)						at 51°·02 C.
Series VII. Calorimeter C. Solid Conductor. Thermometer E, III. Air-free Water.							
XLIX.	24°·94	8°·3727	·579770	20·3878	20·7297	·04083	d = − ·00488,
Jan. 1,	24·94	8·3774	·579087	20·3751	20·7219	·04140	h = + ·05299,
1900.	24·95	8·3435	·355436	12·4554	12·8365	·04567	J = 4·1795,
	24·95	8·3449	·355120	12·4465	12·8282	·04574	at 29°·13 C.
L.	81·56	8·0278	·646259	21·7898	22·5230	·09133	d = − ·00052,
Jan. 6.	81·60	8·0325	·644355	21·7383	22·4762	·09186	h = + ·0930.
Series VIII. Calorimeter C. Solid Conductor. Thermometer E, IV. Box II.							
LI.	28°·15	8°·2035	·645683	22·2468	22·6039	·04358	d = − ·00521,
Feb. 24,	28·15	8·2223	·643769	22·2317	22·5931	·04396	h = + ·05791,
1900.	28·16	8·2468	·404207	14·0003	14·4041	·04897	J = 4·1781,
	28·16	8·2613	·403213	13·9904	14·3966	·04917	at 32°·26 C.

TABLE XVIII.—Summary of Results of Observations—*continued.*

Number and date.	Jacket. Temp. ° C.	Temp. rise. $d\theta$, ° C.	Flow Q. gm./sec.	Product. 4·2 Q $d\theta$.	Watts. EC.	Diff./$d\theta$. D.	Results. *d*, *h*, J.
Series VIII. Calorimeter C. Solid Conductor. Thermometer E, IV. Box II.—continued.							
LII.	69°·85	8°·3152	·622088	21·7257	22·3864	·07947	*d* = − ·00189,
Feb. 28,	69·85	8·3226	·620830	21·7011	22·3672	·08044	*h* = + ·08469,
1900.	69·86	8·4472	·385739	13·6853	14·3733	·08146	J = 4·1920,
	69·86	8·4893	·383723	13·6816	14·3761	·08181	at 74°·05 C.
LIII.	87·42	8·2361	·645077	22·3142	23·1450	·10088	*d* = + ·00042,
Mar. 10,	87·41	8·2513	·642851	22·2783	23·1161	·10155	*h* = + ·10011,
1900.	87·43	8·2768	·402934	14·0069	14·8450	·10130	J = 4·2017,
	87·43	8·3168	·400935	14·0049	14·8398	·10030	at 91°·55 C.
LIV.	76·12	8·5262	·617742	22·1213	22·8806	·08894	*d* = − ·00117,
Mar. 17,	76·12	8·5570	·615198	22·1099	22·8747	·08938	*h* = + ·09218,
1900.	76·12	8·5224	·388311	13·8992	14·6692	·09036	J = 4·1951,
	76·12	8·5433	·387095	13·8897	14·6603	·09021	at 80°·38 C.
LV.	63·84	8·6883	·387767	14·1499	14·8324	·07856	*d* = − ·00262,
Mar 21,	63·84	8·6760	·387527	14·1212	14·8029	·07858	*h* = + ·08283,
1900.	63·82	8·8222	·604663	22·4047	23·0757	·07606	J = 4·1890,
	63·82	8·8494	·601956	22·3732	23·0488	·07634	at 68°·21 C.

Each single line in the above table represents the mean results of the observations of temperature and potential difference taken, as explained and illustrated by the specimen tables of observations, during a period of 15 minutes, for which the corresponding value of the flow was measured. In nearly all cases the observations were repeated during a second period of 15 minutes under conditions as nearly as possible the same, except for a slight diminution of the flow, due to the fall in the water level. The order of accuracy of the readings can be estimated by comparing the corresponding values of D for the two similar flows. The two values of D should agree, except that the falling-off of the flow tends to make the second value in each case slightly the larger when *d* is negative. In comparing the values it must be remembered that 3 in the fifth place of D corresponds to only 1 part in 100,000, with a heat supply of 24 watts and a rise of 8°. The differences seldom exceed 1 in 10,000, whereas with the method of mixtures it is very difficult to obtain an order of agreement of 1 in 1,000 in repeating an experiment under identical conditions.

The values of *d* as directly measured and expressed in the different series just given, I have plotted in fig. 17. From the smooth curve drawn so as to include the observations, I have taken the following values of *d* and calculated the corresponding values of J. These are summarized here (p. 250). The values of J are, of course, in absolute measure, and the values of *d* in terms of a thermal unit equal to 4·2000 joules, which occurs at 9° C. and 88°·5 C. The mean value of

J, 4·18876 joules, is exactly coincident with the values at 15°·7 and at 68° C. In selecting a thermal unit to which the values of the specific heat may be referred, it seems desirable to adopt one at a temperature which, if at the same time at a convenient part of the scale, may also represent the mean value over the whole range. Such a convenient point appears to be indicated at either 15° or 16° C. I propose, at the present time, to adopt the value at 16° C., and shall in consequence express the specific heat of water in terms of this unit, which is equal to 4·1883 joules, and which differs from the mean value by only 1 part in 10,000.

The following table (p. 252) includes the values of the specific heat of water in terms of a unit at 16°. No one simple formula can be fitted to the complete curve between 0° and 100° with any degree of accuracy, on account of the change which occurs at 37°·5, which is the point of minimum specific heat. Two formulæ can be fitted together, however, over the range with great accuracy. Between 5° and 37°·5 the expression representing the specific heat in terms of a unit at 16° C. is

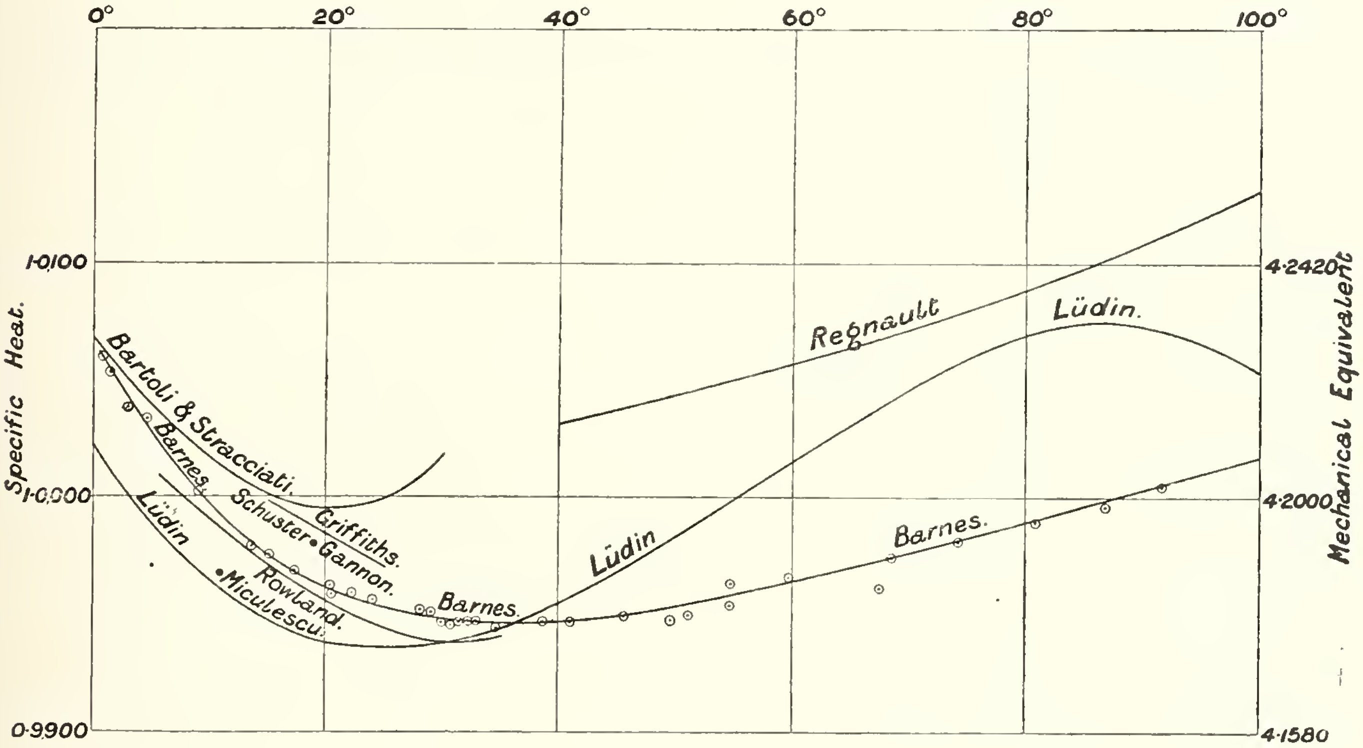

Fig. 17.

$$S_t = \cdot 99733 + \cdot 0000035\,(37\cdot 5 - t)^2 + \cdot 00000010\,(37\cdot 5 - t)^3.$$

The same expression reads above the minimum point, as far as 55°, in this form :

$$S_t = \cdot 99733 + \cdot 0000035\,(t - 37\cdot 5)^2 + \cdot 00000010\,(t - 37\cdot 5)^3.$$

At 55° and upwards the values diverge more and more from this formula, and follow a different curve. The slope of the curve above 60° is very nearly the same as the well-known formula of REGNAULT, but the rate of increase is very much smaller. The following expression, which is very nearly a linear relation, holds between 50° and 100°:

$$S_t = \cdot 99850 + \cdot 000120\,(t - 55^\circ) + \cdot 00000025\,(t - 55)^2.$$

These two formulæ I have represented in the last table in column 3. They represent the variation of the specific heat of water very clearly with the exception of the rapid increase at 0°, and are entirely independent of the values assigned to my electrical units. They can be changed to fit a unit at any other temperature by simply changing the constant term.

Since it would be a matter of great labour to determine the specific heat of superheated water, and since the variation curve of the specific heat shows no discontinuity as the boiling-point is reached at atmospheric pressure, this last formula may be said to hold with some claim to accuracy above 100° throughout the entire range covered by REGNAULT's experiments.

COMPARISON of Observed and Calculated Values.

Temperature.	Observed d.	Calculated d.	J observed.	J. calculated.
Series I. February to March, 1899.				
28·01	− ·00485	− ·00509	4·1796	4·1786
29·09	− ·00469	− ·00517	4·1803	4·1783
29·11	− ·00489	− ·00517	4·1795	4·1783
29·21	− ·00499	− ·00519	4·1790	4·1782
13·79	− ·00208	− ·00210	4·1913	4·1912
17·69	− ·00309	− ·00328	4·1870	4·1862
24·20	− ·00446	− ·00460	4·1813	4·1807
34·46	− ·00561	− ·00545	4·1765	4·1771
4·28	+ ·00330	+ ·00310	4·2138	4·2130
Series II. January 6–22, 1899.				
22·16	− ·00413	− ·00425	4·1827	4·1822
31·40	− ·00542	− ·00532	4·1773	4·1777
32·17	− ·00536	− ·00536	4·1775	4·1775
41·02	− ·00540	− ·00539	4·1773	4·1774
45·49	− ·00514	− ·00515	4·1784	4·1784
49·68	− ·00531	− ·00480	4·1777	4·1799
54·61	− ·00372	− ·00430	4·1844	4·1819
59·80	− ·00341	− ·00370	4·1849	4·1845
32·81	− ·00528	− ·00540	4·1778	4·1773
30·54	− ·00555	− ·00528	4·1767	4·1779

Comparison of Observed and Calculated Values—*continued.*

Temperature.	Observed d.	Calculated d.	J. observed.	J. calculated.
Series III. September 4–18, 1899.				
29·47	− ·00496	− ·00520	4·1792	4·1782
31·22	− ·00544	− ·00530	4·1771	4·1778
38·76	− ·00530	− ·00545	4·1777	4·1771
67·52	− ·00395	− ·00275	4·1834	4·1885
54·57	− ·00473	− ·00430	4·1801	4·1820
Series IV. October 14–19, 1899.				
28·77	− ·00493	− ·00515	4·1793	4·1784
28·52	− ·00497	− ·00510	4·1792	4·1786
Series V. October 27 to November 1, 1899.				
29·92	− ·00542	− ·00523	4·1772	4·1781
20·92	− ·00404	− ·00404	4·1830	4·1830
Series VI. November 3–29, 1899.				
20·18	− ·00383	− ·00384	4·1838	4·1839
17·09	− ·00310	− ·00310	4·1870	4·1870
20·13	− ·00397	− ·00383	4·1833	4·1839
20·45	− ·00420	− ·00400	4·1824	4·1832
15·71	− ·00254	− ·00270	4·1893	4·1887
8·66	+ ·00022	+ ·00020	4·2009	4·2008
1·35	+ ·00512	+ ·00560	4·2215	4·2235
2·68	+ ·00370	+ ·00430	4·2155	4·2181
29·43	− ·00497	− ·00520	4·1791	4·1782
51·02	− ·00513	− ·00470	4·1785	4·1803
Series VII. January 1–6, 1900.				
29·13	− ·00488	− ·00517	4·1795	4·1783
85·60	− ·00052	− ·00036	4·1978	4·1985
Series VIII. February 24 to March 21, 1900.				
32·26	− ·00521	− ·00535	4·1781	4·1776
74·05	− ·00189	− ·00189	4·1920	4·1920
91·55	+ ·00042	+ ·00042	4·2017	4·2017
80·38	− ·00117	− ·00110	4·1951	4·1954
68·21	− ·00262	− ·00270	4·1890	4·1887
Time of flow, 900 seconds automatically recorded.				

SUMMARY of the Specific Heat of Water from Smoothed Curve.

Temperature ° C.	*d.*	J.
5°	+ ·00250	4·2105
10	– ·00050	4·1979
15	– ·00250	4·1895
20	– ·00385	4·1838
25	– ·00474	4·1801
30	– ·00523	4·1780
35	– ·00545	4·1773
40	– ·00545	4·1773
45	– ·00520	4·1782
50	– ·00480	4·1798
55	– ·00430	4·1819
60	– ·00370	4·1845
65	– ·00310	4·1870
70	– ·00245	4·1898
75	– ·00180	4·1925
80	– ·00114	4·1954
85	– ·00043	4·1982
90	+ ·00025	4·2010
95	+ ·00090	4·2038
	Mean value	4·18876

VARIATION of the Specific Heat of Water in Terms of a Thermal Unit at 16° C. = 4·1883 joules.

Temperature ° C.	Observed values from curve.	Calculated values from formulæ.
5°	1·00530	1·00446
10	1·00230	1·00206
15	1·00030	1·00024
20	1·99895	0·99894
25	0·99806	0·99807
30	0·99759	0·99757
35	0·99735	0·99735
40	0·99735	0·99735
45	0·99760	0·99757
50	0·99800	0·99807
55	0·99850	0·99894
60	0·99910	0·99910
65	0·99970	0·99972
70	1·00035	1·00036
75	1·00100	1·00100
80	1·00166	1·00166
85	1·00237	1·00233
90	1·00305	1·00301
95	1·00370	1·00370
Mean value . .	1·00012	

Temperature Coefficient of the Radiation Loss.

It is not possible to obtain a very accurate measure of the temperature coefficient of the radiation correction from the present experiments. At the same time we may, from the different series covering different ranges of temperature, form some idea. During a series of experiments the radiation loss remained exceedingly steady, except that repeatedly after the calorimeter had returned from a high point the heat-loss was found to have been increased, but tended to return to its old value with lapse of time. On account of the slowness of the change, this occurred without producing any serious effect on the measure of the specific heat of the water. These changes were attributed to the effect of the small trace of occluded gases and vapour left in the glass vacuum-jacket. It is interesting in the case of Calorimeter C to trace the gradual alteration in the heat-loss, from series to series, during the time of the experiments.

All of the experiments made at a mean temperature of about 30° are given in the following table :—

Date.	Temperature.	*h* observed.	*h* corrected to 30° C.	Remarks.
February 20. .	29°·09	– ·04944	·05008	
,, 22. .	29·11	·04937	·05000	
March 2 . . .	29·21	·04965	·05021	
June 8 . . .	31·40	·05334	·05235	After trial experiment at 40°.
,, 9 . . .	32·17	·05282	·05138	
,, 20 . . .	32·81	·05429	·05230	,, an experiment at 60°.
,, 22 . . .	30·54	·05364	·05326	
September 4. .	29·47	·05352	·05389	,, experiments at 60° and 70°.
,, 6. .	31·22	·05518	·05432	
November 27 .	29·43	·05316	·05356	,, experiments at 0°.
January 1 . .	29·13	·05299	·05361	
February ·24. .	32·26	·05791	·05631	,, an experiment at 86°.

The values of the heat-loss per degree rise from the experiments on October 14 and October 18, with rises of temperature of 8° and 5° respectively, when the flat heating-wire was used, are :—

October 14	28·77	·05826	·05913
,, 18	28·52	·05870	·05975

These values show a decided increase in the heat-loss, but was due, no doubt, to the wire being in direct contact with the glass flow-tube of the calorimeter.

In regard to the temperature coefficient of the radiation loss, this may be calculated from the observations in any of the different series. Series II. is the most suitable, extending at different temperatures between 22° and 60°, over the middle of the range. The best average of the values of h given in this series is a line represented in the form

$$H_{t_1} = H_t + \cdot000708\,(t_1 - t),$$

where t is the temperature corresponding to the measurement of H_t, and t_1 is the temperature corresponding to the value of H_{t_1}. From further consideration of the changes in the value of h from the other series, this appears to represent the temperature change of the radiation not only for Calorimeter C, but for Calorimeter E, for the two determinations between 30° and 20°.

Taking the different values of Series II., we have, on tabulating the values of the heat-loss, both observed and calculated, and accepting the value at 22° for H_t in the expression given above, the following values :—

Temperature.	H observed.	H calculated.
22°·16	·04619	·04619
31·40	·05334	·05273
32·17	·05282	·05328
41·02	·05939	·05954
45·49	·06306	·06271
49·68	·06669	·06562
54·61	·06867	·06916
59·80	·07220	·07285
32·81	·05429	·05373
30·54	·05364	·05212

The values at 50° and 55° are not very consistent, but it will be remembered that the measurements at these points are not so trustworthy owing to the variation in the experimental conditions.

On returning to 30°, as seen by the last two readings, the value of h has increased in both cases. These two values were obtained with a rise of temperature of 11° and 5° respectively.

In regarding these large variations in the heat-loss from time to time, it must be again emphasised that the value of the specific heat of water, owing to the method of treatment, in no way depends on the absolute value, but only on the constancy throughout the period of an experiment.

To prove that this was so, the order of one of the experiments in Series VIII. at the higher points was reversed, and instead of taking the observations for the large flow first, as was followed for all the other experiments in this series, the observations for the small flow were obtained before those for the large flow. By this, any gradual change in the heat-loss during the time of the experiment would have produced an effect on the value of d in an opposite direction to the values given by the other experiments, and would have produced twice the error.

For Calorimeter E we have the two values at 29°·92 C. and 20°·92, which are

·05994 and ·05414.

These give for the coefficient of t in the radiation expression, the value ·000645 ; or, applying the first formula, the value of the radiation loss at 29°·92 from the value at 20°·92 = ·06051. This is within 6 parts in 10,000, and is comparable in size with the variations from the calculated values for calorimeter C. Doubtless there would be slight differences in the temperature coefficient of the radiation loss for different calorimeters with different degrees of vacuum.

In Series VI., for Calorimeter C, the decrease in the radiation loss takes place with decrease in temperature well in agreement with the other series until the experiments at 0°, when the value of the heat-loss is increased by nearly 3 parts in 1000. The two experiments at 1°·35 and 2°·68, both with the inflowing water at 0°·15 C., agree however very closely with the formula as regards the temperature change in h. The explanation of the apparent increase at these points is not altogether clear, but may be looked for in the very high value of the specific heat of water in the neighbourhood of 0°, which would influence the validity of the method adopted of eliminating the heat-loss from the large and small flows. A similar increase, although much smaller, was noticed in the heat-loss for the same calorimeter at 4°, in Series I. Owing to the small conduction effect at the inflow end of the calorimeter, the water in the large and small flows enters the flow-tube, where it is heated by the electric current, necessarily at a slightly different temperature, as was pointed out before.

Whereas this would produce no error at a part of the range where the value of d was not changing rapidly with the temperature, at the freezing-point, where a very small difference in temperature produces a large change in the value of d, it cannot be regarded as equal in the difference equations for the two flows for the same value of $d\theta$. Taking this into consideration, I have calculated the value of d, for the two experiments under consideration, by extrapolating for the value of the heat-loss from the curve for the other observations in the same series between 20° and 8°. By this means, the value of d for each flow in the same experiment differs nearly 1 part in 1000 in the extreme case. The following are the values so obtained :—

Date.	Mean temperature.	d large flow.	d small flow.
November 18 . . .	1°·35	+ ·0066	+ ·0073
,, 22 . . .	2·68	+ ·0051	+ ·0060
,, . . .	0·67	+ ·0072	

The mean value for each experiment is larger than the value calculated in the usual way, but for the same value of the flow the values of d are very consistent for the different experiments, and all give identically the same temperature coefficient of variation. For the ice experiment on March 24, of Series I., the value of h is very nearly in agreement with the extrapolated value from Series I. and II. Hence the above method of treatment for this experiment would give an almost identical value of d to the one obtained by eliminating the heat-loss from the two flows.

It is important to notice that the value of d in this experiment, obtained from the two flows, is more in agreement with the mean value of d for the other ice experiments, obtained by extrapolating from the values of h in Series VI. than for the values obtained by eliminating the heat-loss in the usual way. This points to the fact that the values given above are more nearly correct than the values given in the tables for the same experiments. If this be so, the indication is, that the value of the specific heat of water rapidly approaches an exceedingly high value at 0°, and in a remarkable way substantiates the suggestions made by ROWLAND in his memoir in regard to this. Further investigation is needed, however, in the neighbourhood of the freezing-point of water, before we can say that the specific heat of water approaches an infinite value as that point is reached. Such questions, as the continuity of the curve for under-cooled water, render the idea quite unthinkable at present. In view of this uncertainty, I have adhered to the lowest of the values of the specific heat given by these measurements, and have consequently included them both in the tables and plot. Even in this case, the change of specific heat with temperature is very rapid, and no effect is shown by the observations taken below 4° which would indicate a change at the point of maximum density. This, however, is not surprising when it is considered that the point of minimum specific heat in no way corresponds to the density curve for water.

Unfortunately, only one complete set of observations could be obtained with Calorimeter D, with the device for getting rid of stream-line motion, owing to a crack which, shortly after, started in the fine flow-tube inside the vacuum-jacket, and admitted water into the jacket. This calorimeter is of special interest, as the vacuum-jacket was supplied with a quantity of phosphorus pentoxide. The value of the heat-loss is larger than for any of the other calorimeters, including calorimeter A, which we exhausted ourselves to a vacuum of at least ·002 millim. of mercury. This indicated that the P_2O_5, instead of improving the vacuum as we at first thought, was really a disadvantage. The values of the heat-loss for the four calorimeters included in these measurements are, at 30° C. :—

Calorimeter A	1·8 millim. flow-tube	·0509 watt.
,, C	2 ,, ,,	·0500 ,,
,, D	2·8 ,, ,,	·0726 ,,
,, E	3·1 ,, ,,	·0600 ,,

Sec. 9.—*Relation of the Present Measurements to the Work of other Observers.*

It will hardly be necessary for me to enter into a lengthy discussion of the work of other observers, more especially as it has been already carefully done in the original memoirs of ROWLAND,* GRIFFITHS,† and SCHUSTER and GANNON.‡ Since the publication of these papers, however, a very elaborate and exhaustive series of experiments has been made by REYNOLDS and MOORBY§ to determine, by a direct mechanical method, using a Reynolds brake and a steam-engine, the energy required to raise water from a temperature slightly above freezing to the boiling-point. The value of the mean mechanical equivalent which they obtained is entitled to a great deal of weight, from the minute accuracy of their measurements and the careful discussion of possible sources of error.

It is fortunately possible, by means of the present series of experiments, on account of their great range, to connect the experiments of REYNOLDS and MOORBY with the experiments of ROWLAND, also by the direct mechanical method, which extends between 6° and 36° C. The absolute value of the mean mechanical equivalent obtained by REYNOLDS and MOORBY is 4·18320 joules, which is obviously less than the same mean value obtained in the present experiments (*i.e.*, 4·18876 joules) by as much as 0·132 per cent.

This discrepancy in the two results may be caused by an error in the present measurements at the extremities of the range, due to the neglecting of some correction factor which would cause the variation curve to increase less rapidly than it does; but it is far more probably due to an error in the value of one of the constants for the determination of the electrical or heat energy. Of this latter possibility the value of the Clark cell is still in doubt, although the value of the ohm is fairly well fixed in absolute measure, as defined in the 'British Association Report' of 1892. All of the thermal measurements are expressed in our two results to the same scale, so that the error resolves itself into an error in the E.M.F. of the Clark cell, which, as it enters into the equation for the determination of the electrical energy to the second power, has twice the effect. This has been already pointed out under the Section devoted to the Clark cell, where it was shown that if all the error between the value of the mean mechanical equivalent obtained by the direct mechanical method and the value obtained by the electrical method (assuming the Clark cell equal to 1·43420 volt and the international ohm equal to 1·01358 B.A. units) could be attributed to the Clark cell, the value 1·43420 would have to be

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[*] 'Proc. Amer. Acad.,' vol. 15, p. 75 (1879).

[†] 'Phil. Trans.,' A, vol. 184, p. 361 (1893).

[‡] 'Phil. Trans.,' A, vol. 186, p. 415 (1895).

[§] 'Phil. Trans.,' A, vol. 190, p. 300 (1898).

reduced to 1·43325 volt at 15° C. Such a reduction is necessary to bring my measurements into absolute agreement with REYNOLDS and MOORBY's result. This reduced value of the Clark cell is so nearly identical with the later absolute dynamometer measurements as to give a most remarkable, if not coincident, agreement between the electrical and mechanical units.

If we compare the value of the mean mechanical equivalent obtained by integrating the values obtained by ROWLAND between 6° and 36°, which have been recently corrected to the Paris Scale by a comparison of ROWLAND's thermometers with the Paris Scale, with the integrated value over the same range from the present experiments, we find the difference between ROWLAND's value, 4·1834 joules, and my value, 4·1872, in terms of the Clark cell value, 1·43420 volt, equal to ·091 per cent. This is a difference of only 1 part in 2000, as deduced from the comparison of the complete curve with REYNOLDS and MOORBY's result, a discrepancy which, if not within the limits of error of our several determinations, is relatively small considering the great range covered by these experiments. The reduced value of the Clark cell according to ROWLAND would be 1·43355 volt, which differs from the value according to REYNOLDS and MOORBY by only ·3 millivolt. Owing to the slight difference in the temperature coefficient of the specific heat between ROWLAND's values and my own, the agreement of our absolute values at any one temperature will be different at different temperatures. At 25° our measurements, when expressing mine in terms of REYNOLDS and MOORBY's, are almost exactly coincident; at 13° my value is lower than ROWLAND's by 1 part in 1000, but at 6° we are in agreement again.

Of the other direct mechanical determinations which have been made recently, we have the work of MICULESCU* in 1892, which is deserving of some mention. Although his work is by no means above criticism, as was clearly pointed out by SCHUSTER and GANNON in their paper, it is of interest as showing the kind of error which may occur between measurements by the direct method, which may be at the same time very carefully and accurately carried out. His value, which appears to be a mean value between 10° and 13°, is 4·1857 joules. ROWLAND's value at the same temperature, about 11° C., is 4·194, while my own in terms of REYNOLDS and MOORBY's value is 4·1903 joules, which, although less than ROWLAND's value, is larger than MICULESCU's.

Perhaps the most difficult part of the comparison of the present experiments with the work of other observers is in relation to the results obtained by the electrical method used by GRIFFITHS and SCHUSTER and GANNON. It is at once apparent from fig. 17 (p. 249) that my values are widely different to the values obtained by both these investigators, although expressed in the same values of the units used. The explanation might at once be looked for in an error in either my Clark cells or resistance standard; but if it is attributed to the Clark cells used in the present work, then the several sets of cells made at different times and from different

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* 'Ann. de Chimie,' vol. 27 (1892).

materials must all have involved the same error, always in the same direction. At the same time my cadmium cells must also have been in error to exactly the same amount and in the same direction, in order to give a ratio to my Clark cells identical with that obtained for the cells at the Reichsanstalt, which have been compared directly with the Cavendish standards used by GRIFFITHS. If the error is attributed to the value of my resistance, then we must reject the signed certificates of 11 standard ohms from the Electrical Standards Committee of the British Association, as well as a true ohm from the German Reichsanstalt, as being in error. It is far more likely that the values of my constants agreed to 1 in 10,000 with those used by GRIFFITHS and by SCHUSTER and GANNON respectively, and that the difference in our results is to be attributed to some constant source of error as yet undiscovered in our methods of calorimetry. However, the values obtained by these observers using the same method differ by nearly 1 part in 1000 from each other, which is not so good an agreement as exists between the measurements of REYNOLDS and MOORBY, ROWLAND, and myself, using widely different methods. At the same time the method used by ROWLAND is essentially the same as that used by GRIFFITHS, and is subject to similar calorimetric errors. Owing to the great care and trouble taken by GRIFFITHS to carry out his experiments, it is difficult to see where the difference between our two results can be. Moreover, the temperature coefficient obtained by GRIFFITHS, although a linear one over the range of his experiments, is almost exactly a mean to the curve in my experiments over the same range.

The individual observations by the present method agree very well amongst themselves, but although it may be correctly said that the mere repetition of observations does not necessarily eliminate errors of experiment, yet it is possible to vary the conditions so thoroughly by the continuous flow method of calorimetry as to leave little room for any systematic error. In addition to varying rise of temperature, water flow and electric current, the present measurements have been made to the same order of accuracy by varying the shape and resistance of the electric heating conductor, by using flow-tubes of different sizes, and by employing calorimeters with different values of heat-loss, this last being identical to the cooling correction in the older methods of calorimetry.

It may be questioned whether the separate determination of the cooling effect by special experiment and its subsequent application as a correction to calorimetric experiments, can be relied on to an accuracy greater than 1 part in 1000. The variations in the radiation loss measured from time to time in the present experiments are so large that unless it had been separately determined and eliminated from the final result for each experiment, large errors would have been introduced. Indeed, it appears that the cooling correction is a far more uncertain factor in methods of calorimetry than has been hitherto sufficiently realized. All questions, however, relating to the absolute values of the standards used in the present results in no way affect the accuracy of the relative results, as regards the variation of the specific heat of water.

It is interesting to compare the absolute value of the Clark cell obtained by assuming GRIFFITHS' absolute value of the mechanical equivalent at 15°, and to express my mean value in terms of his experiments. By so doing the absolute value becomes 4·1975 joules, which differs from REYNOLDS and MOORBY'S value by ·34 per cent, or, assuming the error to be due to the Clark cell, equal to ·17 per cent. on 1·4342, which would reduce this value to 1·4318 volt at 15°. This, however, even referred to the lowest of the latest absolute determinations, seems to be too low a value, by as much as 1 millivolt, to be reconciled with the most probable true value of the Clark cell.

It might be thought advisable, in view of the uncertainty in the electrical units, to accept ROWLAND'S corrected values and express the present series of experiments in terms of his results, which would give a mean value quite sufficiently in accord with REYNOLDS and MOORBY'S mean determination. This could be done either from the integrated value over the range of his experiments, which would tend to eliminate errors in his method at the two extremes of the range, or by accepting his absolute value at a temperature where he could obtain the most accurate measurement. The present experiments over the range between 4° and 60° have already been published ('B.A. Report,' 1899), and were referred to ROWLAND'S absolute measurement at 20° C., but I think that the uncertainty in the thermometric standards used by ROWLAND at that time do not warrant an accuracy greater than 1 part in about 2000, and that the mean result over the complete range of temperature referred to REYNOLDS and MOORBY'S determination is more near the truth.

The value of the mean specific heat between 0° and 100° C., 4·232 joules, obtained by DIETERICI ('Wied. Ann.,' vol. 33, p. 417, 1888) in terms of the electrical units, is obviously too large to be accounted for by an error in the electrical units, or to be reconciled with the direct determination of REYNOLDS and MOORBY. The curve obtained by BARTOLI and STRACCIATI ('Beiblätter,' vol. 15, p. 761, 1891) for the variation of the specific heat of water between 0° and 30° by the method of mixtures in terms of a thermal unit at 15° C. passes through a minimum point at 20° C., above which it shows a far too rapid increase in the specific heat to be reconciled with measurements extending as far as 100° C., unless the values pass through a maximum point.

In 1895, LÜDIN (Dissert. Zürich and 'Beiblätter,' 1897) determined the variation of the specific heat between 0° and 100° by the method of mixtures and showed a minimum point at 25°, but also a maximum point at about 80°. His results are in good agreement with the present series of experiments over a range 0° to 25°, as shown in fig. 17 (p. 249), where I have plotted them in terms of a mean unit between 0° and 100° C. The excessively low minimum point shown by BARTOLI and STRACCIATI and by LÜDIN respectively, both using similar methods, suggests a source of error common to the two. The limitation of the method of mixtures is, however, too well known to give the complete variation curve to any degree of accuracy.

I have arranged in the following table the absolute values of the specific heat of water every 5 degrees between 0° and 100° from my measurements for a value of the Clark cell equal to 1·43325 int. volts, and assuming the true ohm as correct, which gives the values in terms of the mechanical units in Reynolds and Moorby's experiments. For comparison, I also include the measurements of Rowland and Miculescu, and those of Griffiths and of Schuster and Gannon, to the same value of the Clark cell.

The minimum point of the specific heat, which Rowland found at 30°, really occurs at about 37°·5, but this was considered as likely by Rowland, for he says in his memoir (p. 199), "The point of minimum cannot be said to be known, though I have placed it provisionally between 30° and 35° C., but it may vary much from that." And in another place (p. 200) he says, "There may be an error of a small amount at that point (30°) in the direction of making the mechanical equivalent too great, and the specific heat may keep on decreasing to even 40°."

Absolute Value of the Thermal Capacity of Water in Joules per Calorie for Different Temperatures between the Freezing and Boiling-points, expressed in terms of a Clark Cell Value 1·43325 international volts at 15° C., and the Value of the true ohm 1·01358 B.A. Units.

Temperature.	Barnes.	Rowland.	Miculescu.	Griffiths.	Schuster and Gannon.
° C.					
5	4·2050	4·206	—	—	—
10	4·1924	4·196	4·1857	—	—
15	4·1840	4·188	—	4·1927	—
20	4·1783	4·181	—	4·1871	4·1874
25	4·1746	4·176	—	4·1816	—
30	4·1725	4·174	—	—	—
35	4·1718	4·175	—	—	—
40	4·1718	—	—	—	—
45	4·1727	—	—	—	—
50	4·1743	—	—	—	—
55	4·1764	—	—	—	—
60	4·1790	—	—	—	—
65	4·1815	—	—	—	—
70	4·1843	—	—	—	—
75	4·1870	—	—	—	—
80	4·1899	—	—	—	—
85	4·1927	—	—	—	—
90	4·1955	—	—	—	—
95	4·1983	—	—	—	—
Mean . . .	4·18326				
Reynolds and Moorby's value . . . 4·18320.					

ROWLAND's values are those given by W. S. DAY ('Physical Review,' vol. 7, p. 193, 1898), corrected to the Paris scale. GRIFFITHS' values are those quoted by SCHUSTER and GANNON in their paper. At 20° and 25° GRIFFITHS' own temperature coefficient is used. SCHUSTER and GANNON's value is given in their paper at a temperature of 19°·1 C. I have reduced it to 20° by the temperature coefficient obtained in my experiments, which is very similar to GRIFFITHS' over a short range. It will be seen that the values of GRIFFITHS and SCHUSTER and GANNON are brought into closer agreement when corrected to the same value of the Clark cell.

Extrapolating for the values of J above 100° C. we obtain from the formula

$$J_t = J_{55}\,(1 + \cdot000120\,(t - 55^\circ) + \cdot00000025\,(t - 55^\circ)^2)$$

the following values :—

Temperature Centigrade.	J. (J_{55} = 4·1819).	J. (J_{55} = 4·1764).
°		
110	4·2127	4·2072
120	4·2190	4·2135
130	4·2255	4·2199
140	4·2321	4·2265
150	4·2390	4·2334
160	4·2461	4·2405
170	4·2534	4·2479
180	4·2610	4·2554
190	4·2687	4·2631
200	4·2767	4·2711
220	4·2931	4·2875

A glance at the complete curve for the variation of the specific heat of water with temperature reveals at once a most interesting relation. Why should the values drop so rapidly from the freezing point and at 37°·5 the complete character of the curve change? There is no discontinuous or sudden change occurring at this point that is indicated either in the outward physical state or in the density of the water, nor do we see any connection between the curious anomaly in the density curve at 4° C. and the specific heat at that point. It is evident we have to do here with a new, and as yet unexplained, phenomenon.

The ideas advanced by ROWLAND in this connection are not, it seems to me, altogether correct when he says :—"However remarkable the fact may be, being the first instance of the decrease of the specific heat with rise of temperature, it is no more remarkable than the contraction of water to 4°. Indeed, in both cases the water hardly seems to have recovered from freezing. The specific heat of melting ice is infinite. Why is it necessary that the specific heat should instantly fall, and then recover as the temperature rises? Is it not more natural to suppose that it continues to fall even after the ice is melted, and then to rise again as the specific heat approaches infinity at the boiling-point? And of all the bodies which we should select as probably exhibiting this property, water is certainly the first."

The identification of latent heat and specific heat which ROWLAND makes when he says "the specific heat approaches infinity at the boiling-point" and that "the specific heat of melting ice is infinite" is hardly tenable. Moreover, the character of the curve as the boiling-point is reached shows no indication of approaching an infinite value, and is entirely independent of the pressure which determines the boiling-point. The idea of an infinite value of the specific heat at 0° can hardly be reconciled with the idea of the continuity of the curve for under-cooled water. It is highly probable that the specific heat approaches an exceedingly high, but measurable value, as the freezing point is reached, and that the character of the curve below the minimum point indicates an entirely different physical state of the water to that above. The law governing the variation of the specific heat with temperature above 37°·5 is directly in accord with what knowledge we already possess of other substances, and of what our preconceived ideas might lead us to expect.

We can draw no analogies from other liquids, since our knowledge, with the exception, perhaps, of mercury, is now only exceedingly meagre. As the temperature is reduced below 37°·5, may it not be that the water commences to anticipate the formation of the solid phase, even before 0° is reached, and that the rapid increase in specific heat indicates the effort being made to resist parting with the internal energy necessary for formation of ice, and to form a more and more close aggregation? If this be true, it suggests at once the same effect for other liquids. Can we expect to find a minimum point in the specific heat curve for other liquids in the light of the above considerations? I can do no more than suggest such a possibility at present.

INDEX SLIP.

Reynolds, Osborne, and Smith, J. H.—On a Throw-Testing Machine for Reversals of Mean Stress. Phil. Trans., A, vol. 199, 1902, pp. 265–297.

Smith, J. H., and Reynolds, Osborne.—On a Throw-Testing Machine for Reversals of Mean Stress. Phil. Trans., A, vol. 199, 1902, pp. 265–297.

Stress, repeated—Variation of Limiting Range with periodicity of Reversals.
Reynolds, Osborne, and Smith, J. H.
Phil. Trans., A, vol. 199, 1902, pp. 265–297.

Steel, Mild and Cast; Breaking Stress for repeated Stresses of high periodicity. Restoring effect of a period of rest.
Reynolds, Osborne, and Smith, J. H.
Phil. Trans., A, vol. 199, 1902, pp. 265–297.

IV. *On a Throw-Testing Machine for Reversals of Mean Stress.*

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Late Fellow of Victoria University, 1851 *Exhibition Scholar.*

Received March 5,—Read March 20, 1902.

PREFACE.

Although this research is a joint undertaking, I wish to point out that except for the idea and general design of the apparatus all the work in carrying out the design has been done by Mr. Smith, who has made all the calculations and superintended the execution of all the work which he has not executed himself. This undertaking occupied some two years, being not only novel but also approaching fundamental limits which, if passed, would have wrecked the undertaking. He has also made all the tests. Thus whatever success we have had is entirely owing to his knowledge, skill, and perseverance. In saying this, I do not wish to imply that I have not taken great interest in the work, for, on the contrary, I have watched it with interest and admiration, particularly the acumen he has shown in arranging his tests and interpreting the results, by which he has obtained evidence of two general laws which had not hitherto been suspected, one being that under a given range of stress the number of reversals before rupture diminishes as the frequency increases, and the second that the hard steels will not sustain more reversals with the same range of stress than the mild steels when the frequency of the reversals is great.

Owens College,
February 19*th*, 1902.

OSBORNE REYNOLDS.

Contents.

Historical Summary.

In 1860, Sir W. **Fairbairn**, using a riveted girder, carried out a series of experiments, which seem to be the first recorded experiments on Repeated Stress.

From 1860 to 1870, **Wöhler** carried out his laborious and valuable researches on the Fatigue of Wrought Iron and Steel. From his results published in the 'Zeitschrift für Bauwesen,' Berlin, the following important points may be deduced :—

(1) That these materials (wrought iron and steel) will rupture with stresses much *below* the statical breaking stress, if such stress be repeated a sufficient number of times.

(2) That within certain limits, the *range* of stress, and not the maximum stress, determines the number of reversals necessary for rupture.

(3) That as the range of stress is diminished, the number of repetitions for rupture increases.

(4) That there is a *limiting range* of stress for which the number of repetitions of stress for rupture becomes infinite.

(5) That this limiting range of stress diminishes as the maximum stress increases.

Wöhler conducted his experiments on bars of wrought iron and steel, subjecting them to torsional stress, bending stress, equal and opposite bending stresses, and direct tension, with repetitions ranging from 60 to 80 per minute.

In 1874, **Spangenberg** repeated **Wöhler's** experiments, using **Wöhler's** machines, and obtained similar results, also published in the 'Zeitschrift für Bauwesen.' In 1874 also, **Gerber**, in the 'Zeitschrift für Baukunde,' München, suggested the following formula, as representing the results of **Wöhler's** experiments :

$$f\,(\text{max}) = \tfrac{1}{2}\Delta + \sqrt{(f^2 - n\,\Delta f)},$$

where $f\,(\text{max})$ = the maximum stress,

$f\,(\text{min})$ = the minimum stress,

f = the statical breaking stress,

Δ = the range of stress $= f\,(\text{max}) \pm f\,(\text{min})$,

and n = a constant.

Accounts of other experiments and theories bearing on this subject, are given by the following :—

Launhardt (Zeitschrift des Architecten und Ingenieur-Vereins, Hanover, 1873).
Lippold (Organ für die Fortschritte des Eisenbahnwesens, Wiesbaden, 1879).
Professor **Mohr** (Der Civil-Ingenieur, Leipzig, 1881.)

Sir B. BAKER in 1886 gave the results of a series of experiments on iron and steel (*Am. Soc. Mechanical Engineers*), which were obtained with machines similar to WÖHLER's, the bars being rotated in one set of tests and subjected to bending in the other sets, the repetitions taking place 50 to 60 times per minute.

About the same time BAUSCHINGER* published his important memoir on the "Variation of the Elastic Limits," in which it is shown that when the elastic limit in tension is raised, the elastic limit in compression is lowered, and that by subjecting a material to a few alternations of equal stresses, the elastic limits tend towards fixed positions, in which positions he called them the *natural* elastic limits. BAUSCHINGER then proceeded to explain the results obtained by subjecting material to repeated stresses, by showing that the limiting range of stress coincided with the difference of the two elastic limits.

Objects of the Research.

The present research, which was carried out in the Whitworth Engineering Laboratory of the Owens College, was undertaken at the suggestion of Professor OSBORNE REYNOLDS, who proposed an investigation of "repeated stress" on the following lines:—(1) The stress should be direct tension and compression; and (2) of approximately equal amounts, such tension and compression being obtained by means of the inertia force of an oscillatory weight; (3) the rapidity of repetitions should be much higher than in the experiments of WÖHLER, SPANGENBERG, BAUSCHINGER, and BAKER, in fact, ranging as high as 2000 reversals per minute. The importance of these points will be seen from the following considerations:—

(1) By far the greater number of experiments on "repeated stress" have been carried out on bars subjected to bending, the ordinary formula for stress in a bent bar being used to calculate the stress at breaking, that is, in such experiments it has been assumed that the distribution of stress at the breaking-down point is the same as for an elastic bar. Calculations on this assumption are not expected to give the tensile strength of a material for an ordinary cross-breaking experiment. This difficulty is completely overcome, and no such assumptions are necessary, when the stresses are direct as in the present work. The (direct) stress in a bar of metal could easily be obtained by having one extremity rigidly connected to a part of a machine having a known periodic motion, the other extremity being attached to a known weight.

(2) The tensile stress being in all experiments nearly equal to the compressive stress, the elastic limits would, as shown by BAUSCHINGER, soon be changed to their *natural* positions, and the range of stress for unlimited reversals would be this natural elastic range. If then, the limiting range coincides with the natural range it will be constant whatever the rate of reversals. The author considered this point an interesting one, and it will be found that most of the tests recorded in this paper

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* 'Mittheilungen aus dem Mech. Techn. Laboratorium in München,' 1886.

were carried out in such a way as to find the variation of the limiting range of stress as the rapidity of such reversals increased. The apparatus to be described shortly was most convenient for such enquiry, since both the speed and the oscillatory weight could be easily adjusted.

(3) Quite apart from the point mentioned in the last paragraph, the importance of extending the experiments to high speeds—in view of the extensive use in recent times of high speed machinery—is too obvious to need comment.

Short specimens of small diameter (see fig. 4), had to be used throughout, otherwise the apparatus would have been inconveniently heavy, and for this reason any subsequent work on the statical strength and the elastic properties of specimens which had been subjected to repeated stress, could not be done.

Method of Applying the Stress.

A weight is supported vertically by means of the specimen to be tested, and the upper part of the specimen receives a periodic motion in a vertical direction by means of a crank and a connecting rod. The inertia of this weight gives a tension at the bottom end, and a compression at the top end of the stroke, the change from tension to compression being gradual. The specimen and parts are guided by suitable bearings placed in a vertical direction. The motion was made vertical in order to reduce the friction of the bearings to a minimum. The stresses can be changed by varying the diameter of the specimen, the load, and the speed of revolution of the crank. In order to enable one to calculate the stresses in the specimen, the centre of the crank shaft must be at rest, and the crank must move with uniform angular velocity. These conditions are obtained when the crank shaft is driven by a constant turning effort, if the moving parts of the machine are balanced, and if at the same time the total energy of the moving parts is invariable. The apparatus was therefore designed to satisfy these conditions as approximately as possible (see pp. 270 to 272).

The Apparatus.

On examining the drawings (figs. 1 and 2) of the testing machine, which show the working parts, it will be seen to consist of a cast-iron standard having two brass bushed bearings in its upper part. In these bearings a shaft, 4 inches diameter at the front end, and 2 inches diameter at the back end, revolves, driven by a stepped pulley keyed to this shaft at the back part of the machine. The standard is mounted upon a heavy cast-iron bed-plate (weight, 14 cwts.), not shown in the drawings.

The front end of the shaft is cranked, the crank pin being $1\frac{1}{2}$ inch diameter, 2 inches long, and throw $\frac{1}{2}$ inch, and a connecting rod of peculiar form is coupled to the crank pin. One part of this connecting rod gives an oscillatory motion in a vertical direction to the sliding pieces directly below the crank shaft, which pieces

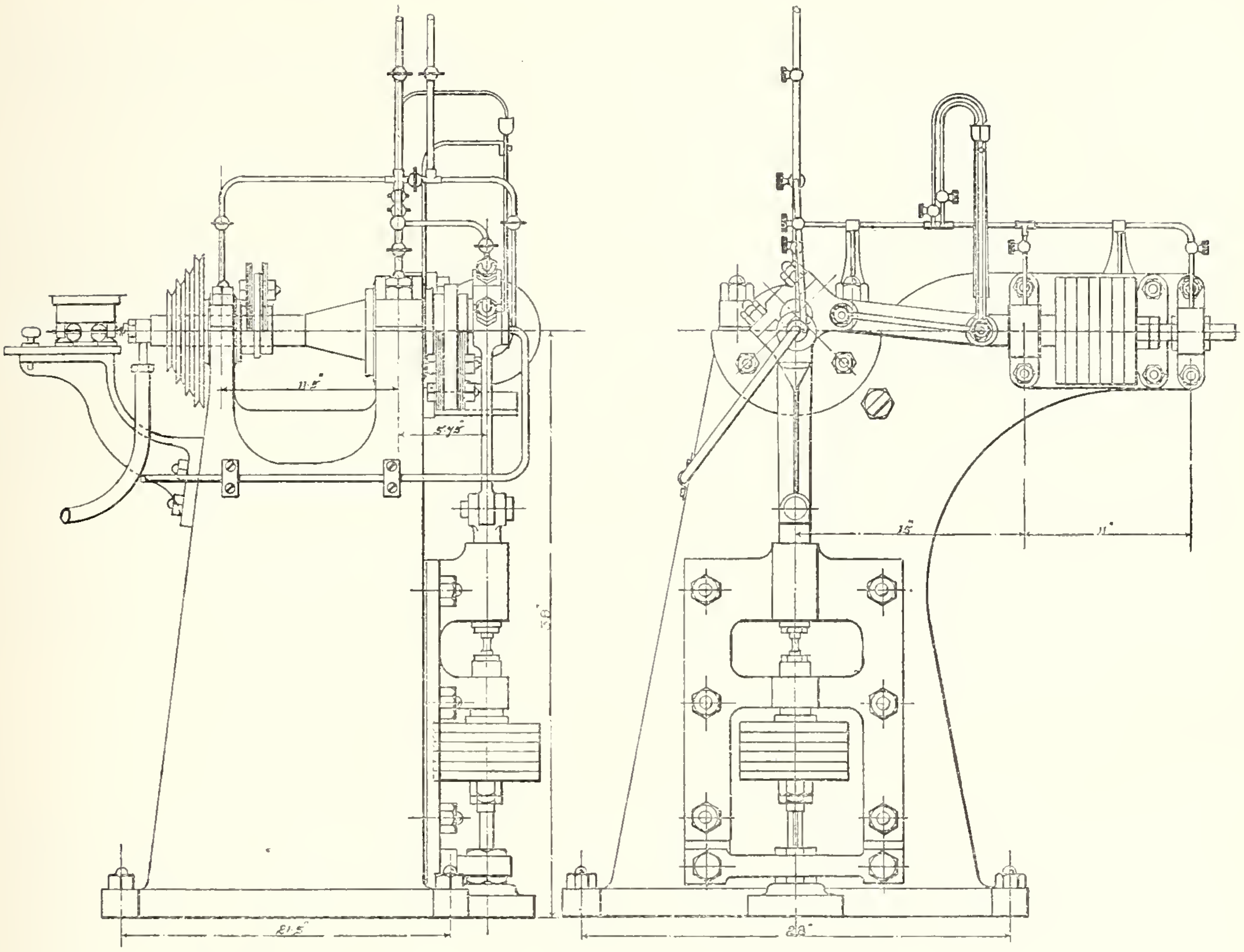

Fig. 1.

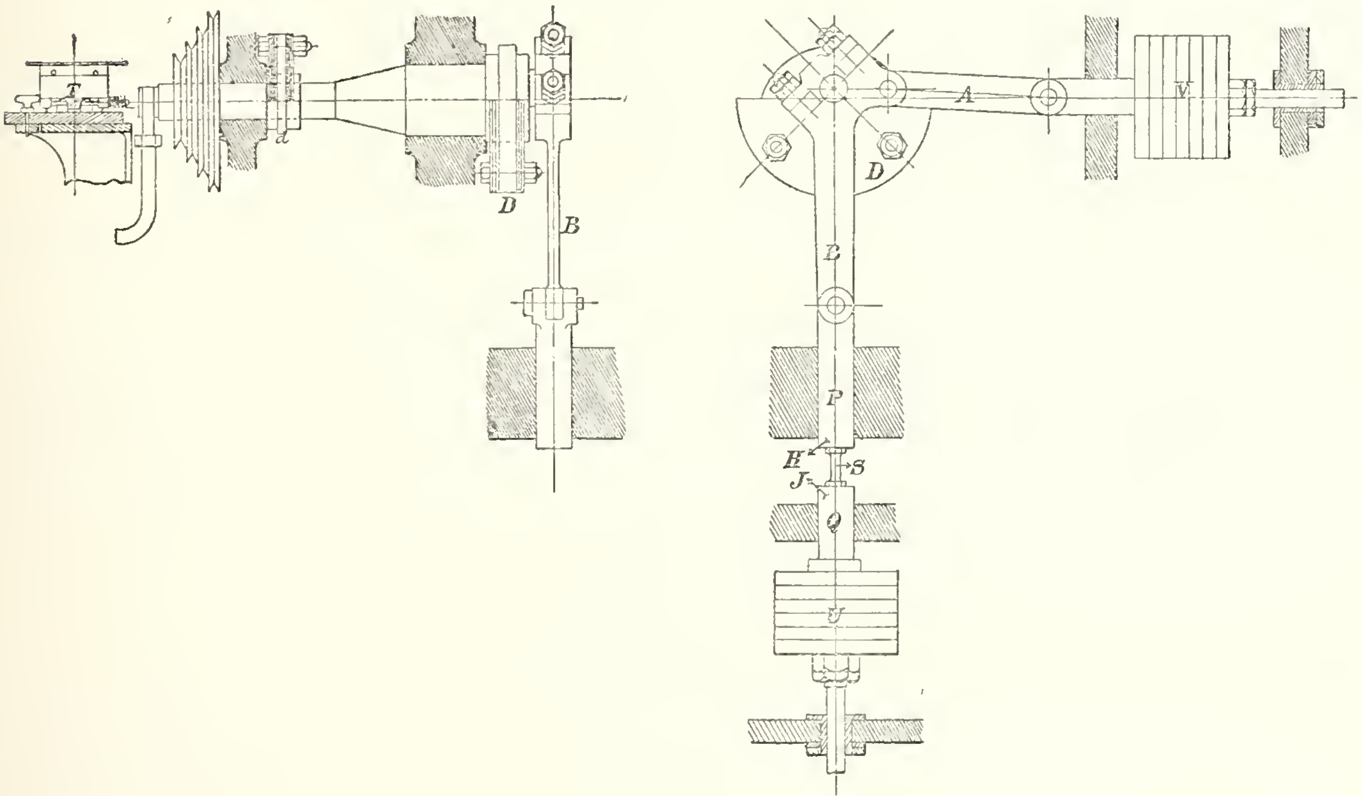

Fig. 2.

include the specimen to be tested. A pin in this connecting rod at the level of the crank shaft gives, by means of a second rod, an oscillatory motion to horizontal sliding pieces, introduced as will be seen later (p. 270) for the purpose of having the energy of the moving parts invariable.

The two parts P and Q of the vertical sliding pieces are connected by means of the specimen S, which is to undergo the test. The chucks H and J for holding the specimen were chased out internally to $\frac{3}{4}$-inch Whitworth thread, and the specimen was locked by means of two lock-nuts, one at each end. The specimen was prevented from rotating by means of a key placed in the lower bearing of the vertical sliding piece, which fitted accurately in a keyway cut in the moving spindle. The lower bearing was bushed to allow of adjustment, and a suitable locking arrangement was provided for it.

All the working parts were well made and exceptionally strong, of mild steel, tensile strength 24 tons per square inch; the pins in the connecting rod were all casehardened and afterwards ground to fit. The greater part of the tool work was done by the author in the College Laboratory.

Energy of the Parts.

The horizontal sliding piece was introduced in order to make the energy of the moving parts constant. Since the vertical connecting rod is 24 times, and the horizontal connecting rod 18 times, the throw of the crank, the motions of both sliding pieces will be very approximately simple harmonic motions, and, as both these pieces receive their motion from the same crank pin, the velocity of one will vary as the *sine*, and the other as the *cosine* of the angular displacement of the crank. The sum of the squares of their velocities will be constant. The kinetic energy of the parts will thus be constant if the total mass moving in the horizontal direction is equal to that moving in the vertical direction.

The masses of the parts were adjusted to satisfy this condition in the following manner:—The connecting rod and the spindles were weighed in the two positions shown in fig. 3.

Firstly, the shorter connecting rod A was supported horizontally and the load on the crank pin weighed; secondly, the longer connecting rod B was supported horizontally and the weight on the crank pin again taken. The masses of these parts were then adjusted until the loads on the crank pin were the same in the two cases.

The Balancing of the Machine.

Having adjusted the masses of the horizontal and vertical sliding pieces, it was now possible to balance these parts by placing a suitable mass diametrically opposite to the crank pin. This balance weight was made in the form of a steel eccentric D (fig. 2), $8\frac{1}{2}$ inches diameter, ·7 inch thick, and throw $1\frac{1}{4}$ inches, and was keyed to the shaft as near as possible to the crank pin.

This arrangement introduces an unbalanced couple in a plane passing through the centre line of the crank shaft and rotating with the shaft, and to balance this couple a smaller eccentric *d* (fig. 2) of diameter $5\frac{1}{2}$ inches, thickness $\frac{1}{2}$ inch, and throw 1 inch was placed near to the far end of the shaft with its centre in the axial plane passing through the crank pin.

So far then—neglecting the obliquity of the connecting rods, which were respectively 24 and 18 times the throw of the crank—the unloaded machine was balanced, and the kinetic energy of the parts was constant.

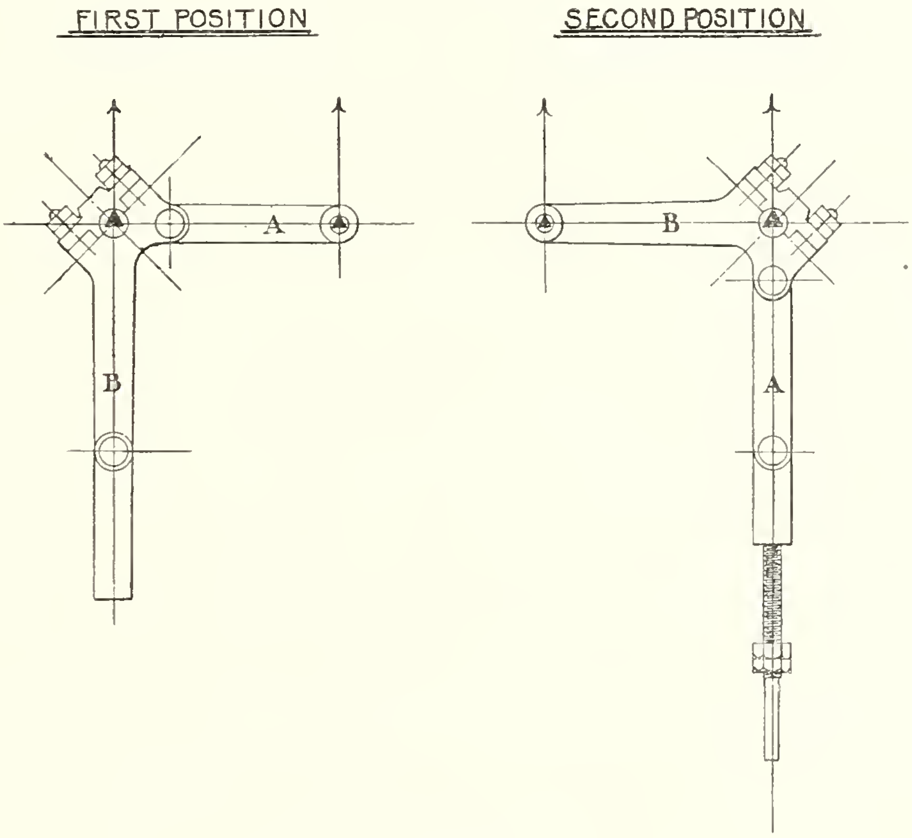

Fig. 3.

In loading the machine the system of weights used was so designed that when one cast-iron weight of $6\frac{1}{4}$ pounds was added to each of the oscillating pieces (U, V, fig. 2), and one semicircular $\frac{1}{16}$-inch steel plate was added to each side of each eccentric balance weight (D and *d*) the machine was still balanced. It was necessary to use the two balance weights to each eccentric (one on each side) in order to keep the plane of the unbalanced force due to each pair in a constant position, that is, in the central plane of the eccentric perpendicular to the shaft. Fig. 2 shows the working parts of the machine fully loaded.

To prevent any vibration from being transmitted to the building when the machine was running unbalanced, and to hold the machine in position, the bed-plate was supported by four spiral springs (made of $\frac{1}{2}$-inch steel of square section), 3 inches diameter, which were fitted into cases specially cast on the under side of the bed-plate for them, their other extremities being sunk into the floor of the laboratory. The machine was mounted on the bed-plate in such a manner as to bring the vertical line of the oscillating piece into the centre line of the bed-plate, and about 3 cwts. of cast-iron was then bolted to the inside of the bed-plate, and its position adjusted so as to bring the surface horizontal.

The machine was driven from the countershaft by means of a $\frac{3}{8}$-inch rope and large stepped grooved pulley, 30 inches diameter, a movable pulley being used to adjust the tension of the driving cord.

At the left side of the bed-plate there was attached a speed indicator designed and constructed by Mr. T. Foster, Mechanical Expert in the Whitworth Engineering Laboratory. The form of the indicator is simple, the speed being indicated by the rise of water in a tall glass tube due to the "centrifugal force" produced by setting it in rotation by means of a spindle driven by the machine. The author is indebted to Mr. Foster, not only for this, but for many valuable suggestions and many excellent pieces of his workmanship during the construction of the apparatus.

A central gunmetal spindle, driven from the crank shaft by a small gut band, has attached to it four radial vanes which revolve in a cylindrical brass box filled with water. A glass tube rising vertically is connected to the lower part of the case, and has a scale attached which is graduated by means of a revolution-counter to measure revolutions per minute. The case containing the water was arranged so that the amount of water used could be accurately regulated. Coloured water was first used, but it was found better to use pure water as the colouring matter was deposited on the tube, and after a few weeks made the taking of readings difficult.

In addition to this, at the back end of the machine a cast-iron bracket is bolted to the standard. This has its upper surface planed, and on it a small table having a revolution-counter (T, fig. 2), attached to it. The table slides on the surface, being guided so as to allow the counter to pass in and out of gear with the end of the crank shaft. A steady pin was used to hold the counter in its different positions.

A lead buffer is used to receive the blow from the vertical oscillatory weight when the specimen breaks. Two cast-iron pieces F and G (fig. 5, p. 279), keep the buffer central and are so arranged that when F is lifted G can be removed. A conical piece of lead is inserted in the centre of the piece F, and is directly under the vertical spindle. The pieces of lead can easily be replaced, and it was found necessary to replace them after every three or four tests.

Method of Lubrication.

A great amount of difficulty was experienced in supplying the oil to the various bearings. A very thick oil was used for the crank pin, and an ordinary machine oil for the other parts. In the final arrangement of the apparatus, the oil was supplied from two large glass vessels supported by brackets fixed to the wall behind the machine. The oil was led by means of two $\frac{3}{8}$-inch brass pipes to the machine, one pipe being arranged to feed into a brass cup at the extremity of the crank pin, the other having a number of branches passing to the various bearings in the upper part of the machine.

The brass cup supplies the oil to the crank pin by centrifugal force, by means of a hole passing along parallel to the centre line of the shaft and then at right angles into the crank pin bearing. The two pins in the horizontal connecting rod were supplied with oil from two vertical pipes having cups to receive the oil at their upper extremities, which pipes are connected together and oscillate about a pin supported by a bracket attached to the frame of the machine. From one pipe the oil is led directly up the centre of the pin connected to the horizontal sliding piece, and from the other the oil is led to the same pin but passes along a pipe attached to the connecting rod to the pin at the other end of the rod.

Sheet iron shields are placed about the revolving parts, and these collect the oil thrown off, carry it down the vertical rod, and allow it to drain into a cup and pipe for carrying the oil so drained to the lower pin of this rod. The bearing of the vertical sliding piece, above the load, receives the oil drained from the upper parts of the machine; the bearing below the load receives the oil from passages cut in the sliding spindle through which the oil passes on its downward course. The crank shaft bearings and the horizontal sliding piece bearings have each a separate oil supply pipe.

A sheet iron trough is inserted between the frame of the machine and the bed-plate to catch the oil. The oil is taken out of the troughs, passed through a filter, and again used. The thick oil was used for nothing but the crank pin for some time, but, owing to the mixing of the oils in the lower trough, the oil all became gradually of a heavy variety, so that in about a few months the same oil was used for all the bearings.

The machine, it was found, worked well after a few months' running, but on changing from slow to high speeds, or *vice versâ*, a little trouble was always experienced owing to the bearings heating. To help to keep the crank shaft bearings cool,—as it was these bearings which heated most easily,—a hole was drilled right through the whole length of this shaft, and a brass junction was specially made for the back end; to this junction an india-rubber pipe conveying a stream of water was connected. The water passed along the hole in the crank shaft to the front of the machine, where, on passing out, it was received by a pipe of larger diameter, through which it was drained away.

Determination of Stress.

If W is the weight below the specimen, R the radius of the crank, L the length of the vertical connecting rod, ω the angular velocity of the crank pin, and Δ the area of the specimen, then the compressive stress in the specimen at the upper end of the stroke is equal to

$$\frac{W\,\omega^2\,R}{g\,\Delta}\left(1-\frac{R}{L}\right)-\frac{W}{\Delta},$$

and the tensile stress at the lower end of the stroke to

$$\frac{W\,\omega^2\,R}{g\,\Delta}\left(1+\frac{R}{L}\right)+\frac{W}{\Delta}.$$

The range of stress is equal to the sum of these, or is equal to

$$2\,W\,\omega^2\,R \div g\Delta.$$

The values of W, the weights of the vertical loads used below the specimen, were determined to one hundredth of a pound, and were as follows:—

Spindle and lock-nut	6·15	pounds.
,, lock-nut, and one weight	12·42	,,
,, ,, ,, two weights	18·69	,,
,, ,, ,, three ,, ...	24·96	,,
,, ,, ,, four ,, ...	31·23	,,
,, ,, ,, five ,, ...	37·50	,,
,, ,, ,, six ,, ...	43·77	,,

The error in the determination of the stress due to the maximum error in the estimation of these weights would not in any case exceed ·3 per cent.

The throw of the crank was measured to a ten-thousandth of an inch, the value obtained being ·5067 inch. The maximum error in this measurement would not affect the stress by more than ·1 per cent.

The areas of the specimens were determined by finding their diameters by means of an ordinary micrometer gauge which was graduated to ten-thousandths of an inch. Assuming that the greatest error in actual measurement would not be more than three ten-thousandths of an inch, then the error from this cause for a specimen $\frac{1}{4}$ inch diameter would not exceed ·25 per cent.

It is thus seen that the errors incurred in the estimation of W, R and Δ are negligible.

There are three sources of errors in the estimation of the angular velocity. They are—

(1) The variation due to fluctuation in the energy of the parts;

(2) The variation due to fluctuation of the velocity of the engine in a cycle; and

(3) The variation due to the fluctuation of velocity over a long interval arising from the difficulty of regulating the motive power.

(1) To determine the extent of the variation due to the first cause, the curves of displacement for the oscillating parts were carefully drawn to a large scale, and the harmonics of the motion found by the usual graphical method. The harmonics were, however, very small, and as the kinetic energy of the reciprocating parts is only about $\frac{1}{30}$th of the total kinetic energy of the rotating parts, it is evident that the fluctuation of energy of the parts could only introduce infinitesimal fluctuations in angular velocity.

(2) The fluctuations of velocity of the engine in a cycle, loaded as it was by a heavy fly-wheel and rope pulley, and connected with a long line of shafting having a large number of heavy pulleys attached, are also negligibly small. Thus the only real difficulty in eliminating errors in the measurement of ω was found in overcoming the secular variations of velocity.

(3) In the first series of experiments, the machine was driven by a Crossley's oil engine of three horse-power, but the fluctuations of velocity were not small enough, even when the engine was working with full load, for this mode of driving to be considered satisfactory. Although the author was not content with the results obtained under these conditions, yet, for the sake of comparison, the results of one set of 20 tests are given in this paper.

The machine was finally driven by the low-pressure engine of the triple expansion experimental engines. These engines are described in a paper on 'The Mechanical Equivalent of Heat,' by Professor OSBORNE REYNOLDS and W. H. MOORBY, 1898.[*] The secular changes of velocity were again found to be great, and it was only after a great number of trials that the following method (suggested by Professor REYNOLDS) was hit upon to reduce them to a minimum, it being the only method suitable for this work.

The boiler was worked at 120 lbs. pressure, and the steam was throttled so as to reach the engine at 5 lbs. per square inch. In this way, small variations of boiler pressure were rendered less effective in causing variations of velocity.

The engines were run so as to give out approximately 20 horse-power, and drove by means of a rope a long line of shafting from which the power was taken to the counter shaft of the machine by means of a 2½-inch belt. The surplus work was dissipated in a hydraulic brake, also described in the paper just referred to. The brake was not loaded in the ordinary way, but was allowed to bed against an upright or dead-stop behind the brake; a fairly constant flow of water was supplied to the brake, and the resistance offered by the brake was varied by regulating the quantity of water passing out of it.

A speed indicator, similar to the one attached to the testing machine, and previously described (see p. 272), was driven directly from the engine, and the heights of the water columns in the two indicators were constantly watched by

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[*] 'Phil. Trans.'

means of a telescope and mirror, so arranged as to bring the images of the two columns next to each other. The fluctuations of velocity of the engine and the machine could thus be easily compared, and any slipping at once detected.

It was found that, using this method of regulation, the fluctuations of velocity of the machine and engine corresponded with one another, and that the fluctuation could be kept within very small limits, namely, about $\frac{1}{5}$th per cent. A certain amount of experience was necessary to ensure this steady motion for a long period, as in varying the water passing out of the brake, a little too much either one way or the other, oscillations of speed were set up which took some time to die away. It was also found that the reading of the two speed indicators did not correspond at once when the machine was started after a period of rest, but that after a few minutes' run they settled down to corresponding positions.

The telescope and mirror were discarded after some time, but the speed indicators were occasionally checked in each experiment. Mr. JOSEPH HALL, the engine attendant in the Whitworth Engineering Laboratory, soon became quite expert in keeping the variations of speed within surprisingly narrow limits, even when an experiment extended over seven or eight hours without a stop.

The author often found it impossible to be in attendance the whole time occupied by long tests, and in such cases the machinery was left in charge of Mr. HALL. The author found that he could leave the apparatus in his charge with the utmost confidence.

The maximum error in the determination of the stress, due to errors in the measurement of ω, is finally estimated at ·3 per cent.

Modes of Vibration of a Specimen.

The specimen may vibrate during a test in three ways, longitudinally, transversely, and torsionally, and it is important that, either the periods of the free vibration of the specimen do not coincide with the period of any unbalanced force in the machine, or that the vibrations are prevented from taking effect by the use of suitable guides.

The central cylindrical part of most of the specimens was half an inch long and ·25 inch diameter. The greatest load suspended from it was 43·77 lbs., and the smallest 12·42. Taking 30×10^6 as YOUNG's modulus for mild steel, the number of longitudinal vibrations per minute was calculated and found to be between the limits 130,000 and 50,000 approximately.

The highest speeds at which the machine was driven with the greatest and least loads were 1,800 and 2,500 revolutions per minute respectively. It is thus evident that the free period of the longitudinal vibration of the specimen can never coincide with, or be any simple multiple of, the speed of the machine, and hence can never coincide with any periodic force arising from the imperfect balancing of the moving parts.

The number of free vibrations per minute of the specimen vibrating transversely was calculated, considering the specimen as a bar fixed at its end, and found to be about 500,000 per minute, so that in this case also the free vibration need not be considered as influencing the results.

The number of vibrations per minute executed by a specimen when oscillating torsionally was also estimated. The calculation gives for the heaviest and lightest loads used 1200 and 2800 vibrations per minute respectively, so that it is quite possible that the free period of torsional vibration of the specimen might coincide with the speed of the machine.

The key attached to the vertical sliding spindle, which works in a key-slotted bush which can be adjusted and locked, prevents such vibration *above a certain amplitude* taking place, and they are damped also by the viscosity of the oil in the bearings of the spindle. Still, it is evident that this key and keyway cannot be fitted so accurately as to completely extinguish a twist in the specimen as it slides with the weight.

With a view to eliminating the effect of the torsional vibrations of specimens, a number of tests were carried out under different conditions. It was found that when the speed corresponding to the free period of torsional vibrations was reached, a change in the moment of inertia of the load seemed at once to eliminate the vibrations, whilst the unlocking of the lower bearing greatly increased them, causing the specimen to break with fewer reversals. When the speed did not correspond with the free period, neither the change of moment of inertia nor the conditions ot locking effected the results (see footnote, Table III., set C).

The results of these tests are given later (p. 289), and it is seen that only when the free vibration of the specimen coincides with the speed of the machine has this vibration any influence on the results.

Preparation of the Specimens.

The materials used in the tests, of which the results are given in this paper, were mild steel, best cast steel, and best Lowmoor iron. By far the greater number of tests were carried out on specimens having dimensions given in fig. 4.

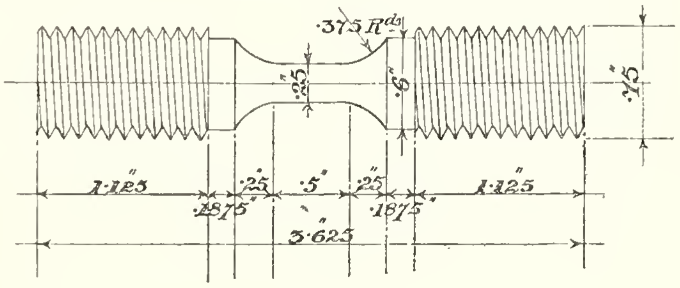

Fig. 4.

Bars ¾ inch diameter were cut up into short lengths of 6 inches. The centres were marked and small holes were drilled up these centres for each piece, and the pieces were then square-centred in the ordinary way. A rough cut was then taken over the whole length, and the cutting of the screw, over 5 inches in length, was then commenced. This part was then finished by means of a chaser to a Whitworth Standard $\frac{3}{4}$-inch thread. The pieces were marked off to a standard length and the ends cut down well below the thread. The central part was roughed out and turned carefully as the size required was approached, a template being used for the curved ends, which were cut to an arc of a circle $\frac{3}{4}$ inch diameter.

The specimens were next rotated between centres and ground to size by means of a small emery wheel which rotated rapidly in the opposite direction to the specimen, and which was moved backwards and forwards parallel to the axis of the specimen. The amount taken off during the grinding process was usually about one-thousandth part of an inch all over the central parallel part.

In the early part of the work the specimens were turned, ground, and finished in the College Laboratory, but during the latter part they were prepared by Messrs. CARTERS and Co., Engineers, Salford.

A number of specimens were turned and ground very roughly in order to see the effect of any bad workmanship, but the results were found to agree almost as well as if the specimens had been turned and ground in the careful manner above described.

In the case of the cast-steel specimens the bars were sawn up and the short pieces were then annealed in a gas furnace before commencing the turning process.

The Annealing of the Specimens.

The finished specimens which were to be annealed were placed inside a piece of wrought-iron piping, 6 inches diameter, and the pipe was closed at both ends by means of two cast-iron covers. The case so formed containing the specimens was placed so as to stand with the specimens vertical, inside a gas furnace, and heated.

The jet of hot gases was prevented from playing directly on the case by using a cast-iron plate which was placed opposite to the jet, and the case was rotated frequently to ensure uniform heating. The supply of gas and air to the burner could be adjusted as required. The process of heating up to a red-heat usually took about half an hour, during which time the specimens were occasionally examined by moving the upper cast-iron cover; the gas supply was then diminished so as to keep the furnace at a constant temperature for another half-hour, after which the burner was taken away, the passages for outlet and inlet of hot gases plugged up by pieces of cast-iron, and the whole allowed to cool, the cooling process usually taking from 10 to 12 hours.

On taking the specimens from the annealing furnace the thin coat of oxide was removed from the central parallel part by rubbing it with the finest emery cloth. This coat was, as a rule, easily removed, but in a few cases the specimens were polished in a lathe, as the skin was found to be very hard.

The diameter of the central part was next measured by means of an ordinary micrometer gauge, and if this part was found to be slightly tapered, the diameters at the centre and each end were measured.

Method of Fixing the Specimens.

A lock-nut was screwed on to each end of the specimen, a hardened steel ball, $\frac{1}{2}$ inch diameter, was inserted in the upper chuck H (fig. 5), and that end of the specimen which contained the centre mark was screwed into this chuck, but not screwed home. The oscillatory weight was then next brought up and the chuck J, which contained another hardened steel ball, was screwed on the lower end of the specimen until the specimen bedded against the ball, the specimen being prevented from rotating by means of a pair of gas-tongs with which the short parallel part *m* was gripped. The lock-nut *n* was screwed tight, thus fixing the specimen to the oscillatory weight.

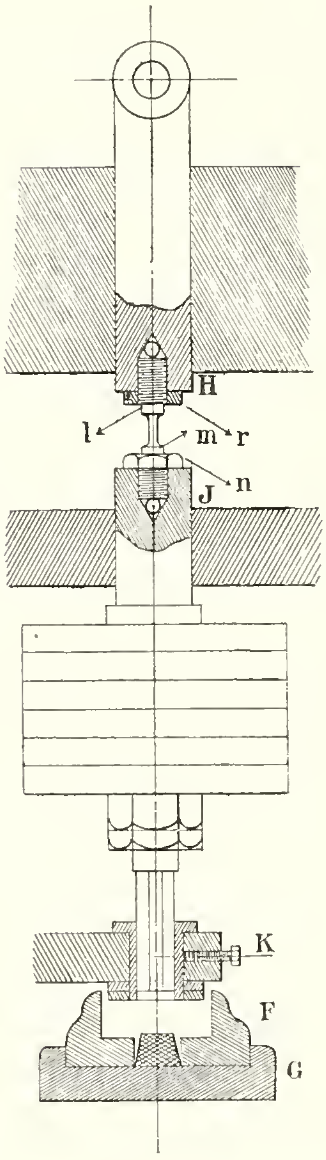

Fig. 5.

The weight was now supported, and the specimen screwed up so as to bed against the steel ball in the upper chuck, the small force necessary for this being supplied by gas-tongs, with which, in this case, the parallel part *l* was gripped. The lock-nut *r* was then screwed tight, thus fixing the specimen to the chuck H.

By the above method, one was certain of getting the specimen into the machine without straining it, whereas, had the specimen been fixed first to the upper chuck, it is quite possible that the material would have been subjected to severe torsional strains in connecting up the oscillating weight.

In the tests carried out with the apparatus driven by the oil engine, the steel balls were not used, and they were also discarded in the tests on wrought iron and cast steel, since it was found that the specimens could be easily locked in the manner described above without using the balls.

In a great many of the tests the specimens were not prevented from rotating, for, as previously explained, it was found unnecessary to do so, but when necessary, to prevent oscillations, the lower bearing was locked by means of a small brass set-screw *k*, $\frac{1}{4}$ inch diameter, which was screwed so as to press against the outside of the loose bush which formed this bearing, thus by frictional force preventing torsional oscillations.

Method of Conducting Tests.

The boiler fire was generally made about 8.30 in the morning; steam was up and the engine was started a little before 9.30. During this time the oil supply pipes of the testing machine and engine were attended to, the cocks being adjusted to give the necessary flow for each bearing; the large oil vessels on the wall were filled up; the rope was placed on a suitable step of speed pulley, and the movable pulley was adjusted to give the requisite tension for driving; a specimen was inserted in the manner previously described; the counter reading was taken; the water inlet cock connected to the hydraulic brake was adjusted so as to give the necessary flow of water through the brake; and the apparatus was then ready for the carrying-out of a test.

Having decided upon the particular speed at which the machine was to run, the speed of the engine to obtain this was found from the tabulated results of a series of experiments previously made; the flow of water from the engine brake was regulated (see p. 275) by means of the water outlet valve, attached to the spindle of which was a long arm, which enabled one to delicately adjust the valve opening (so as to bring the engine to the chosen speed); the machine was started after the engine had been working steadily for a few minutes.

At the commencement of a test the author usually watched the speed indicator attached to the machine; the engine attendant watched the engine speed indicator and adjusted the outlet valve of the brake if necessary. The speed of the machine gradually rose; the time taken to rise to the required speed varied from 60 to 100 seconds when the machine was started first thing in the morning, but the speed was attained in about 20 seconds when the machine had been running for a short time before beginning the test.

It was very important to carefully watch the speed indicator columns on starting, as the speed of the engine had to be reduced always one or two revolutions per minute in the first few minutes of the run, which appeared to be the time necessary to obtain steady lubrication of the bearings; moreover, a great amount of trouble was saved when the brake had been carefully adjusted at the commencement of the test, for in many experiments, when this adjustment had been made, it was found unnecessary to touch the outlet cock for periods of 30 minutes or even longer. On arriving at the steady speed, it was only necessary to watch the speed indicator on the engine, since the fluctuations of the two speed indicators were found to agree, but still the indicator connected to the machine was examined about every 10 minutes.

Throughout the test the boiler was attended to, so as to keep the pressure as nearly constant as possible.

The time at which the machine attained the required speed was taken by means of a watch; and when the speed of the engine had become steady, the counter on the testing machine was pushed home, and the number of revolutions taken for from 10 to 100 minutes, according to the length of the time taken for the test; after one minute's interval, during which the counter reading was taken, the counter was again pushed home, and so on throughout the test.

The time at which the specimen broke was taken, and the total time from attaining full speed to breaking was deduced and the total reversals were estimated from this and the mean speed.

In the case of very short tests the speed was found either before or directly after the test, in which case the oscillatory weight was connected up by a specimen of large diameter specially kept for such work, and the machine was run for 10 minutes to the mark on the speed indicator at which the test was done.

It is thus seen that the reversals of stress to which the materials were subjected during the rise of speed were not taken into account. This might make a slight difference in the short tests, but could certainly have very little effect on the results in the case of long tests, namely, those extending over a period greater than two or three hours. To reduce this effect as much as possible, short tests were never carried out without previously running the machine for some time at the speed at which they were done.

If, during a test, the lubrication of any of the bearings of the engine, shafting, or machine failed, it was at once detected, since the speed indicator column on the engine fell and the pitch of the (unmusical) note given out by the machine was lowered. In such cases, the machine was at once stopped and the time taken; the bearing was attended to, and a new start made.

In the case of very long tests, the machine was run for five or six hours each day according to convenience. The engine could not be used for driving on Tuesday or Wednesday afternoons, as it was employed during those times by the students for the experimental trials, which form part of the College Laboratory course; so that a test which required ten or twelve hours to complete could not be conveniently carried out without a stop which, in some cases, extended over two or three days.

It was important to find the effects of these periods of rest on the number of reversals required for rupture, and after several preliminary tests were completed, a series of experiments were undertaken to investigate this matter. An account of these experiments is given later (see p. 283).

Preliminary Tests for Mild Steel.

A great number of preliminary tests were carried out during the time in which the oil-engine was used as the source of power and also on first using the steam-engine. In some cases the oil-engine had an ordinary pulley and cord brake attached, so as to cause the engine to work at full load, thus reducing the fluctuations of velocity, whereas in other cases it was used to drive the machine without any brake.

The ordinary statical test for this material gave the following results:—

Yield stress	18·64 tons.
Maximum stress	25·83 ,,
Breaking stress	22·09 ,,
Percentage elongation at maximum stress	22.
,, ,, rupture	29.

The results of the endurance tests given in Table I. were obtained whilst working under the conditions mentioned above. The specimens were turned and finished in the College Laboratory, and approximately corresponded to the final specimen shown in fig. 3. The diameters were not quite the same for all specimens, but varied from ·21 to ·26 inch; the specimens were not annealed. The machine was working with the full load, 43·77 lbs.; the speeds used varied from 1200 to 1500 revolutions per minute.

The fluctuation of velocity, as shown by the speed indicator attached to the machine, usually ranged from 4 per cent. to 6 per cent. The revolutions per minute were determined by dividing the total revolutions by the total time from the beginning to the end of the test.

TABLE I.—Unannealed Mild Steel.

Oscillatory weight, 43·77 lbs. Diameter of Specimens, ·22 inch to ·26 inch.

Number.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
1	18·97	−16·36	35·33	2,360
2	17·94	15·48	33·42	2,330
3	16·43	14·17	30·60	5,960
4	15·99	13·80	29·79	10,240
5	14·82	12·90	27·72	53,200
6	14·73	12·72	27·45	39,700
7	14·19	12·19	26·38	17,200
8	13·68	11·87	25·55	89,200
9	14·09	12·15	26·24	68,900
10	13·67	11·73	25·40	65,400
11	13·36	11·39	24·75	71,400
12	13·24	11·43	24·67	97,800
13	13·08	11·36	24·44	132,000
14	12·41	10·70	23·11	251,000
15	11·97	10·30	22·27	332,000
16	11·76	10·01	21·77	396,000
17	11·72	10·01	21·73	404,000
18	11·57	9·91	21·48	710,000
19	10·42	8·84	19·26	1,930,000 (Not broken.)
20	11·12	9·45	20·57	3,920,000 (Not broken.)

On comparing these results with those of WÖHLER for a similar material—although it is impossible to choose from his list one exactly the same as the steel used here—one sees the general similarity of the results, but is struck by the great difference between the total reversals for any given range of stress. It is easy to see that this difference is greater as the stress range, and therefore as the speed increases, thus suggesting that there is a relation similar to WÖHLER's for every speed.

If the mean variation of speed is taken at 5 per cent., the variation of stress range due to this will be 10 per cent. This great variation would seem to reduce the value of these tests, but the author introduced them mainly to enable one to compare results got in this way with those obtained after the fluctuations of speed had been reduced to a minimum. In some cases, this fluctuation is of no consequence, as will be seen from the following.

On comparing Tests 18 and 20 (Table I.) we see that for a drop of ·91 ton per square inch in the range of stress, the reversals for rupture have increased from $7·1 \times 10^5$ to over $3·9 \times 10^6$. If, then, a fluctuation of range of stress of 10 per cent. had been taking place for a test at about this particular range, it is evident that only a very small fraction of the actual reversals recorded could be effective in damaging the material. One thus sees that, as long as the rate of change of reversals with range of stress is small, slight fluctuations of velocity will not appreciably affect the results, whereas, when this rate is great, it is important to keep the speed as steady as possible.

If the limiting range of stress increases as the speed diminishes, it will be more rapidly approached with the method of lowering the range used here, than in that used by Wöhler, for the diminution of range is got by diminishing the speeds when the specimens are of constant diameter. Hence, after a certain point, it will not be worth while doing long tests, since these fluctuations of velocity, however small, would render the results doubtful.

Finding that the reversals for rupture with any given range of stress are diminished with the speed, the author decided to limit his tests more particularly to cases for which the reversals were less than one million. In a few cases, however, specimens have been subjected to a greater number of reversals.

Nearly the whole of one year was spent in an attempt to get more regular results by improving the method of preparing the specimens, by annealing, by subjecting each specimen to a number of reversals with a small range of stress, and by diminishing the fluctuations of speed in the manner described previously; and, strange as it may seem, the results were not so regular in many of the final series of tests as in those recorded in Table I. The only possible explanation is that the material used for Experiment I. was of more uniform quality than that used subsequently.

On the Restoring Effect of a Period of Rest.

Since in the long tests, namely, those extending over several days, the experiments could not be conveniently carried out without stopping, and therefore allowing the specimen to rest, it is important to find the effect of these periods of rest on the total reversals required for breaking. With this object in view, tests were made with a number of specimens of mild steel, some of which were broken without stopping the machine, while others were allowed to rest for various periods after having been subjected to about half the number of reversals required to break them. The speed of the machine and the suspended load (24·96 lbs.) were kept the same in all cases. The results of these tests are given in Table II.

TABLE II.—Mild Steel.

Oscillatory weight, 24·96. Diameter of Specimens, ·265 inch to ·269 inch.

Unannealed.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals.	Total reversals.
1	1948	11·56	10·23	21·79	114,000	114,000
2	1949	11·35	10·06	21·41	122,000	122,000
3	1947	11·53	10·21	21·74	124,000	124,000
4	1940	11·54	10·22	21·76	47,500	47,500
5	1947	11·69	10·37	22·06	58,400	—
(After 3 days)	1933	11·51	10·21	21·72	53,800	112,200
6	1935	11·37	10·08	21·45	58,100	—
(After 5 days)	1938	11·41	10·11	21·52	60,200	118,300
7	1938	11·38	10·09	21·47	58,200	—
(After 5 days)	1942	11·53	10·02	21·55	80,600	138,800
8	1937	11·49	10·17	21·66	58,200	—
(After 11 days)	1932	11·43	10·11	21·54	58,500	116,700
9	1940	11·39	10·09	21·48	58,200	—
(After 11 days)	1936	11·37	10·07	21·44	7,500	65,700
10	1944	11·58	10·26	21·84	58,300	—
(After 4 months)	1942	11·56	10·23	21·79	30,800	89,100
11	1944	11·57	10·24	21·81	58,300	—
(After 4 months)	1950	11·63	10·31	21·94	32,100	90,400
Annealed.						
Diameter of Specimens, ·25 inch.						
12	1947	13·14	11·62	24·76	30,600	30,600*
13	1947	13·14	11·63	24·77	30,500	30,500*
14	1947	13·09	11·58	24·67	15,600	—
(After 4 months)	1938	12·98	11·46	24·44	20,250	35,850
15	1947	13·87	11·21	25·08	15,600	—
(After 4 months)	1936	16·40	13·35	29·75	12,600	28,200

No. 15 had extended during the first part of the test, and the diameter had changed from ·2487 to ·2271.

In these experiments, two sets of specimens were prepared all from the same bar. The material was the same as that employed in the tests recorded in Table III. The first set consisted of 11 specimens, which were tested without annealing. The length of each was ·63 inch, and their diameters varied from ·265 to ·269 inch.

Specimens 1, 2, 3, and 4 were broken without stopping the machine. Specimens

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* These two tests are also included in Table III., Set C, Nos. 37, 38.

5 to 11 were put into the machine and run for 30 minutes each—about half the length of time required to break Specimens 1, 2, and 3. Specimen 5 was carefully put away for three days, after which the test was completed by putting it in the machine and running it till rupture took place. The other specimens were treated in a similar manner, Specimens 6, 7, and 8 resting for five days, Specimens 8 and 9 for eleven days, and Specimens 10 and 11 for four months. The result for Specimen 4 is irregular, and is therefore rejected.

The second set of specimens was treated at a later time. They were annealed before testing. All the specimens of this set had the dimensions shown in fig. 4, which was adopted as the standard size in all succeeding tests.

These results show that, if a specimen is allowed to rest when the test is half completed, there is no appreciable recovery if the period of rest is for a few days only. They suggest that if the period of rest extends over some months the specimens may or may not recover slightly; the extent would appear to depend on the treatment which it has received previous to the test.

To settle definitely the restoring effect of a long period of rest, a great many more experiments would have to be done, but as far as this work is concerned where the specimens were seldom allowed to rest for more than two days, the effect of this rest on the total reversals for rupture is negligible.

Relation of Limiting Range to Periodicity of Reversals.

Under this head are given the results of experiments to determine the variation of the range of stress with speed when the number of reversals for rupture is constant, viz., one million.

Six bars of mild steel were purchased together, and the whole of the specimens for which the results given in Tables II. and III. were obtained were cut from these bars. Six samples, each 18 inches long, were cut, one from each bar, and were tested for statical breaking-stress, &c., in the Owens College Laboratory Testing Machine, which is a Buckton 100-ton machine of the Wicksteed horizontal lever type; the extensions were measured over 8 inches. The figures obtained in these tests were as follow:—

	Yield-stress.	Maximum stress.	Breaking stress.	Percentage elongation at maximum stress.	Percentage elongation at rupture.
Maximum . .	17·44	24·70	21·08	24·6	31·5
Minimum . .	16·81	22·93	19·34	23·0	29
Mean . . .	17·12	24·54	20·47	23·5	30

Three annealed specimens of the form used in the endurance tests (dimensions according to fig. 4) were also broken in the same testing machine, and the maximum stress measured. The mean for these three tests was 25·81 tons per square inch; the yield-stress and extensions could not be conveniently measured.

During the preliminary tests (described on p. 281), it had been noticed that the reversals for rupture for any given range of stress diminished as the rapidity of reversals increased, and the author decided to carry out a number of tests to investigate this point. He decided to carry out six sets of tests with the standard form of specimen (fig. 4).

In each set of tests, specimens from every one of the six bars were used; the load supported by the specimen was kept constant and the speed varied. The load was changed from set to set so that there might be six tests for any given range of stress, each carried out at a different speed. The first test of each set was, as a rule, done at the highest speed at which the machine could be run. The range of stress was varied for the subsequent tests in the set by reducing the speed. It was decided to limit, in general, the experiments to tests taking not more than two million reversals for rupture. The results of these tests are given in Table III.

TABLE III.

Set A.

Annealed Mild Steel.

Oscillatory weight, 12·42 lbs. Diameter of Specimens, ·245 inch to ·247 inch.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
1	2380	10·00	8·95	18·95	28,090
2	2306	9·43	8·43	17·86	22,100
3	2240	9·01	8·05	17·06	80,700
4	2191	8·59	7·66	16·25	136,000
5	2126	7·99	7·11	15·10	248,700
6	2047	7·51	6·67	14·18	416,000
7	1956	6·81	6·02	12·83	334,000
8	1954	6·87	6·08	12·95	682,000
9	1909	6·51	5·74	12·25	1,138,000
10	1888	6·26	5·50	11·76	1,787,000 (Not broken.)
Unannealed Mild Steel. Diameter of Specimens, ·24 inch to ·255 inch.					
11	2492	11·83	10·65	22·48	43,000
12	2438	11·17	10·03	21·20	34,100
13	2382	10·54	9·46	20·00	66,700
14	2356	10·09	9·02	19·11	59,000
15	2346	9·91	8·87	18·78	61,000
16	2238	9·03	8·07	17·10	73,800
17	2190	8·33	7·44	15·77	66,000
18	2122	8·03	7·17	15·20	226,500
19	2071	7·34	6·54	13·88	162,700
20	2015	6·72	5·96	12·68	2,025,000 (Not broken.)

TABLE III.—*continued.*

Set B.

Annealed Mild Steel.

Oscillatory weight, 18·69 lbs. Diameter of Specimens, ·247 inch to ·249 inch.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
21	2285	13·86	12·39	26·25	4,100
22	2250	13·33	11·91	25·24	6,200
23	2150	12·36	11·00	23·36	35,500
24	2170	12·29	10·96	23·25	58,900
25	2113	11·60	10·33	21·93	86,000
26	2032	10·83	9·62	20·45	124,700
27	1934	9·88	8·74	18·62	199,700
28	1860	9·30	7·20	17·50	350,000
29	1807	8·68	7·65	16·33	438,000
30	1790	8·77	7·71	16·48	528,000
31	1749	8·08	7·09	15·17	843,000
32	1715	7·79	6·82	14·61	1,840,000
33	1696	7·65	6·70	14·35	5,076,000 (Not broken.)

Set C.

Annealed Mild Steel.

Oscillatory weight, 24·96 lbs. Diameter of Specimens, ·248 inch to ·25 inch.

34	2150	16·09	14·32	30·41	0
35	2032	14·34	12·73	27·07	13,500
36	1962	13·52	11·97	25·49	30,900
37	1947	13·14	11·62	24·76	30,600*
38	1947	13·14	11·63	24·77	30,500†
39	1903	12·62	11·13	23·75	55,250
40	1845	11·83	10·41	22·24	143,200
41	1758	10·89	9·56	20·45	348,000
42	1693	10·10	8·82	18·92	283,000
43	1682	9·88	8·64	18·52	783,200

Set D.

Annealed Mild Steel.

Oscillatory weight, 31·23 lbs. Diameter of Specimens, ·245 inch to ·249 inch.

44	1920	16·43	14·52	30·95	4,400
45	1887	15·74	13·89	29·63	11,090
46	1831	15·03	13·25	28·28	14,300
47	1776	14·31	12·57	26·88	22,600
48	1729	13·31	11·66	24·97	72,700
49	1698	12·72	11·12	23·84	92,900
50	1642	11·99	10·45	22·44	149,400
51	1609	11·63	10·12	21·75	112,000
52	1589	11·14	9·66	20·80	400,300
53	1544	10·69	9·24	19·93	540,100

* Keyed bush of lower bearing free to turn.
† ,, ,, ,, locked.

Table III.—*continued.*

Set E.

Annealed Mild Steel.

Oscillatory weight, 37·50 lbs. Diameter of Specimens, ·244 inch to ·249 inch.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
54	1832	18·35	16·15	34·50	·0
55	1776	17·44	15·33	32·77	2,900
56	1689	16·04	14·05	30·09	13,900
57	1645	14·82	12·92	27·74	20,100
58	1587	13·81	11·98	25·79	39,600
59	1583	13·78	11·95	25·73	21,400
60	1544	13·16	11·38	24·54	46,600
61	1499	12·45	10·74	23·19	112,400
62	1475	11·63	10·02	21·65	298,200
63	1441	11·03	9·46	20·49	650,100

Set F.

Annealed Mild Steel.

Oscillatory weight, 43·77 lbs. Diameter of Specimens, ·238 inch to ·249 inch.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
64	1617	17·63	15·37	33·00	16,140
65	1539	15·12	13·10	28·22	17,440
66	1491	14·05	12·10	26·15	20,150
67	1501	13·99	12·09	26·08	45,200
68	1449	13·26	11·42	24·68	54,400
69	1401	12·50	10·69	23·19	96,600
70	1402	12·31	10·52	22·83	273,100
71	1372	11·98	10·21	22·19	348,400
72	1345	11·43	9·73	21·16	679,000
73	1316	11·74	9·08	19·82	542,000

Unannealed Mild Steel.

Diameter of Specimens, ·238 inch to ·250 inch.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
74	1660	17·28	15·10	32·38	43,000
75	1550	14·45	12·48	26·93	73,600
76	1494	14·44	12·44	26·88	67,200
77	1462	13·94	12·00	25·94	60,600
78	1356	12·57	10·70	23·27	199,400
79	1398	12·28	10·51	22·79	106,800
80	1399	12·17	10·41	22·58	233,200
81	1326	11·86	10·07	21·93	448,000
82	1305	11·41	9·64	21·05	1,141,000

These results are probably not so regular as they might have been with specimens all cut from one bar. The second column of Table III. gives the speed at which the machine was run during the test; the reversals are given in the sixth column. The latter were determined from the mean speed, found from the readings of the revolution counter over times ranging from 10 to 100 minutes, and the total time between starting the machine and rupture.

The following tests carried out as part of Set B, Table III., have not been included in that table :—

	Reversals.	Speed.
a.	132,700	1855
b.	127,000	1855
c.	17,800	1777
d.	51,250	1737
e.	329,000	1775

These tests were carried out after Nos. 24, 25, 26, and 27 of Set B. Owing to the specimen used in (*a*) breaking in a shorter time than was expected, the test was repeated with the result (*b*). The lower bearing, which had for tests (*a*) and (*b*) been locked, was now allowed perfect freedom to rotate, and tests (*c*) and (*d*) were carried out. The lower bush was now removed and a new keyway and key were made and very accurately fitted. Then test (*e*) was carried out. The large plate weights on the oscillating spindle were changed for others of smaller diameter but of the same weight, and the remaining tests of Table III., Set B, were completed. It is evident from the above that in the tests (*c*) and (*d*) the free period of torsional oscillation of the specimen corresponded with that of the machine (see p. 276).

In Tables IV., V., and VI. are given the corresponding results obtained for tests for Lowmoor iron, cast-steel, and cast-iron, respectively.

The statical tests for these materials gave the following results :—

		Yield stress.	Maximum stress.	Breaking stress.	Percentage elongation at maximum stress.	Percentage elongation at rupture.
Lowmoor iron	Maximum .	16·46	23·58	23·08	24	29·4
	Minimum .	16·40	23·55	21·10	21	27·5
	Mean . . .	16·43	23·56	22·27	22·8	28·5
Cast-steel . .	Maximum .	40·20	60·80	60·80	—	5·9
	Minimum .	39·45	55·30	55·30	—	2·5
	Mean . . .	39·85	58·10	58·10	—	3·8

The breaking stress for *annealed* specimens of the type used in the endurance tests was 23·1 tons for Lowmoor iron, and 48 tons for cast-steel. In the case of the cast-iron used, the breaking stress was 9·4 tons. As the specimens used were short, the extensions were not measured.

By far the greater number of specimens broke without any appreciable change in diameter or length. A fair number, however, had their diameters greatly increased, but there does not appear to be any definite connection between these changes of dimensions and the range of stress or speed, as far as the author has observed. In only one test, namely, No. 15, Table II., was a change of diameter observed on stopping the machine *before* rupture. The author is led to believe that the change in dimensions occurs, if at all, just before breaking. In only one case had flaws been observed on stopping the machine before the breaking-point was reached, namely, No. 15, Table IV. It showed most peculiar flaws at both ends.

TABLE IV.—Annealed Lowmoor Iron.

Set A.

Oscillatory weight, 12·42 lbs. Diameter of Specimens, ·245 inch to ·249 inch.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
1	2380	10·15	9·08	19·23	33,350
2	2308	9·33	8·35	17·68	49,200
3	2298	9·53	8·51	18·04	36,200
4	2217	8·82	7·86	16·68	43,250
5	2122	7·99	7·10	15·09	252,500
6	2038	7·28	6·47	13·75	89,700
7	2034	7·31	6·50	13·81	192,300
8	1969	6·73	5·97	12·70	399,600
9	1893	6·23	5·50	11·73	111,600
10	1890	6·21	5·48	11·69	1,236,000

Set B.

Oscillatory weight, 24·96 lbs. Diameter of Specimens, ·245 inch to ·248 inch.

11	2217	13·03	11·53	24·56	16,270
12	2131	12·19	10·74	22·93	43,800
13	2066	11·54	10·17	21·71	63,000
14	2019	10·77	9·45	20·22	85,800
15	1975	10·50	9·20	19·71	413,000
16	1917	9·76	8·52	18·24	342,000

Set C.

Oscillatory weight, 31·23 lbs. Diameter of Specimens, ·248 inch to ·25 inch.

17	1916	12·87	11·25	24·12	62,700
18	1836	11·77	10·25	22·02	80,200
19	1701	10·28	8·88	19·16	243,800
20	1630	8·48	8·14	17·62	760,100

Set D.

Oscillatory weight, 43·77 lbs. Diameter of Specimens, ·248 inch to ·249 inch.

21	1486	13·81	11·90	25·71	54,000
22	1397	12·15	10·37	22·52	100,400
23	1367	11·69	9·96	21·65	299,500

Table V.—Annealed Cast Steel.

Set A.

Oscillatory weight, 12·42 lbs. Diameter of Specimens, ·245 inch to ·25 inch.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
1	2382	10·22	9·16	19·38	35,680
2	2313	9·35	8·38	17·73	50,900
3	2303	9·51	8·50	18·01	36,900
4	2226	8·66	7·74	16·40	97,000
5	2216	8·94	7·97	16·91	47,700
6	2117	7·70	6·85	14·55	273,000
7	2116	7·75	6·93	14·68	95,200
8	2034	7·21	6·40	13·61	472,000
9	1963	6·77	6·00	12·77	402,000
10	1892	6·29	5·56	11·85	1,327,000

Set B.

Oscillatory weight, 24·92 lbs. Diameter of Specimens, ·246 inch to ·248 inch.

11	2215	13·06	11·56	24·62	37,700
12	2163	12·56	11·09	23·65	49,400
13	2076	11·46	10·07	21·53	86,700
14	2012	10·91	9·56	20·47	129,300
15	1972	10·37	9·08	19·45	189,300
16	1917	9·95	8·70	18·65	337,500
17	1838	9·17	7·98	17·15	687,400

Set C.

Oscillatory weight, 31·23 lbs. Diameter of Specimens, ·248 inch to ·25 inch.

18	1975	13·73	12·05	25·78	31,200
19	1841	11·98	10·44	22·42	107,400
20	1694	10·10	8·72	18·82	341,600
21	1650	9·74	8·39	18·13	2,270,000

Set D.

Oscillatory weight, 43·77 lbs. Diameter of Specimens, ·248 inch to ·249 inch.

22	1474	13·46	11·60	25·06	92,600
23	1395	12·19	10·41	22·60	157,000
24	1363	11·59	9·89	21·48	265,400
25	1326	11·07	9·40	20·47	718,000
26	1303	10·64	9·00	19·64	918,000

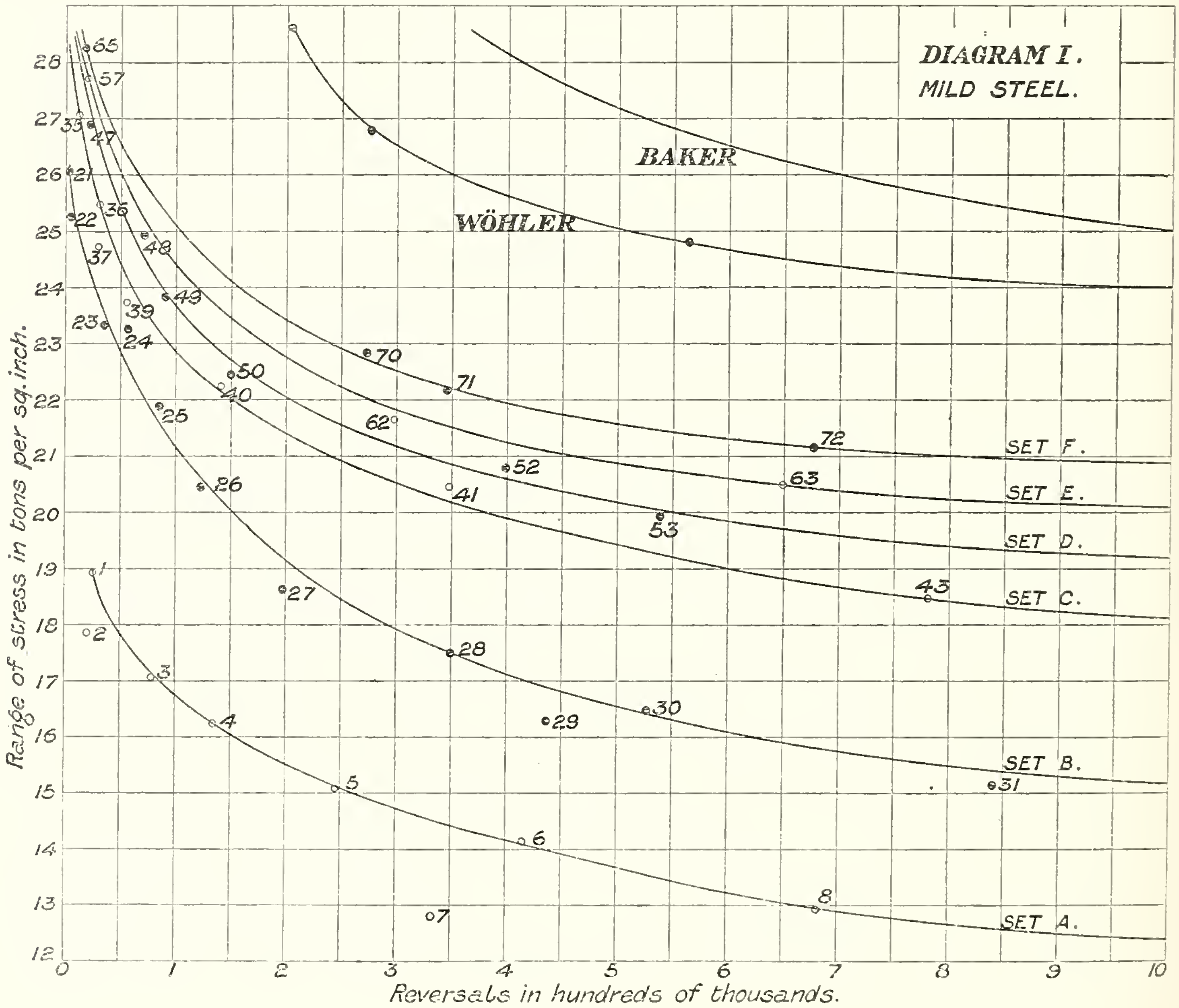
TABLE VI.—Cast-iron.

Oscillatory weight, 24·96 lbs. Diameter of Specimens, ·345 inch to ·35 inch.

Number.	Revolutions per minute.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
1	1941	6·67	5·91	12·58	0
2	1493	4·01	3·46	7·47	39,200
3	1496	4·02	3·47	7·49	36,600
4	1399	3·53	3·02	6·55	6,000
5	1396	3·51	3·01	6·52	111,600
6	1350	3·35	2·84	6·19	0
7	1305	3·10	2·62	5·72	620,000

Summary of Results.

The results of tests for mild steel, given in Table III., are plotted in Diagram I., the range of stress being taken as ordinate, and the reversals for rupture as abscissa.



The method used was to plot all the results of a set of tests and then draw a curve through the best results, that is, those giving the greatest number of reversals. These are indicated by the small circles in the diagram. To prevent confusion, points lying much below the curves are not shown.

The results obtained by Wöhler and Baker were plotted on the same scale as Diagram I., but on a much larger sheet. It was found that none of Baker's and only three of Wöhler's results came on that part of the sheet included in Diagram II. The three points corresponding to Wöhler's figures will be found on the diagram.

The results chosen from Wöhler's experiments were those carried out on rotating bars (steel axles) made by Messrs. Vickers, Sons & Co. The tenacity of this material ranged from 26·3 to 29·2 tons per square inch, and the percentage extension from 15·8 to 19·5. The material experimented on by Baker was soft steel of tensile strength 26·8 to 28·6 tons, and percentage extension 28.

The results of Wöhler and Baker for their materials are given in the following tables :—

Number of bar.	Maximum stress.	Minimum stress.	Range of stress.	Repetitions before fracture.
		Wöhler's.		
63	16·3	−16·3	32·6	51,240
64	15·3	15·3	30·6	72,940
65	14·3	14·3	28·6	205,800
66	13·4	13·4	26·8	278,740
67	12·4	12·4	24·8	564,900
68	11·5	11·5	23·0	3,275,860
69	10·5	10·5	21·0	8,660,000 (Not broken.)
		Baker's.		
1	16·1	−16·1	32·2	40,510
2	16·1	16·1	32·2	60,200
3	15·2	15·2	30·4	68,400
4	15·2	15·2	30·4	92,070
5	15·2	15·2	30·4	107,415
6	15·2	15·2	30·4	128,650
7	15·2	15·2	30·4	155,295
8	11·6	11·6	23·2	14,876,432

The materials used by Wöhler and Baker in their tests given above, do not correspond very well with that used in the tests carried out by the author, but they are, however, the only results which could be reasonably used for the purposes of comparison.

It appears from Diagram I. that the range of stress for a definite number of reversals diminishes rapidly as the periodicity of the reversals increases. The following Table has been deduced from Diagram I., and shows corresponding values of the range of stress—for rupture at one million reversals—and speed.

Mild Steel.

Range of stress for rupture with 10^6 reversals.	Reversals per minute.	Ratio of range for 10^6 reversals to yield stress.
25 (Baker)	50 to 60	—
24 (Wöhler)	60 to 80	—
20·9	1337	1·22
20·1	1428	1·17
19·2	1516	1·12
18·1	1656	1·06
15·2	1744	·89
12·4	1917	·72

The author does not consider the number and regularity of the tests on wrought-iron sufficient to enable him to trace the curves for the various loads used, but wishes to point out that the results, with one exception, are similar to, and nearly in agreement with, those obtained for mild steel. The exception is No. 15, Table IV. Finding that the results with wrought-iron were not coming out anything like so regular as in the case of the mild steel specimens, and as the time for the completion of the work was limited, more attention was paid to the cast-steel specimens in the hope (which was realised) of obtaining more uniformity.

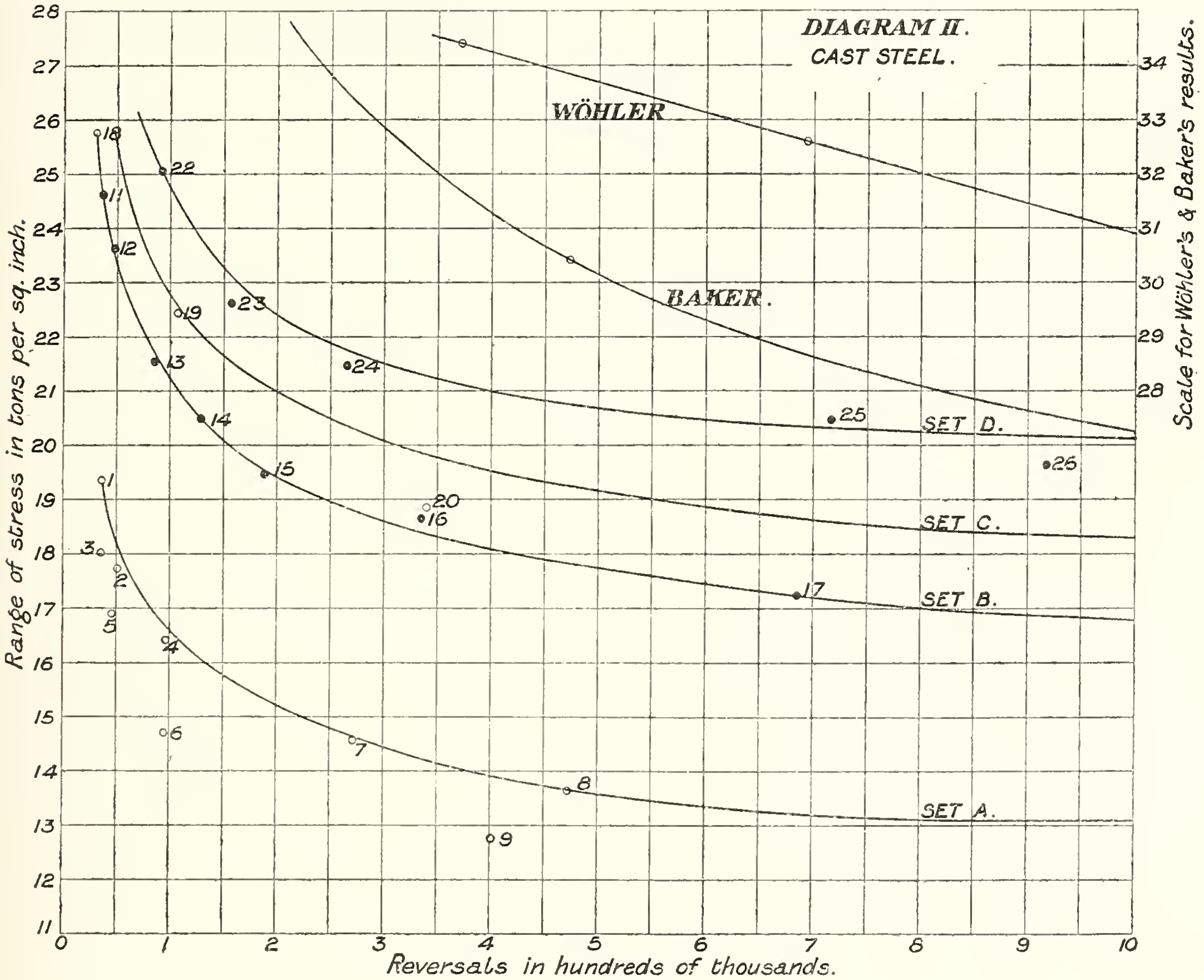
The results of the tests for cast-steel are plotted on Diagram II. They show the same lowering of the range of stress, for any fixed number of reversals for rupture as the speed is increased. The material experimented upon by Wöhler which corresponds most nearly to the cast-steel used here was tool steel made by Firth and Sons, of tensile strength 55 tons, and extension 9·1 per cent. The range for one million reversals, as deduced from Wöhler's results, is 30·9 tons per square inch.

Wöhler's results are for bars rotated and bent :—

Number of test.	Maximum stress.	Minimum stress.	Range of stress.	Number of repetitions for rupture.
70	17·2	− 17·2	34·4	370,975
71	16·3	16·3	32·6	694,450
72	15·3	15·3	30·6	233,700
73	14·3	14·3	28·6	1,528,550

It should be noticed that in these results of Wöhler, the rate of change of reversals with range of stress was *finite* at the point corresponding to one million reversals for rupture. This shows that what is understood as the limiting range was not by any means nearly approached. Diagram II. shows that in these experiments (Table V.) the limiting range for cast-steel was approached very rapidly as the speed was diminished.

It is almost impossible to compare the results obtained here with those given by Baker, as the total reversals in his case were limited to less than half-a-million.



Baker's results for "fine drift steel," of tensile strength 54 tons, elongation 14 per cent., are as follows :—

Number.	Maximum stress.	Minimum stress.	Range of stress.	Reversals for rupture.
9	29·9	−29·9	59·8	5,760
10	29·1	29·1	58·2	7,560
11	23·9	23·9	47·8	14,600
12	23·9	23·9	47·8	16,300
13	20·8	20·8	41·6	26,100
14	22·8	22·8	45·6	32,445
15	18·1	18·1	36·2	157,815
16	15·2	15·2	30·4	472,500

The range of stress for one million reversals, which these tests of BAKER seem to point to, lies between 27 and 28 tons.

Taking the results given in Table V. along with those of WÖHLER and BAKER, we see that in the case of cast-steel there is a great lowering of the range of stress—for rupture with a given number of reversals—as the speed is increased.

In the following table the author's results are added to those of WÖHLER and BAKER in order to show the relation between the range of stress and the reversals per minute for rupture with one million reversals :—

Cast Steel.

Range of stress for rupture with 10^6 reversals.	Reversals per minute.	Ratio of range for 10^6 reversals to yield stress.
30·9	60 to 80 (WÖHLER)	—
27·5	50 to 60 (BAKER)	—
20·1	1320	·50
18·3	1660	·46
16·8	1820	·42
13·1	1990	·33

In the case of cast-iron the range of stress for one million reversals obtained in the author's experiments is approximately 5·5 tons at 1300 revolutions per minute. WÖHLER obtained 4·78 tons as the range for one million reversals for bars subjected to repeated tensions, the limits being 0 and 4·78 tons; if we assume that cast-iron behaves in the same general way as wrought-iron and steel, WÖHLER'S limit would have been much greater if the stress range had been between equal and opposite limits, pointing possibly to the same lowering of the range as the speed increases.

It is, therefore, impossible, in the case of cast-iron, to say definitely whether the range is diminished as with the other metals experimented upon.

Conclusion.

There are many points which the author would have liked to investigate, but was unable to owing to the great amount of time which would be required. The only satisfactory method of procedure with experiments of the kind dealt with in this paper is to carry out a large number of tests bearing upon any particular point, in order to eliminate the effects of irregularities or inequalities of the materials of which the specimens are composed. It is only in this way that one can be certain of avoiding the inclusion of anomalous results among those from which the deductions are made.

A little time had been spent on the effect of annealing specimens after subjecting them to a number of reversals. The author refrains from publishing the results, which he considers not sufficient to establish anything definite, since they vary a great deal; but desires to mention that the effect of such annealing appeared in general to shorten the life of the specimen and not to restore it, as is usually supposed.

As mentioned early in this paper, complete statical tests of specimens of size shown in fig. 3, could not be performed, since extensions could not be measured; moreover, as the 100-ton testing machine had to be used, the measurements were not too delicate. However, two specimens which had been subjected to reversals, and must have been nearly on the point of fracture, showed a distinctly greater maximum stress than the unused specimens.

The author desires to thank Professor OSBORNE REYNOLDS, to whom he is indebted for many suggestions and much valuable advice and criticism during the progress of the work, and also for the facilities which he afforded for the carrying on of the experimental work.

INDEX SLIP.

AYRTON, Hertha.—The Mechanism of the Electric Arc.
Phil. Trans., A, vol. 199, 1902, pp. 299–336.

Arc, Electric—Mechanism of.
AYRTON, Hertha. Phil. Trans., A, vol. 199, 1902, pp. 299–336.

Back Electromotive Force, apparent, of the Electric Arc—Its probable Cause.
AYRTON, Hertha. Phil. Trans., A, vol. 199, 1902, pp. 299–336.

Resistance, true, of the Electric Arc.
AYRTON, Hertha. Phil. Trans., A, vol. 199, 1902, pp. 299–336.

V. *The Mechanism of the Electric Arc.*

By (Mrs.) HERTHA AYRTON.

Communicated by Professor J. PERRY, *F.R.S.*

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EVER since the first discovery of the Electric Arc, nearly 100 years ago, the secret of its mechanism has been one of the most fascinating mysteries of science. To account for its abnormally high temperature, and for the fact that a higher P.D. is required to send a small current than a large one through it, the arc has been endowed with unique properties, such as a back E.M.F. of many volts, and even a negative resistance. The measurement of this resistance alone has been the object of a large number of experiments, made under all conceivable conditions.

The object of the present paper is to see how far this peculiar behaviour of the arc might have been logically predicted from the known conditions of its existence, viz., that it is a gap in a circuit, furnishing its own conductor by the evaporation of its own material; and to show that it is quite unnecessary to invoke the aid of a negative resistance, or even of a large back E.M.F., to account for this behaviour.

What happens on making the Gap.

The usual explanation given for the formation of a spark or flash, on opening an electric circuit, is that it is caused by self-induction. The interesting question therefore arises, could an arc be struck and maintained if there were no self-induction whatever in the circuit? I think it could. For the surfaces of all solids are irregular, and therefore all parts of the carbons cannot be separated at the same instant. The parts that remain in contact will still conduct the current, but the fewer of them that remain the greater will be their resistance. The heat caused by this resistance must, at last, be great enough to volatilise the carbon at the remaining points of contact, and, by the time that no part of one carbon is touching any part of the other, the small gap will be full of carbon vapour. [As the carbon points at each junction must volatilise as soon as they are hot enough to do so, this vapour will be given off at a constant temperature, viz., the lowest at which carbon can volatilise. —March 23, 1902.]

To explain the further formation of the arc, we must remember that when the carbons are separated still more all the material in the gap cannot retain its high temperature. The access of the cold air must, I consider, turn some of the vapour into *carbon mist* or *fog* as distinct from *carbon vapour*, just as the steam issuing from a kettle is turned into visible mist at a short distance from its mouth. The interior globular portion A (fig. 1), which is purple in the image of the arc, is, I suggest, composed of such carbon mist, while there is an indication of a space between this mist and the positive carbon which is occupied, I believe, by a thin film of true carbon vapour.

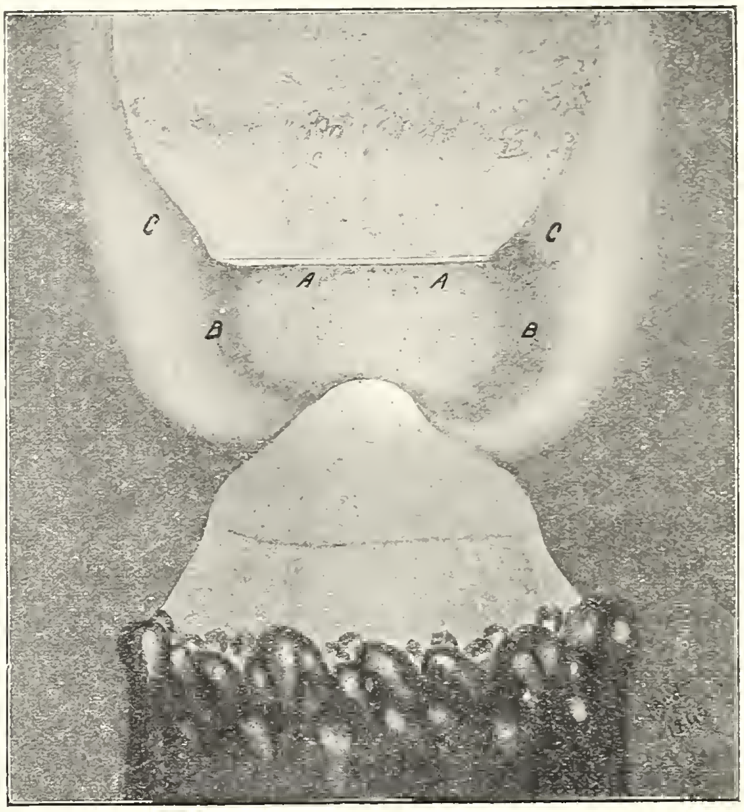

Fig. 1. Enlarged image of arc and carbons with positive carbon on top. AA, purple mist, BB, shadow, CC, green flame.

Next the dissimilar action of the poles, met with in so many electric phenomena, begins. Instead of *both* poles volatilising, so that there is a thin layer of carbon *vapour* over each with a mass of carbon *mist* between them, the positive pole alone volatilises, while the negative appears simply to burn away.

Besides the film of vapour and the bulb of mist, other volatile materials must go to make up the whole substance of the arc. For the surrounding air must not only cool the carbon vapour, but it must unite chemically with a certain thickness of the mist, thus forming a sheath of burning gases surrounding both vapour and mist, and even portions of the solid carbons themselves. This sheath of gases, which is of a brilliant green colour with solid carbons, may be seen at C (fig. 1), while B, the shadow between it and the mist, probably indicates where the two mingle. There must be three sorts of material in the gap, therefore, marking the three stages through which the vapour is continually passing.

1. It starts as a thin film of carbon *vapour* spread over the end of the positive carbon.
2. It then changes into the *mist* that lies between this vapour film and the negative carbon.
3. Finally it burns and forms a sheath of burning gases which encloses not only the fresh vapour and mist, but also the ends of the solid carbons themselves.

The Conducting Power of the Vapour, Mist, and Flame.

The specific resistances of true vapours have been shown to be high, therefore I conclude that the film over the end of the positive carbon has a high resistance, even though it be very thin. The mist, on the contrary, is composed, I think, of minute solid particles of carbon, and must, therefore, I anticipate, have a lower specific resistance. My experiments on the flame have shown, on the other hand, that its specific resistance is so high, compared with that of the inner purple mist, that it is relatively an insulator, a result confirming that obtained by LUGGIN[*] in 1889. The current, therefore, flows through the vapour and the mist, and practically not at all through the sheath of burning gases.

The Production of the High Temperature at the Crater.

To explain the great production of heat at the end of the positive carbon, as well as the sudden change of potential that is known to exist there, it has been supposed that a back E.M.F. of some 35 to 40 volts existed at the junction of the crater and the arc. But if, as I suggest, there be a high resisting vapour film in contact with the crater, the current passing through this must generate much heat, and this heat is utilised mainly in continuously forming fresh carbon vapour, at the lowest temperature at which carbon will volatilise—to be itself turned into mist, and then into flame. Hence it seems probable that the high and constant temperature of the crater is kept up by the current flowing, not against a back E.M.F., but through the resistance of a thin vapour film of constant temperature lying over the surface of the crater. In other words, *it is not the crater itself that is the source of the heat of the arc, but a thin film of carbon vapour, at constant temperature, in intimate contact with it.*

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[*] 'Wien. Sitzungsberichte,' vol. 98, p. 1, 233.

Why the End of the Positive Carbon has its Particular Shape.

As only the part of the positive carbon that is in actual contact with the vapour film can be at the temperature of volatilisation, evaporation can only take place at that surface, and hence I suggest that, unless the vapour film is as large as the whole cross-section of the positive carbon, it must dig down into the carbon and leave the surrounding parts unvolatilised, *i.e.*, the part of the positive carbon against which the film rests must become concave. These surrounding parts, however, are heated sufficiently by conduction from the evaporating surface and by the hot gases surrounding them to burn away, and so there must be a race between volatilisation of the centre portion and burning away of the edges, which must, in all cases, determine the shape of the surface of volatilisation. When, all other things being equal, the gap between the carbons is small, so that the end surface of each carbon is well protected from the air, volatilisation will gain over burning and the pit may become very deep. When, on the other hand, the gap is large, so that the air can easily reach all parts of the carbon except that actually covered by vapour, these parts may burn away as fast as, or even faster than the inner portion is volatilised, and in that case the surface of volatilisation will be flat, or even slightly convex. It is evident, therefore, that this surface cannot, from the very nature of things, help being concave when the distance between the carbons is short, and flat or convex when it is long. And this is true, whether the volatilisation is due solely to a large back E.M.F., as some have supposed, or to the resistance of a thin film of carbon vapour, as I have suggested, or partly to one and partly to the other.

When only a small bit of the end of the positive carbon is being volatilised, the outer edge of the carbon will *not* be made hot enough to burn, and the tip will remain relatively blunt. When, on the contrary, the area of volatilisation is large, the edge of the carbon will be burnt away and a long tapering end will be formed, terminating in the surface of volatilisation. Further, the shorter the arc, the less easily will the heat be able to escape from between the carbons, so that the more remains in them to produce burning, and, consequently, the longer must be the tapering part. Experience shows these conclusions to be true.

Why the End of the Negative Carbon assumes its Particular Shape.

The negative carbon is shaped entirely by burning away; the heat that raises it to burning temperature being furnished partly by the mist that touches it, and partly by radiation from the vapour film lying against the positive carbon. The part that the mist rests on is protected by it from the action of the air, and does not, therefore, burn away. At the same time this part must be hotter than the remainder of the carbon, and so the portion of the carbon near it burns away more readily than the rest, leaving a mist-covered tip which is longer and slenderer, because its sides are hotter and burn away more readily, the larger the crater and the shorter the arc.

Hence, with a small crater and a long arc, the negative carbon remains fairly flat, as in *a*, (fig. 2); whereas, as the crater becomes larger, *its* action alone shapes the negative carbon as dotted in *b*, (fig. 2), and the extra heating due to the mist combined with the protection which the mist offers as shown in the full line. With a short arc, on the contrary, a small crater alone would produce an end as dotted in *c*, (fig. 2), while the combined effect of the crater and mist produce the end outlined by the full line. Finally, with a large crater and a short arc, the crater alone would produce an end as dotted in *d*, (fig. 2), while the crater and mist together would shape the negative carbon as given by the full line in *d*. Experience shows that the negative carbon does shape itself in this way under the various conditions.

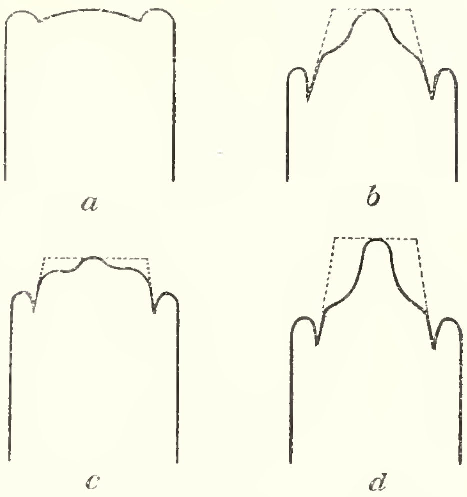

Fig. 2. Negative carbons. *a*, long arc, small crater; *b*, long arc, large crater; *c*, short arc, small crater; *d*, short arc, large crater.

Why the Area of the Crater is not Directly Proportional to the Current, but Depends also on the Length of the Arc.

Suppose that the current and the distance between the ends of the carbons have been kept constant long enough for all the conditions of the arc to have become steady, so that it is "*normal*," and that then the resistance in the outside circuit is suddenly diminished. At the first instant the P.D. between the carbons must be increased, a larger current will have to flow through a vapour film of the old dimensions, and consequently the heat developed in it per second will increase. The temperature of the existing vapour film cannot rise, because there is no increase of pressure, consequently it must expand, and spread over a larger area of solid carbon. The moment the film had expanded in the slightest degree, it would begin volatilising carbon from a part of the surface hitherto inactive, and thus a larger quantity of vapour per second would be volatilised. At the next instant, therefore, the quantity of carbon volatilised per second would have increased, and the resistance of the vapour film would have become lower, and its tendency to expand would, therefore, be diminished on both accounts. Thus, at each instant after the change of current the volatilising surface would increase, but more and more slowly, till its area was such that the heat developed per second in the vapour film only just sufficed, after all losses from conduction, &c., to keep up the volatilisation. After that, the vapour film would cease to expand, and the surface of volatilisation would have reached its maximum area for the new current.

The vapour film, besides radiating heat in all directions from its free surface, must lose a certain extra amount of heat all round its edges by conduction through a ring of the solid carbon that it does not actually touch. The heat thus lost must be subtracted from the edges of the part of the solid carbon that the vapour film does touch, and this part will, therefore, be just *below* the temperature of volatilisation, as will also the small ring of solid carbon outside the vapour film. Suppose, for instance, that the full line in fig. 3 is the part of the positive carbon that is in contact with the vapour film, then the inner dotted line will enclose the area that is actually volatilising fresh carbon, and the space between the two dotted circles will be at a temperature just below that of volatilisation, because the conduction of heat from the edges of the vapour film will bring the outer circle up and the inner circle down to a temperature a little below that of the vapour film itself. The slightly lower temperature of the space between the dotted circles would make it perhaps a little less brilliant than the volatilising surface, but it would still be very much more brilliant than the remainder of the positive carbon, so that it must form the outer circle of what we are accustomed to call the crater, viz., the most brilliantly white part of that carbon. The area of the crater is thus rather larger than the cross-section of the vapour film, while the actively volatilising surface is slightly smaller.

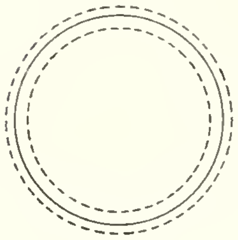

Fig. 3.

When the carbon vapour proceeds from a given area, the cross-section of the vapour film will be greater the more it is protected from the cold outer air by the end of the positive carbon. If, for instance, AB, fig. 4, were the diameter of the volatilising surface, the cross-section of the vapour film would be greater if the end of the carbon were CD, than if it were C′D′, or, since the end of the positive carbon is thicker the longer the arc, *the cross-section of the vapour film is greater the longer the arc.* This film will also be able to keep a larger ring of solid carbon at a temperature just below the lowest at which volatilisation can take place, when the end of the carbon is CD, than when it is C′D′, therefore the whole space that is just below the lowest temperature of volatilisation, *i.e.*, that included between the dotted circles in fig. 3, will be greater with a long arc than with a short one, when the

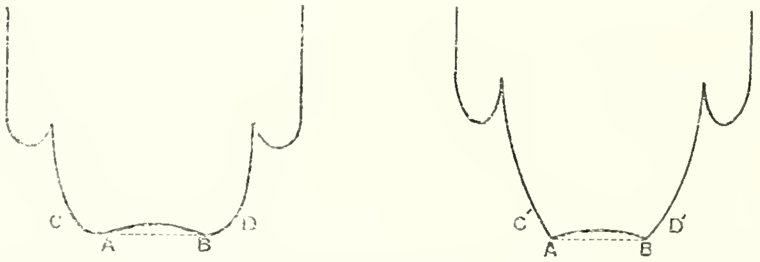

Fig. 4. Positive carbons having the same area of volatilisation. CABD with a long arc. C′ABD′ with a short arc.

surface of volatilisation is the same in each case. In other words, the area of the crater increases with the length of the arc with a given surface of volatilisation. Now, I shall show presently that, in the normal state of the arc, the area of the volatilising surface is directly proportional to the current, but is independent of the length of the arc; it follows, therefore, that with a given constant current the area of the *crater increases* with the length of the arc, as I have found it to do by actual measurement.*

The area of the crater, then, if we define it as that part of the positive carbon that is far brighter than the rest, is not a function of the current only, as has hitherto been affirmed. It is a function of the current, the length of the arc, and, until the arc has become normal after any changes have occurred in the length or the current, of the time after the change was made. The cross-section of the vapour film, on the other hand, *is* proportional to the current, as we shall now see.

The Film of Vapour in Contact with the Positive Carbon acts like a Back E.M.F.

Let a be that area of the film that uses its heat in volatilising fresh carbon, and let x be the part of which the heat is lost by conduction, radiation, &c. Then the whole area of the film is $a + x$, and its resistance, if we consider the thickness of the film to be constant, is $\frac{p}{a + x}$, where p is a constant. The heat generated per second in the film varies as $\frac{pA^2}{a + x}$ and, of this, only $\frac{a}{a + x}$ is used in volatilisation.

The quantity of carbon volatilised per second is, therefore, proportional to

$$\frac{a}{a + x} \cdot \frac{pA^2}{a + x}, \text{ or } \frac{apA^2}{(a + x)^2}.$$

But, therefore, since the temperature at which volatilisation is taking place is a constant one, viz., the lowest possible, the quantity of carbon volatilised per second must be proportional to the area of the surface from which it is volatilised, *i.e.*, to a.

$$qa = \frac{paA^2}{(a + x)^2}, \text{ where } q \text{ is constant,}$$

That is, $a + x$, the area of the vapour film, is proportional to A, the current.

Again, from the above,

$$\frac{a + x}{p} = \frac{A^2}{(a + x)\,q};$$

but

$$\frac{a + x}{p} = \frac{1}{f}, \text{ where } f \text{ is the resistance of the film,}$$

therefore

$$f = \frac{q\,(a + x)}{A^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1).$$

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* 'The Electric Arc,' p. 154.

Or, since $a + x$ is proportional to A,

$$f = \frac{k}{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

where k is constant; that is, Af, the P.D. used in sending the current through the vapour film, is constant.

Hence, no back E.M.F. at the crater is necessary to account for the great fall of potential between it and the arc, for the film of high resistance vapour, whose existence I have suggested, could cause the P.D. between the positive carbon and the arc to remain constant, exactly as if this junction were the seat of a back E.M.F.

The Apparent Negative Resistance of the Arc is caused by the True Positive Resistance diminishing more rapidly than the Current Increases.

It has been mentioned (p. 301) that the specific resistance of the green flame is so high as to make it, to all intents and purposes, an insulator, so that nearly the whole of the current flows through the mist. It follows, therefore, that the resistance of an arc of given length must depend (apart from the resistance of the vapour film) simply on the cross-section of the carbon mist, which, as it appears purple in the image of the arc, can easily be measured. To see how this cross-section varies when the current is increased while the length of the arc is kept constant, I have drawn, in fig. 5, diagrams traced from actual images, after the arc had been burning long enough with each current and length for the P.D. between the carbons to have become quite constant, great care having been taken to trace as accurately as possible the exact limits of the purple centre and the green outer flame.

The resistance of the carbon mist (as distinct from that of the vapour film) may be defined, practically, as being the resistance of that portion of the mist that lies between the parallel planes passing through the mouth of the crater and the tip of the negative carbon.

The mean cross-section of the mist D^2, given in column 3 of Table I., has been obtained by taking the means of the squares of the three lengths AB, CD, and EF. The next column, giving the ratio of D^2 to the current A, shows that the cross-section of the mist increases more rapidly than the current. Column 5 gives numbers proportional to the resistance of the mist, while columns 6 and 7 contain numbers proportional to the power spent in the mist, as obtained from these experiments and from the equation to be subsequently referred to.

The mist carries practically the whole of the current, and, since D^2 increases more rapidly than A (column 4), it follows that in the normal arc the resistance of the mist diminishes more rapidly than the current increases. But equation (2) above shows that the resistance of the vapour film varies inversely as the current. Hence, *with* *solid carbons, the whole resistance of the normal arc diminishes more rapidly than the current increases,* and consequently the P.D. must diminish as the current increases.

Thus, if, in the normal arc, δV be a change made in V, and δA be the corresponding change produced in the current, $\frac{\delta V}{\delta A}$, has a negative value, even although the resistance of the arc is positive, simply because that resistance diminishes faster than the current increases, and *vice versâ.*

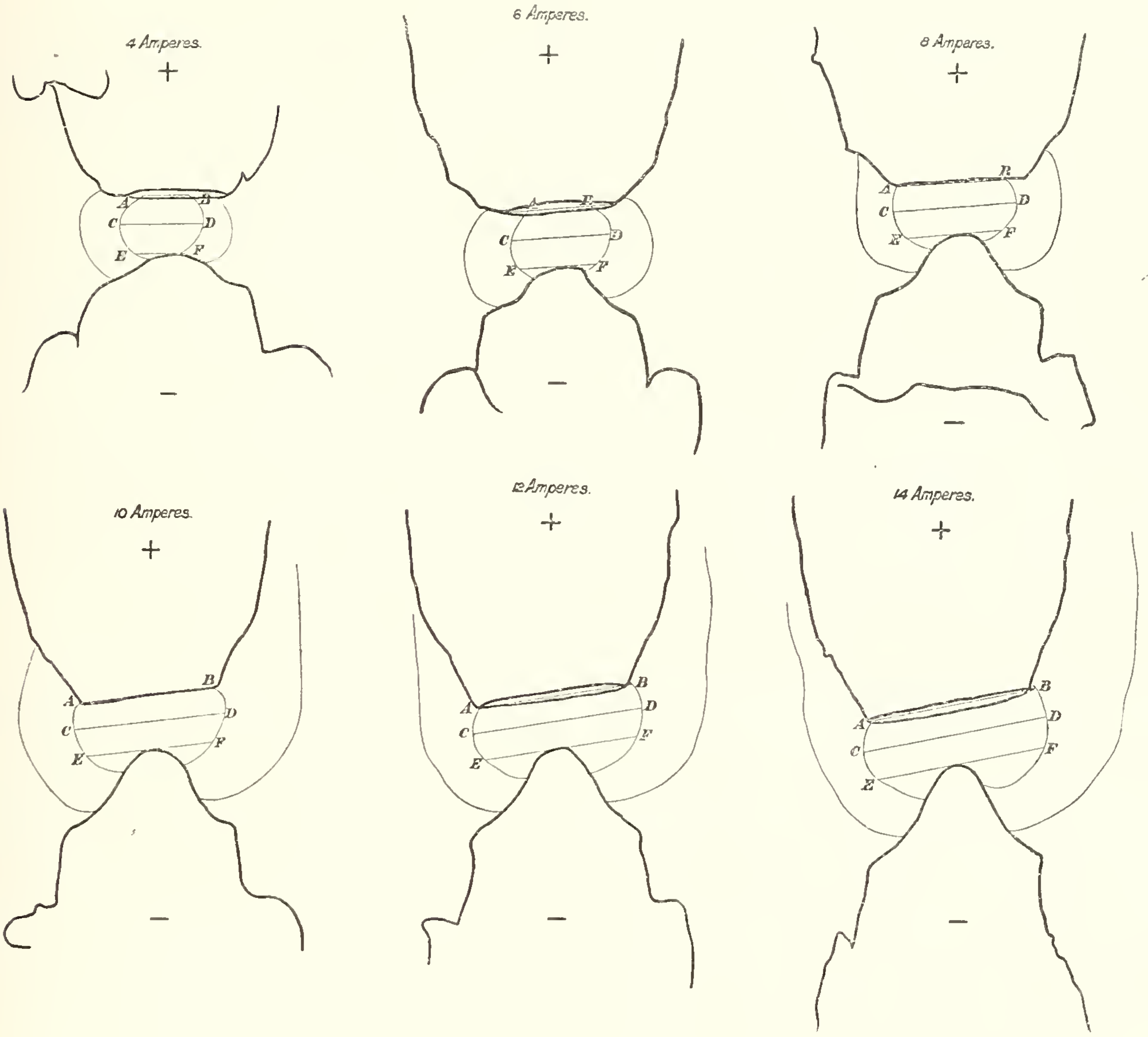

Fig. 5. Diagram of 2-millim. normal arc between solid carbons, positive 18 millims. and negative 15 millims. in diameter.

Table I.—Mean Squares of Diameters of Mist with Corresponding Currents A, and Potential Differences V, between the Carbons. Numbers proportional to Resistances of Mist (Column 5), and Powers Expended in Mist (Column 6). Normal Arc.

Constant Length of Arc = 2 millims.

Solid Carbons, Positive 11 millims., and Negative 9 millims., in diameter.

1.	2.	3.	4.	5.	6.	7.
A.	V.	D^2.	$\frac{D^2}{A}$.	$\frac{1}{D^2}$.	$\frac{A^2}{D^2}$. From Experiment.	$\frac{A^2}{D^2}$. From Equation.
4	51·7	4·8	1·20	0·208	3·33	3·4
6	49·0	9·8	1·63	0·102	3·67	3·68
8	48·0	16·2	2·02	0·061	3·95	3·95
10	47·0	23·4	2·34	0·043	4·27	4·22
12	45·7	34·9	2·91	0·029	4·13	4·49
14	45·1	41·2	2·94	0·024	4·76	4·76

There is Nothing to show that the P.D. between the Carbons Divided by the Current is not the True Resistance of the Arc.

Fig. 6 shows that the curve connecting the values of A^2/D^2 given in the sixth column of Table I., with those of the current given in the first column, is a straight line having the equation

$$A^2/D^2 = 0{\cdot}136\ A + 2{\cdot}86.$$

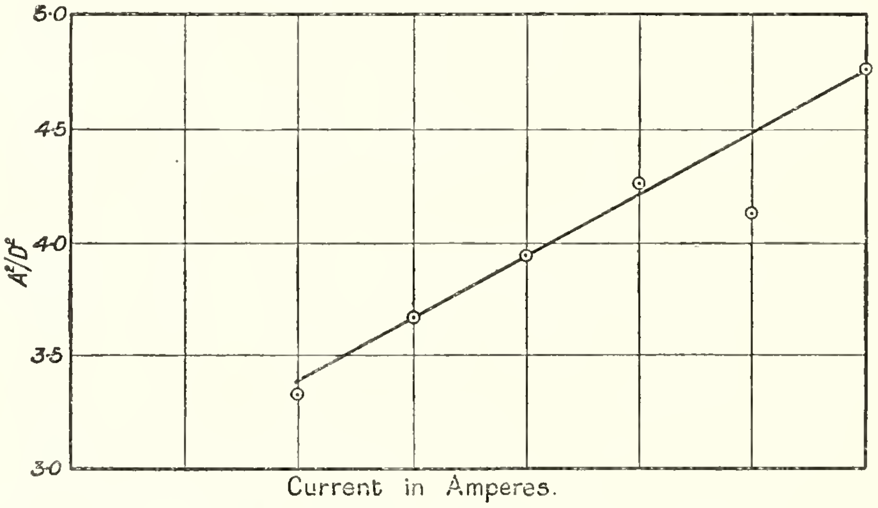

Fig. 6. Curve connecting the power expended in the arc mist with the current. Solid carbons, 11 millims. and 9 millims. in diameter. Length of arc, 2 millims.

Hence, for a normal arc of given length, the power expended in the carbon mist is proportional to a constant plus a term which varies directly with the current. Dividing by A^2, we obtain m, the resistance of the *mist*,

$$m = \frac{0{\cdot}136}{A} + \frac{2{\cdot}86}{A^2}.$$

Combining this with f, the resistance of the vapour film on p. 306, we have for the total resistance of the normal arc an expression of the form

$$f + m = \frac{\alpha}{A} + \frac{\beta}{A^2}.$$

But I have shown* that an equation of the form

$$V = a + bl + \frac{c + dl}{A}$$

exactly fits not only all the numerous measurements that I have myself made ot simultaneous values of the P.D. between the carbons, the current, and the length of the arc, but also all the similar experiments made by other observers when both carbons are solid. When l, the length of the arc, is constant, this equation becomes

$$V = \gamma + \frac{\delta}{A},$$

where γ and δ are constants. Hence, dividing by A, we have, for the total apparent resistance of an arc,

$$r = \frac{\gamma}{A} + \frac{\delta}{A^2}.$$

Thus, by considering only the way in which the resistances of the vapour film and of the carbon mist respectively must vary with the current, we arrive at an equation for the resistance of exactly the same form as is obtained by dividing by the current the values found experimentally for the P.D. between the carbons. So that instead of an arc consisting of a circuit of low resistance combined with a back E.M.F., it may well be that its *apparent* resistance, *i.e.*, the ratio of V to A, is its *true* resistance; or it may be that, if there is any back E.M.F. at all, it is very much smaller than has hitherto been supposed.

Both the Resistance of the Arc and the P.D. between the Carbons depend not only on the Current and the Length, but also on How Lately a Change has been made in Either and on What that Change was.

The whole resistance of the arc depends on the cross-sections of the vapour film and the mist, and on the distance between the carbons. Now I have shown that

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* 'The Electric Arc,' p. 186.

when the P.D. between the carbons is changed—increased, say—the *first* result must be an increase of current, while the *second* is a corresponding increase in the cross-sections of the vapour film and the mist, causing a *diminution* of the resistance, and, consequently, of the P.D. between the carbons. *Thirdly*, if the new current is kept constant long enough, the end of the negative carbon burns away to a longer slenderer point, allowing more of the mist to escape, so that it takes a smaller cross-section, and, consequently, both the resistance and the P.D. increase again, although they never reach such high values as they had with the smaller current.

Fig. 7 is useful as showing at a glance how the resistance and the P.D. depend upon the time that has elapsed after a change of current. When the arc is normal, in the first instance, A B, A′ B′, and A″ B″ represent the curves connecting the P.D., the current, and the true resistance of the arc respectively with the time. When the P.D. is increased from B to C, the resistance does not alter at the first instant, but the current rises to C′. If it is then kept constant at C′, the surface of volatilisation next increases in area, the resistance falls to D″, and the P.D. consequently falls to D. After this the carbons begin to grow longer points; the cross-section of the mist diminishes, the resistance, therefore, increases to E″, and the P.D. with it to E. The arc has now become normal again, so that the curves are all now parallel straight lines, the current higher than before, and the P.D. and resistance lower.

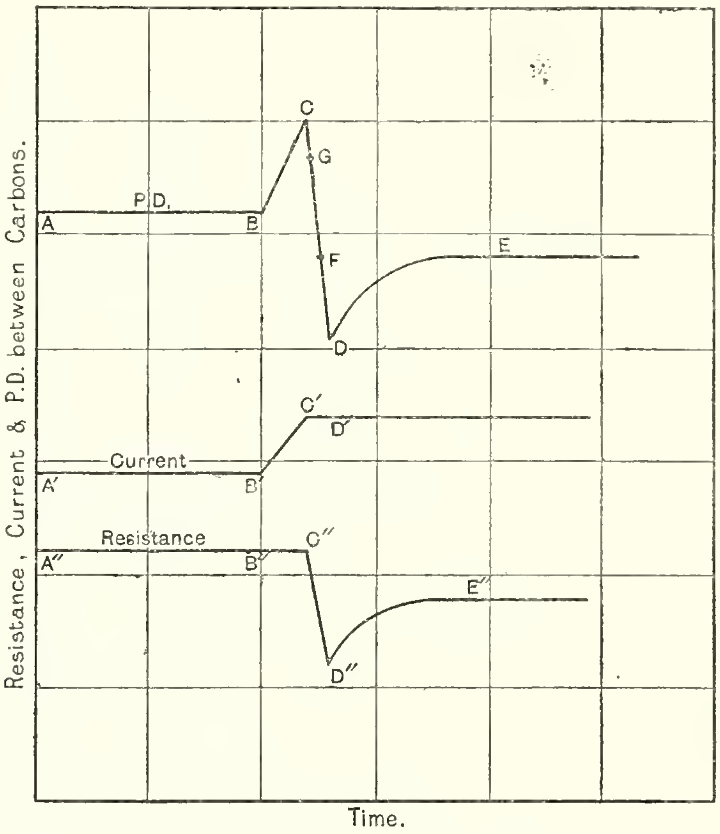

Fig. 7. Suggested simultaneous time-changes of P.D., current and resistance.

Thus any alteration that is made and maintained in the arc sets up a series of changes in its resistance and, consequently, in the P.D. between the carbons, that cease only when the arc becomes normal again. In other words, when an arc of given length, with a given current flowing, exists between given carbons, neither the resistance nor the P.D. between the carbons has any fixed value, except when the arc is, and continues to be normal. In all other cases each varies, within certain limits, according to the time that has elapsed since either the current, or the length was altered, and according to what change was then made.

That the P.D. does actually undergo alterations of the kind just described, after a change of current, is evident from fig. 8, the curves in which were plotted from actual experiments made in 1893. For these curves, the current was suddenly altered when the arc was quite normal, and was then kept constant at the new value while the P.D. continued to alter, the time change of P.D. being noted. The first change of P.D.—the *rise* or *fall* that must have instantaneously accompanied the change of current, when the resistance outside the arc was suddenly diminished—was too quick to detect. Indeed, it was only after assisting in carrying out these experiments that it occurred to me that we ought to have seen it, and that, on trying, I found I could sometimes detect it and sometimes not.*

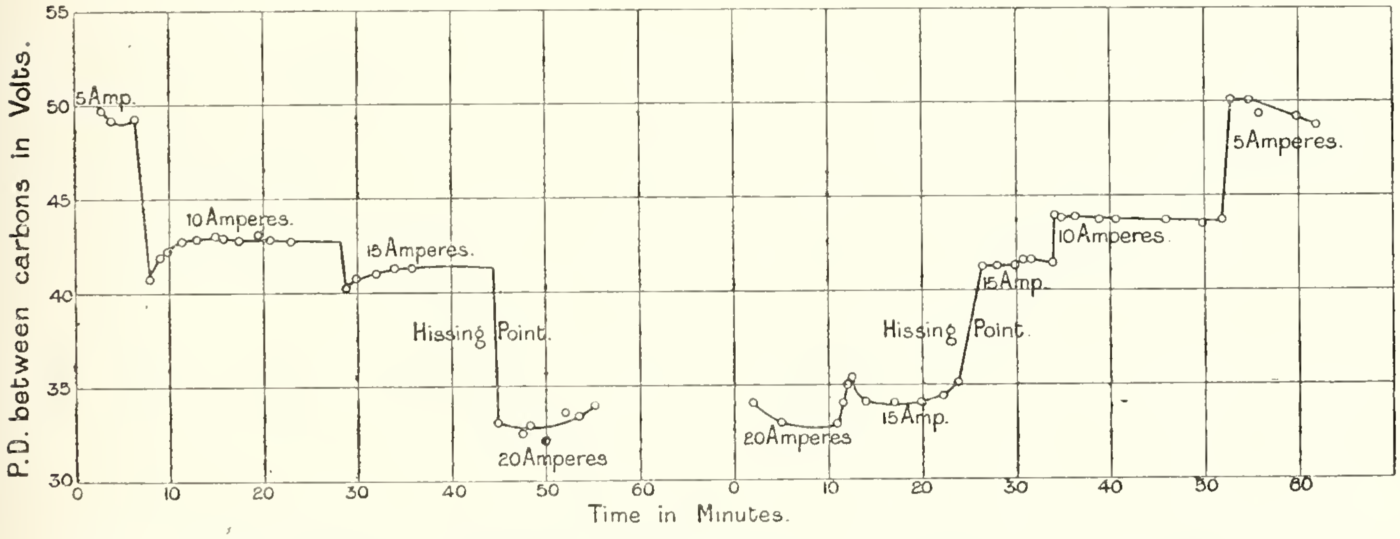

Fig. 8. Experimental curves showing simultaneous time-changes of P.D. and current with a constant length of arc of 1 millim. Solid carbons, 18 millims. and 15 millims. in diameter.

The rapid change in the P.D. while the area of the crater and the cross-section of the mist were altering, is very marked, however, as well as the slow rise or fall of P.D. accompanying the diminution or increase in the cross-section of the arc due to the change in the cross-section of the carbon ends.

Why Measurements of the Resistance of the Arc made under the same Apparent Conditions Differ in Value and even in Sign with Different Experimenters.

The dependence of the resistance of the arc on its previous history, as well as on the actually existent length and current, has an important bearing on the question

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[*] It is only when the carbons are cored that it can be detected. The reason will be explained later.

of measuring the resistance by means of a small superimposed alternating current. Such a method has been employed by many experimenters, but the results have not shared the similarity of the methods; for while VON LANG and ARONS found, in 1887, that the arc had a *positive* resistance, Messrs. FRITH and RODGERS, in 1896, found that it had a *negative* one with solid carbons.

We shall now see the reason of this disparity, and first it may be well to recall shortly the reasoning on which the method is based.

The equation $V = E + Ar$ may be taken to represent the connection between the P.D. between the carbons, the current, and the length of the arc, whether it has a variable E.M.F., a constant E.M.F., or none at all. For in the first case E will be variable, in the second constant, and in the third zero. In any case $\delta V/\delta A = r$, *only when such a small quick change is made in V and A that neither E nor r is made to vary by it.*

Instead of a single small quick change of current, the experimenters superimposed a small alternating current on the direct current of the arc, and measured the *average* value of $\delta V/\delta A$, or its equivalent. Obviously, if the alternating current left the resistance and any back E.M.F. that might exist in the arc unaffected, this was a *true* measure of the resistance of the arc. But if the alternating current changed both or either of these, then instead of being equal to r, we should have

$$\frac{\delta V}{\delta A} = r + \frac{\delta E}{\delta A} + A\frac{\delta r}{\delta A} \quad . \quad . \quad \text{if there is a back E.M.F., and if both it and the resistance varied with the alternating current;}$$

$$\frac{\delta V}{\delta A} = r + \frac{\delta E}{\delta A} \quad . \quad . \quad . \quad . \quad \text{if there is a back E.M.F., and if it alone varied;}$$

$$\frac{\delta V}{\delta A} = r + A\frac{\delta r}{\delta A} \quad . \quad . \quad . \quad . \quad \text{if there is no back E.M.F., or if the resistance alone varied.}$$

None of the experimenters, as far as I am aware, applied any but a few imperfect tests to see whether the alternating currents they employed affected the resistance of the arc or not, and it was, I believe, because the resistance *was* affected, in every case, that such diverse results were obtained. The low frequency of the alternations was the probable source of error, for I shall now show that, with a given root mean square value of the alternating current, the average value of $\delta V/\delta A$ varies not only in magnitude, but even in sign, with the frequency of that current.

Effect of the Frequency of the Superimposed Alternating Current on the Value and Sign of $\delta V/\delta A$.

I have shown (p. 310) that when a sudden increase of the current is made and maintained the P.D. has three successive stages of variation. It first rises (BC, fig. 7), then falls (CD), then rises again (DE), but not so high as before, and after this it remains constant. In dealing with a superimposed alternating current there is, of course, no sudden increase and diminution, everything is gradual. The three changes of P.D. do not, therefore, act separately—they overlap. At any moment, for instance, when the current is increasing say, the increase may be considered due to the addition of successive small increments of current, so that the P.D. has a tendency to rise on account of the last added increment of current, to fall on account of the diminution of resistance due to the last but one, and to rise on account of the re-shaping of the carbons following the last but two. If the frequency of the alternating current is very low indeed, so that the current changes very slowly, all three of these tendencies will be in force at each moment, and the actual change of P.D. will be the resultant of the three. If the frequency is so high that the shapes of the carbons never change at all, but so low that the area of the volatilising surface can alter, only the first two tendencies will be operative; while, if the frequency is so high that the area of the volatilising surface remains constant, the resistance of the arc will not alter at all, the current and P.D. will increase and diminish together and proportionately, and, unless the arc contains a variable back E.M.F., $\delta V/\delta A$ will measure the true resistance of the arc.

The influence of the frequency of the alternating current on the magnitude and sign of $\delta V/\delta A$ is traced in fig. 9. PR represents the time occupied by one complete alternation, whatever that time may be. If, for instance, the frequency is 50 complete alternations per second, PR represents one-fiftieth of a second; if the frequency is 5000, PR represents one-five thousandth of a second. PSQTR represents the time change of current with any frequency. When the alternations are so slow that the arc remains normal, the change of P.D., δV, for a given small change of current, WS say, is the resultant of three such changes as BC, CD, and DE (fig. 7), and it is in the opposite direction from the change of current. The P.D. time curve is something like PXQYR (fig. 9) therefore, and $\delta V/\delta A$ is the mean of such ratios as ZX/WS, and is therefore negative.

When the frequency is raised, so that the carbons never have time to alter their shapes completely before the current changes, the third variation, DE, (fig. 7, p. 310) is smaller than with the normal arc, so that δV is greater negatively, and $\delta V/\delta A$ must, therefore, have a larger negative value than when the arc is normal, and such a curve as PX_1QY_1R would be the P.D. time curve in this case.

When the frequency was so high that the carbons never altered their shapes at all, but the volatilising surface underwent the maximum alteration, the third variation (DE fig. 7) would be absent altogether, and therefore δV would undergo the greatest change it was susceptible of in the opposite direction to the change of current, so that PX_2QY_2R is then the P.D. time curve,, and $\delta V/\delta A$ has then its maximum negative value, and is the mean of such ratios as Z_2X_2/WS.

With a further increase of frequency, the area of the volatilising surface would never have time to change completely, so that δV would be the resultant of two such changes as BC and CF, say, (fig. 7) only; $\delta V/\delta A$ would therefore have a *smaller* negative value than with the lower frequency last mentioned, and the curve denoting the time change of P.D. might again be PX_1QY_1R, or it might be PX_3QY_3R, if the frequency were high enough. When the frequency was so great that the two P.Ds., BC and CD (fig. 7) were exactly equal, the P.D. would not alter at all when the current was changed, $\delta V/\delta A$ would be zero, and the straight line PQR would be the time change of P.D. curve. When the frequency was further increased, the change of P.D. would be the resultant of two such changes as BC, CG (fig. 7), the total change of P.D. would therefore be in the *same* direction as the change of current, the P.D. time curve would be like PX_4QY_4R, and $\delta V/\delta A$ would be $+ Z_4X_4/WS$. Finally, when the frequency was so great that the area of the volatilising surface never altered at all, the change of P.D. would be BC (fig. 7) alone, the P.D. time curve would be PX_5QY_5R, δV would be Z_5X_5, and $\delta V/\delta A$, or Z_5X_5/WS would measure the *true* resistance of the arc, even if there is a back E.M.F. in the arc, unless that back E.M.F. varies with the current.

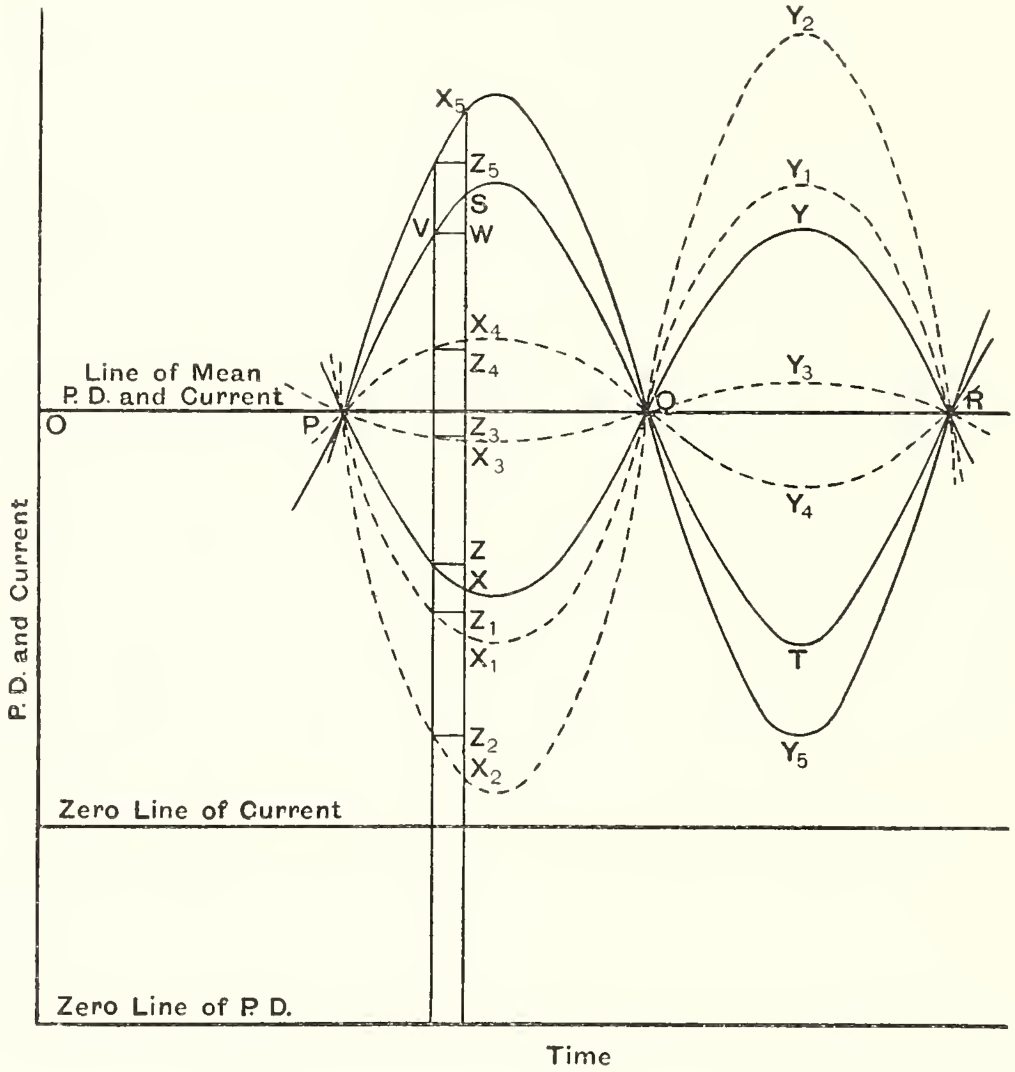

Fig 9. Suggested curves connecting current and P.D. with time for different frequencies of the same small superimposed alternating current, when the direct current and length of the arc are constant.

Thus, by applying the same alternating current, but with different frequencies, to a direct current arc, $\delta V/\delta A$ can be made to have any value from a fairly large negative value to the true positive value. It is easy to see, therefore, how different experimenters might get very different values and even different signs for the resistance of the arc, when they measured it by means of a superimposed alternating current; and fig. 9 shows the imperative necessity of some rigorous proof that the alternating current has not affected the resistance of the arc before any such measurements can be accepted as final. I shall presently show how such a proof can be obtained, but first it will be interesting to see how, with an arc of given length, and with a given current flowing, the value of $\delta V/\delta A$ is connected with the frequency of the alternating current, and what sort of frequency is required in order that the resistance of the arc shall not be affected by this current.

To find the Curve connecting $\delta V/\delta A$ with the Frequency of the Superimposed Alternating Current, and to see with what Frequency $\delta V/\delta A$ Measures the True Resistance of the Arc.

Take an arc of 2 millims. with a direct current of 10 amperes flowing. For the arc to remain normal when the small alternating current is superimposed on it, the frequency must be practically zero, for each alternation must take many seconds instead of only a small fraction of a second. Now the equation I have found* between V, A, and l, in the normal arc with solid Apostle carbons is

$$V = 38{\cdot}88 + 2{\cdot}07l + \frac{11{\cdot}66 + 10{\cdot}54l}{A};$$

therefore the normal $\delta V/\delta A = -\dfrac{11{\cdot}66 + 10{\cdot}54l}{A^2} = -0{\cdot}33$, when $l = 2$, and $A = 10$.

The first point on the curve connecting $\delta V/\delta A$ with the frequency of the alternating current has, therefore, the co-ordinates 0, and $-0{\cdot}33$ (A, fig. 10).

The value found for $\delta V/\delta A$ by Messrs. FRITH and RODGERS† with the same carbons, direct current, and P.D. was about $-0{\cdot}8$, more than double the normal value, which shows that the alternating current they superimposed was making the resistance of the arc vary to an extent that made the P.D. follow some such curve as PX_2QY_2R (fig. 9). They also found that varying the frequency from 7 to 250 complete alternations per second made no difference in the value they obtained for $\delta V/\delta A$. Therefore the curve connecting $\delta V/\delta A$ with the frequency must fall steeply from A, the point of no frequency, to B, the point for a frequency of 7, and must be practically horizontal from B to C (fig. 10). Hence Messrs. FRITH and RODGERS' observations cover the portion BC of the curve.

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* 'The Electric Arc,' p. 184.

† 'Phil. Mag.,' 1896, vol. 42, Plate 5.

The next point D, is obtained from Mr. DUDDELL'S work. In his remarkable paper[*] on "Rapid Variations in the Current through the Direct Current Arc," he said, "I tried to record the transient rise in P.D. for the solid arc by means of an oscillograph, the sudden increase of the current being obtained by discharging a condenser through the arc. This experiment was successful, and a transient rise in P.D. was observed, *the P.D. and current increasing together, but only for about* 1/5000 *second*." It is clear from this that $\delta V/\delta A$ must at least *begin* to be positive with a frequency of 2,500 complete alternations per second; and D where OD = 2,500 may be taken to be the point near which $\delta V/\delta A$ changes its sign.

To the right of D the curve must continue to rise, as indicated in fig. 10, more and more slowly, as it approaches the horizontal line whose distance from the axis of frequency represents the value of $\delta V/\delta A$ which is the *true* resistance of the arc. The curve must finally become asymptotic to this line, since when once a frequency is nearly reached with which the alternating current does not practically affect the resistance of the arc, increasing the frequency will not alter the value of $\delta V/\delta A$.

My equation above shows that the resistance of the particular 2-millim. 10-ampere normal arc under discussion cannot be greater than 4·63 ohms, nor less than 0·62 ohm; for if there is no back E.M.F.,

$$r = \frac{38{\cdot}88 + 2{\cdot}07 \times 2}{10} + \frac{11{\cdot}66 + 10{\cdot}54 \times 2}{100}$$
$$= 4{\cdot}63;$$

and if there is the largest possible back E.M.F., viz., $38{\cdot}88 + \frac{11{\cdot}66}{A}$ volts (for it is impossible to imagine that terms involving the length of the arc can belong to a back E.M.F.), then $r = \frac{2{\cdot}07 \times 2}{10} + \frac{10{\cdot}54 \times 2}{100} = 0{\cdot}62$.

Thus the curve cannot rise higher than the horizontal line $\delta V/\delta A = 4{\cdot}63$, and it must rise at least as high as $\delta V/\delta A = 0{\cdot}62$. Consequently, as the lower curve in fig. 10 shows, the true resistance of this particular arc could not be measured with a superimposed alternating current having a frequency of less than at least 8000 complete alternations per second, even if there were a back E.M.F. as great as 40 volts. And if, as I have suggested, the back E.M.F. is zero, or at least very much smaller than 40 volts, the frequency would have to be many times as high for $\delta V/\delta A$ to be on the horizontal part of the curve, *i.e.*, for the alternating current not to alter the resistance of the arc.

The Form of the P.D. Time Curve indicates whether the Resistance of the Arc is Affected by the superimposed Alternating Current or Not.

The final test as to the frequency being high enough not to affect the resistance of the arc must, of course, be the finding, with the same root mean square value of the

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[*] 'Journal of the Institution of Electrical Engineers,' vol. 30, p. 232.

alternating current, of two frequencies, differing by many thousands of alternations per second, that would both give the same value of δV/δA. This would show that the horizontal part of the δV/δA frequency curve (fig. 10) had been found.

A very good *first* test, however, is furnished by the curve connecting the P.D. between the carbons with the time, for this curve is unsymmetrical with respect to the corresponding current curve, when the resistance *is* affected, for the following reasons.

I have shown that the change in the area of the volatilising surface of the crater that is due to any change of current follows *after* the change of current and requires time for its completion. If, therefore, a superimposed alternating current is affecting the resistance of a direct current arc, the P.D. required for any given current must be higher when the current is increasing than when it is diminishing. A current of 10 amperes, for instance, would require a higher P.D. when it came after 9 and before 11 amperes than when it came after 11 and before 9 amperes, because in the first case it would be flowing through an arc of which the cross-section had been made by some current *less* than 10 amperes, and in the second by some current *greater* than 10 amperes.

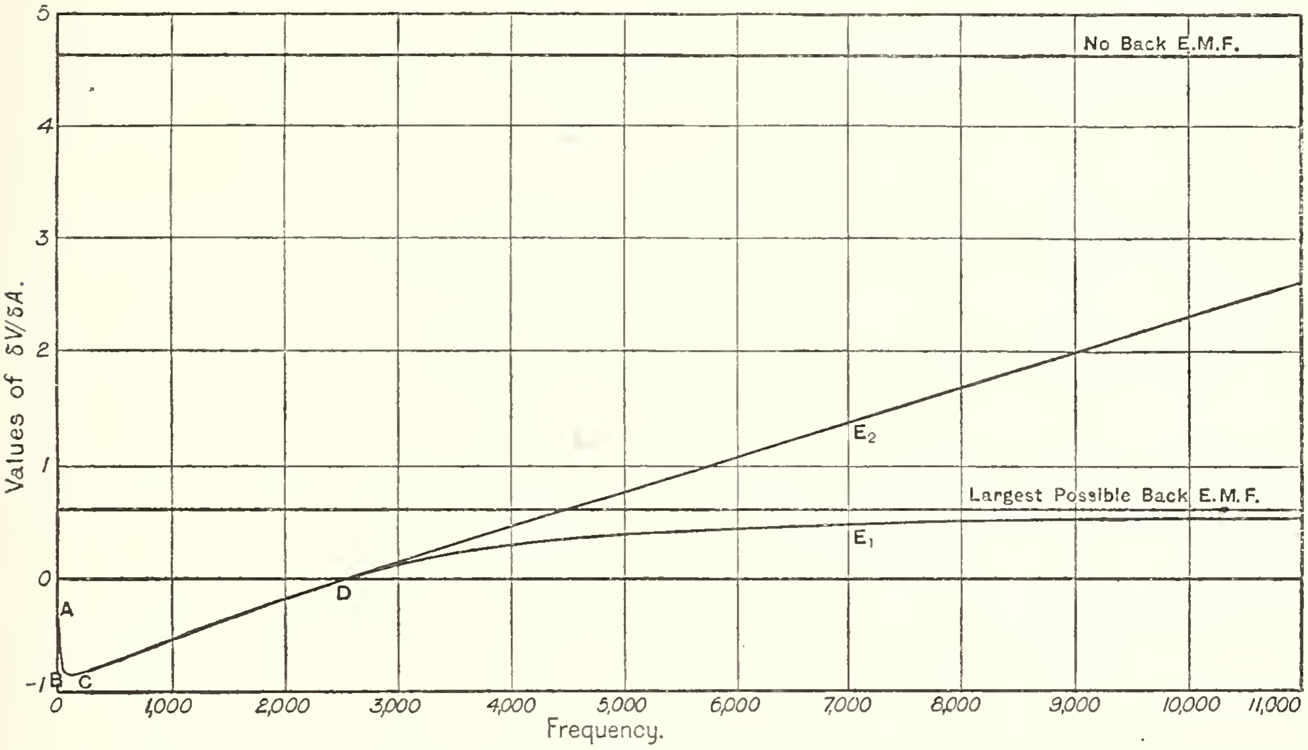

Fig. 10. Suggested curve connecting δV/δA with the frequency of a superimposed alternating current of constant root mean square value, when the direct current and the length of the arc are constant.

I have applied this test, with very satisfactory results, to some experiments in which it is quite certain that the alternating currents must have affected the resistances of the arcs, because they had frequencies of only 47 and 115 alternations per second respectively.

The experiments formed part of a valuable series carried out in 1896 by Messrs.

Ray and Watlington, two students at the Central Technical College, in continuation of the researches of Messrs. Frith and Rodgers. The carbons were solid, and the direct current normal arc carried a current of 10 amperes with a P.D. of 45 volts. Simultaneous values of the current and P.D. were taken with the Joubert point by point method. Some of these are given in Table II., in which the columns headed V_i are the P.D.'s with increasing currents, and those headed V_d with diminishing currents; while V_s and V_l belong to the smallest and largest current respectively.

It may be seen at a glance that in every single instance the P.D. for the same current is higher when the current is increasing than when it is diminishing. For instance, with the lower frequency the P.D. corresponding with a current of 11 amperes is 42·4 volts when the current is increasing, and only 41·8 volts when it is diminishing. And with the higher frequency it is 43·2 volts with increasing current, and only 42·0 with a falling current. Hence, we are supplied with a very simple test as to whether the superimposed alternating current changes the resistance of the arc or not. It is only necessary to take the wave form of P.D. and current by means of an oscillograph, and to observe whether the P.D. corresponding with each current is the same with increasing as with diminishing currents. If the two P.Ds. are different, the resistance is being altered, if they are alike, it is not.

Table II.—Instantaneous Values of Corresponding Currents and P.Ds. with Small Alternating Current Superimposed on Direct Current of 10 Amperes in the Arc. P.D. with Direct Current alone, 45 volts.
Solid Apostle Carbons: Positive, 11 millims.; Negative, 9 millims.

		Frequency, 47.					Frequency, 115.		
A.	V_s.	V_i.	V_l.	V_d.	A.	V_s.	V_i.	V_l.	V_d.
8·425	45·6	—	—	—	8·65	46	—	—	—
9·0	—	44·8	—	44·0	9·0	—	45·6	—	44·9
9·5	—	44·2	—	43·3	9·5	—	45·2	—	44·2
10·0	--	43·7	—	42·8	10·0	—	44·6	—	43·5
10·5	—	43·1	—	42·1	10·5	—	43·9	—	42·9
11·0	—	42·4	—	41·8	11·0	—	43·2	—	42·0
11·5	—	42·0	—	41·4	11·25	—	—	42·2	—
12·0	—	41·7	—	41·2	—	—	—	—	—
12·25	—	—	41·4	—	—	—	—	—	—

How to Ascertain with Certainty whether there is a Constant or a Variable Back E.M.F. in the Arc or None, and how to find the True Back E.M.F. if there is One.

Returning to the equation

$$V = E + Ar,$$

we have

$$\frac{\delta V}{\delta A} = \frac{\delta E}{\delta A} + r + A\frac{\delta r}{\delta A}, \text{ when both E and } r \text{ vary,}$$

and hence

$$V - A\frac{\delta V}{\delta A} = E - A\frac{\delta E}{\delta A} - A^2\frac{\delta r}{\delta A}.$$

If the alternating current with which $\delta V/\delta A$ is measured is of such high frequency that it does not alter the resistance of the arc, and if, also, the back E.M.F. is constant, or, being variable, the alternating current is too small to affect it, then

$$V - A\,\delta V/\delta A = E.$$

To see whether the arc has any back E.M.F. at all, therefore, it is only necessary to measure $\delta V/\delta A$ with a superimposed alternating current of a frequency that has been found not to affect its resistance and to subtract $A\,\delta V/\delta A$ from V. If the result is zero, the arc has *no* back E.M.F. If it is not zero, $\delta V/\delta A$ must be measured in the same way for other arcs differing widely in current and length. If all the values of $V - A\,\delta V/\delta A$ thus obtained are equal, or nearly so, the arc has a constant back E.M.F. which is equal to this value. If $V - A\,\delta V/\delta A$ is *not* the same for all the arcs, but varies according to some definite law, then there is a *variable* back E.M.F. which may or may not be affected by the alternating current used to measure $\delta V/\delta A$.

Suppose, for instance, that two measurements of $\delta V/\delta A$ were made, using the same direct current and length of arc, but different alternating currents. If one of the alternating currents had a root mean square value equal to one per cent. of the direct current, and the other a value equal to five per cent., one would be five times as great as the other, and yet both would be small compared with the direct current. It would, of course, be possible to make the frequency of each of these currents so great that the resistances of the arcs to which they were applied were not altered by them. Yet it would not necessarily follow that when this had been done the two values of $\delta V/\delta A$ thus obtained would be equal. For the back E.M.F. might vary not with the *frequency* of the alternating current, but with its *magnitude*. If, therefore, it were found that E was variable, it would be necessary to measure $\delta V/\delta A$ with smaller and smaller alternating currents, till two were found which, while differing considerably from one another, both gave the same value of $\delta V/\delta A$. Only a value obtained in this way could be accepted as measuring the *true* resistance of the arc, and $V - A\,\delta V/\delta A$ would be the *true* back E.M.F. of the same arc.

THE CHANGES INTRODUCED INTO THE RESISTANCE OF THE ARC BY THE USE OF CORED CARBONS.

Next let us consider the explanation of the marked effects produced by introducing a core into either or both of the carbons. These are of a two-fold character; first, those such as Professor AYRTON published at Chicago in 1893, viz.:

(1.) The P.D. between the carbons is always lower for a given current and length of arc, when either or both of the carbons are cored, than when both are solid.

(2.) With a constant length of arc and increasing current, the P.D., which diminishes continuously when both carbons are solid, either diminishes less when the positive is cored, or after diminishing to a minimum remains constant over a wide range of current, or even increases again.[*]

(3.) It requires a larger current with the same length of arc to make the arc hiss when the positive carbon is cored than when both are solid.

Secondly, there are the facts connected with the influence of cores on the small *change* of P.D. accompanying a small *change* of current, to which attention was first drawn by Messrs. FRITH and RODGERS in 1896.[†] These facts, which were physically correct, although, as I have already shown, they were wrongly interpreted at the time, are embodied in the following wider generalisations which I have deduced from the results of my experiments, and from theoretical considerations.

(1) When, on a direct current arc, an alternating current is superimposed which is small, but yet large enough for the resistance of the arc to be altered by it, the average value of $\delta V/\delta A$ is always more positive[‡] when either carbon is cored than when both are solid, and most positive of all when both are cored, all other things being equal.

(2) The frequency of the alternating current that makes $\delta V/\delta A$ begin to have a positive value is lower when either carbon is cored than when both are solid, and lowest when both are cored.

(3) The value of $\delta V/\delta A$, with a given root mean square value of the superimposed alternating current, depends not only on the nature of the carbons and on the frequency of that current, but also on the magnitude of the direct current, and on the length of the arc.

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[*] NEBEL observed the fact that the P.D. fell to a minimum and then rose again, in 1886, but as he used *cored* positive carbons *only*, he did not discover that this form of curve was peculiar to those carbons.

[†] "The Resistance of the Electric Arc," 'Phil. Mag.,' 1896, vol. 42, p. 407.

[‡] I call $\delta V/\delta A$ *more positive* in one case than in another when it has either a larger positive value, or a smaller negative value in the first case than in the second.

There are two ways in which the P.D. between the carbons, for a given current and length of arc, may be lowered by the core; (1) by an increase in the cross-section of the vapour film, or the mist, or both; (2) by a lowering of their specific resistances. To see whether I could observe any change in the cross-sections, I have traced a series of enlarged images of the arc with four sets of Apostle carbons, using (1) + Solid − Solid, (2) + Solid − Cored, (3) + Cored − Solid, (4) + Cored − Cored carbons.

The positive carbon was 11 millims. and the negative 9 millims. in diameter, and the arc 2 millims. in length in each case, while the currents were 4, 6, 8, 10, 12, 14 amperes. The diagrams were traced not only when the arc was normal in each case, but also immediately after each change of current, so that the effect on the cross-section of the arc of both an instantaneous and a normal change of current might be seen. Fig. 5 (p. 307) showed the first set of diagrams of the normal arc; the others are too numerous to publish, but the mean cross-sections of the purple part—the mist—in each, measured as in fig. 5, may be found in Table III., those marked "non-normal" belonging to the arc *immediately* after the change of current, and those marked "normal" to the arc after all the conditions had become steady again.

TABLE III.—Mean Cross-Sections of Mist between + Solid − Solid, + Solid − Cored, + Cored − Solid, and + Cored − Cored Apostle Carbons, 11 millims. and 9 millims.

Length of Arc, 2 millims.

Current in amperes.	Normal.				Non-normal.			
	S.S.	S.C.	C.S.	C.C.	S.S.	S.C.	C.S.	C.C.
4	4·8	6·95	4·0	3·3	—	—	—	—
6	9·8	8·3	6·05	5·6	9·5	8·4	6·25	3·5
8	16·2	14·2	11·0	8·9	17·6	11·1	12·0	5·8
10	23·4	20·75	13·55	11·9	21·5	19·0	18·7	11·1
12	34·9	27·6	17·7	16·55	34·1	26·9	20·1	16·7
14	41·2	35·0	24·5	20·0	—	39·4	—	18·7

With a single exception, every number in each set is smaller than the corresponding number in the preceding column. Hence, with both normal and non-normal arcs the mean cross-section of the mist, for a given current, is largest when both carbons are solid, smallest when both are cored, and is more diminished by coring the positive than by coring the negative. Fig. 11, besides showing well this marked difference in the influence of the cores, makes it apparent that the difference increases, in every case, with the current, for such currents as were there used.

We cannot measure the cross-section of the vapour film directly, but, for a constant length of arc, it must be roughly proportional to the cross-section of the mist where it touches the crater. These cross-sections, which are given in Table IV., do not, naturally, vary nearly so regularly as the mean cross-sections, but still we can judge pretty well what are the effects of the various cores. Coring the positive carbon, for instance, distinctly diminishes the cross-section of the vapour film; for every number in column (7) is less than the corresponding one in column (5), and all but one in column (3) are less than those in column (1). Coring the negative carbon, on the other hand, only seems to affect the cross-section that the vapour film assumes *immediately* after a change of current, for while in the *non-normal* section each number in (6) is less than in (5), and in (8) less than in (7), in the *normal* section the numbers in (2) are sometimes less and sometimes greater than those in (1), and those in (4) are nearly all greater than those in (3).

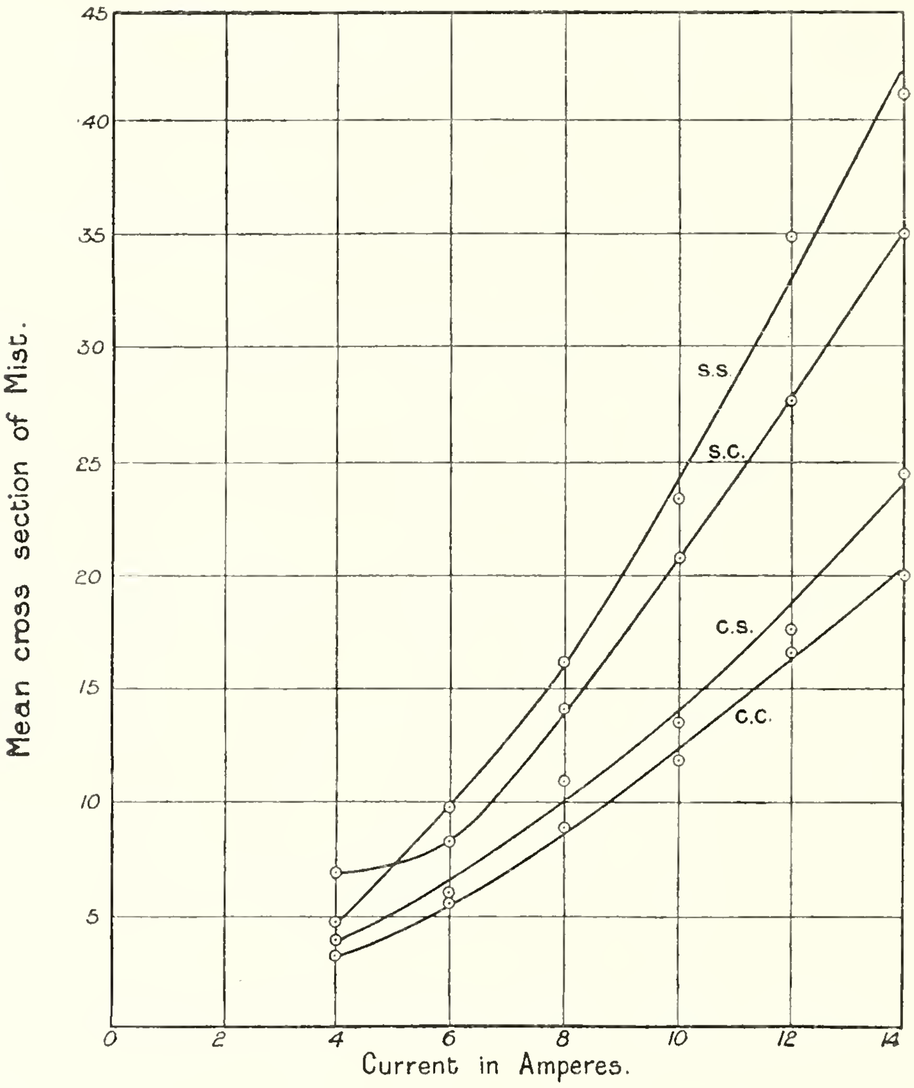

Fig 11. Curve connecting the mean cross-section of the arc mist with the current for + solid, − solid, + solid − cored, + cored − solid, and + cored − cored carbons respectively. Apostle carbons, 11 millims. and 9 millims. Length of arc, 2 millims.

TABLE IV.—Cross-section of Mist where it touches Crater, with + Solid − Solid, + Solid − Cored, + Cored − Solid, + Cored − Cored Carbons.

APOSTLE Carbons, 11 millims. and 9 millims.

LENGTH of Arc, 2 millims.

Current in Amperes.	Normal.				Non-normal.			
	(1) S.S.	(2) S.C.	(3) C.S.	(4) C.C.	(5) S.S.	(6) S.C.	(7) C.S.	(8) C.C.
4	2·9	7·8	3·2	2·9	—	—	—	—
6	6·8	9·0	5·3	5·8	10·9	6·25	6·25	3·6
8	16·0	13·0	10·9	14·4	16·0	9·0	10·9	6·25
10	23·0	26·0	12·25	21·2	19·4	16·8	15·2	15·2
12	32·5	25·0	17·6	22·1	31·4	23·0	17·6	21·2
14	39·1	36·0	23·0	24·0	—	33·6	—	19·4

Thus, taking Tables III. and IV. together, we find that a core in the positive carbon keeps both the mist and the vapour film from being as large as they would be with a solid positive, both immediately after a change of current and when the arc is normal again. Coring the negative, on the other hand, while it has the same effect on the cross-section of the *mist* as coring the positive, only diminishes the cross-section of the *vapour film* immediately after a change of current. If, therefore, coring either carbon produced nothing but an alteration in the cross-section of the arc, the resistance of the arc, and, consequently, the P.D. between the carbons would be *increased* by the coring. It follows, therefore, that the diminution of the P.D. between the carbons actually observed with cored carbons must be caused by a lowering of the specific resistance of the vapour film or of the mist, or of both; and this lowering must be so great that it must more than compensate for the diminution in their cross-sections.

It is easy to see how the vapour and mist from a core in the *positive* carbon must alter the specific resistance of the arc, but, since the *negative* carbon does not volatilise, there seems to be no reason why coring *it* should have the same effect. The core, however, consists of a mixture of carbon and metallic salts; and metallic salts have a lower temperature of volatilisation than carbon, so that these salts may easily be volatilised by the *mist* touching them, and, mingling with it, lower its specific resistance.

Now take the fact that, with a constant length of arc, on increasing the current the P.D. always diminishes less if the positive carbon is cored than if it is solid, and that the reduction of diminution is sometimes so great that the P.D. remains constant for a large increase of current, and sometimes even increases somewhat, instead of steadily diminishing, as it does when both carbons are solid.

Every increase of current, whether the carbons are solid or cored, entails an enlargement of the cross-section of the arc, and a consequent tendency of the P.D. to diminish. While the current is so small, with cored carbons, that the volatilised surface does not completely cover the core, the increase of cross-section is unaccompanied by any change in the specific resistance of the arc. When the current is so large, however, that the solid carbon round the core begins to volatilise, each increase of current is accompanied by two tendencies in the P.D., the one to *fall*, on account of the larger cross-section, the other to *rise*, because of the higher specific resistance of the vapour and mist coming from the solid portion of the carbon. The curve connecting the P.D. with the current must, therefore, be compounded of two. One, such as A B C (fig. 12), which would connect the P.D. with the current if the positive

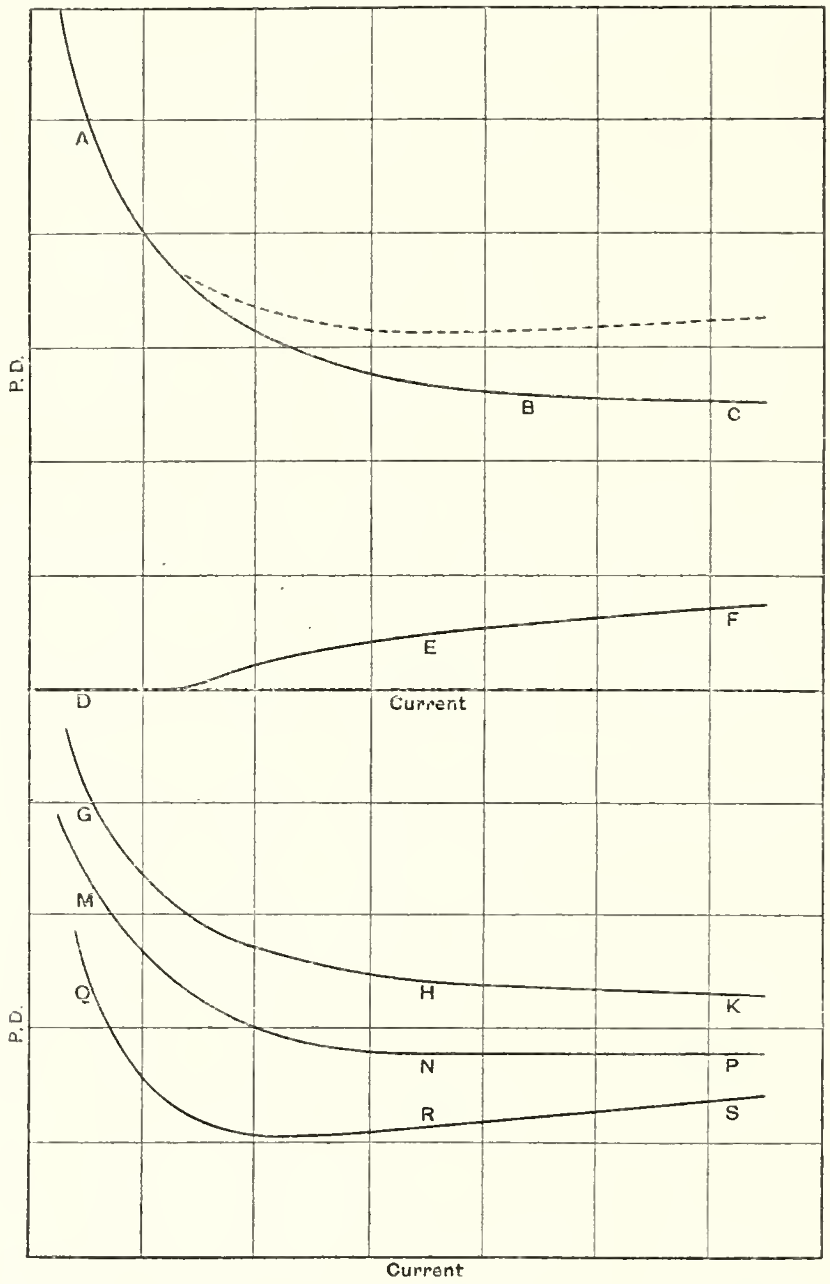

Fig. 12. Curves exemplifying the changes introduced into the curves connecting P.D. with current for a constant length of arc by coring the positive carbon.

carbon were composed entirely of core, and the other, D E F, connecting the rise of P.D., due to the increase of the specific resistance, with the current. The curve connecting the true P.D. with the current is found by adding each ordinate of D E F to the corresponding ordinate of A B C, as indicated in the dotted line. Whether this resulting curve has the form G H K, or M N P, or Q R S (fig. 12) depends, evidently, upon the relation between the increase of the cross-section and the rise of specific resistance, *i.e.*, on the relative structures and cross-sections of the core and the outer carbon.

The fact, already obtained from Table IV., that, for the same current and length of arc, the vapour film, and, consequently, the crater, is smaller with a cored than with a solid positive carbon, explains why the arc can carry such a much larger current without hissing when the positive carbon is cored than when it is solid. For I have shown* that hissing is the result of that direct contact of the crater with the air which follows when the crater grows too large to cover the end only of the positive carbon and so extends along its sides, and this must happen with a smaller current the larger the crater is with a given current, *i.e.*, it must happen with a smaller current when the positive carbon is solid than when it is cored.

How the Change in the Cross-Sections of the Mist and the Vapour Film, due to a Change of Current, is Affected by Coring Either or Both Carbons.

Consider next the facts concerning the influence of the cores on the values of $\delta V/\delta A$, when a small alternating current is superimposed on a direct current *normal* arc, that the resistance of the arc is affected by this superposition. Here we have to deal, not with the whole P.D. between the carbons, but with the *change* in that P.D. that accompanies a given small *change* of current, and I shall show that the effect of the core on this change must always be to *add* a positive increment to $\delta V/\delta A$, the amount of which depends on the value of the direct current, the length of the arc, and the frequency of the alternating current.

The influence of the core on the value $\delta V/\delta A$ is two-fold; it alters the amount by which the cross-sections of the vapour film and the mist change, with a given change of current; and it makes their specific resistances vary with the current. We will take each separately, the change of cross-section first. I shall call the part of $\delta V/\delta A$ that depends on the change of cross-section $\delta V_c/\delta A$, and the part that depends on the variation in the specific resistance $\delta V_s/\delta A$, so that $\delta V_c/\delta A + \delta V_s/\delta A = \delta V/\delta A$.

I have already pointed out (p. 306) that if, when the current is increased, the ratios of the new cross-sections of the mist and the vapour film to the old are greater than

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* "The Hissing of the Electric Arc," 'Journal of the Proceedings of the Institution of Electrical Engineers,' 1899, vol. 28, p. 400.

the ratio of the new current to the old, then the resistance of the arc must have been diminished more than the current was increased, and that hence the P.D. must have diminished as the current increased, and $\delta V/\delta A$ must be negative (provided always that the specific resistance of the arc had not been altered). Similarly, when the ratio of the cross-sections are smaller than that of the current $\delta V/\delta A$ must be positive.

In order to see the effect of the cores on these ratios, in the experiments of which the results are given in Tables III. and IV., Tables V. and VI. have been drawn up, in which the cross-section ratios are found by dividing the cross-section for each current by the cross-section for the next smaller current; and the current ratios by dividing each current by the next smaller current. For the non-normal ratios the larger cross-sections were taken from the *non-normal* sets in Tables III. and IV. and the smaller from the *normal*, because it is the effect of the core when the alternating current is superimposed on a *normal* arc that we are considering, and because also the non-normal numbers in these Tables were found by suddenly *increasing* the current when the arc was normal. For the normal ratios *both* currents were taken from the normal sets.

For instance, the normal cross-section for a current of 8 amperes with the + solid-— cored carbons in Table III. (p. 321) is 14·2, and the non-normal cross-section for 10 amperes is 19·0, while the normal cross-section for the same current is 20·75. Thus, when the current is increased from 8 to 10 amperes, the current ratio is $\frac{10}{8} = 1{\cdot}25$, the non-normal cross-section ratio with these carbons is $\frac{19}{14{\cdot}2} = 1{\cdot}34$, and the normal is $\frac{20{\cdot}75}{14{\cdot}2} = 1{\cdot}46$. In this case, therefore, $\delta V_c/\delta A$ was negative, both when the change of current was non-normal and when it was normal, for both the cross-section ratios, 1·34 and 1·46, are greater than 1·25, the current ratio. Of course to imitate the effect of an alternating current completely it would be necessary to suddenly diminish the current as well as suddenly increasing it, but as this would only alter the signs of both δV and δA, without materially changing their relative values, it is not necessary for our purpose.

The non-normal ratios show the effect of the core on the change in the cross-section, *i.e.*, in the resistance of the arc, and therefore on δV, when the frequency of the alternations is so great that the carbons do not change their shapes; and the normal, when it is so small that the changes are slow enough for the arc to remain practically normal throughout.

TABLE V.—Ratios of Mean Cross-Sections of Mist taken from Table III.

LENGTH of Arc, 2 millims.

Change of Current.	Current Ratios.	Ratios of Mean Cross-Sections.							
		Normal.				Non-normal.			
		S.S.	S.C.	C.S.	C.C.	S.S.	S.C.	C.S.	C.C.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
4 to 6	1·5	2·04	1·2	1·51	1·7	1·98	1·21	1·56	1·06
6 ,, 8	1·33	1·65	1·71	1·82	1·6	1·8	1·33	1·98	1·04
8 ,, 10	1·25	1·44	1·46	1·23	1·33	1·33	1·34	1·70	1·25
10 ,, 12	1·20	1·49	1·33	1·31	1·39	1·46	1·30	1·48	1·40
12 ,, 14	1·17	1·18	1·25	1·38	1·21	—	1·43	—	1·13

The most important point to observe in these tables is whether $\delta V_c/\delta A$ is negative or positive with each set of carbons, *i.e.*, whether the cross-section ratios are greater or less than the current ratios. Take first the non-normal ratios. When the positive carbon alone is cored, the *sign* of $\delta V_c/\delta A$ is decidedly negative, just as it is when both carbons are solid, for all the cross-section ratios in column (9) of both Tables V. and VI. are greater than the corresponding current ratios in column (2). Moreover, with this particular length of arc, and these currents, the non-normal *value* of $\delta V_c/\delta A$ does not appear to be altered by coring the *positive* carbon alone, for the non-normal cross-section ratios in column (9) of each table are in some cases greater and in others less than those in column (7). When the *negative* carbon alone is cored, the non-normal value of $\delta V_c/\delta A$ appears to be negative, but approaching the zero point; for in Table V., one cross-section ratio in column (8) is less than the corresponding current ratio, one is equal, and three are greater; while in Table VI., three are less and two are greater. When *both* carbons are cored, the non-normal value of $\delta V_c/\delta A$ is positive; for three out of the five of the numbers in column (10) of Table V., and the whole of those in the same column of Table VI. are greater than the corresponding numbers in column (2).

TABLE VI.—Ratios of Cross-Sections of Mist where it Touches the Crater, taken from Table IV.

LENGTH of Arc, 2 millims.

Change of Current.	Current Ratios.	Ratios of Cross-Sections at Crater.							
		Normal.				Non-normal.			
		S.S.	S.C.	C.S.	C.C.	S.S.	S.C.	C.S.	C.C.
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
4 to 6	1·50	2·34	1·07	1·66	2·00	3·76	0·80	1·95	1·24
6 „ 8	1·33	2·35	1·44	2·05	2·50	2·35	1·00	2·06	1·08
8 „ 10	1·25	1·44	2·00	1·12	1·47	1·21	1·29	1·40	1·05
10 „ 12	1·20	1·41	0·96	1·44	1·04	1·37	0·88	1·44	1·00
12 „ 14	1·17	1·20	1·44	1·31	1·09	—	1·34	—	0·88

Turning next to the normal ratios, we find that when the positive carbon alone is cored, $\delta V_c/\delta A$ has still much the same negative value as when both carbons are solid, since the numbers in column (5) differ on the whole very little from those in column (3). When, on the other hand, it is the negative carbon alone that is cored, there is a change, for instead of being a little below zero, $\delta V_c/\delta A$ is decidedly negative, since in Table V. all but one of the numbers in column (4), and in Table VI. all but two are greater than the corresponding numbers in column (2). When *both* carbons are cored, there is an even greater difference between the normal and non-normal values of $\delta V_c/\delta A$. For in Table V. all the numbers in column (6), and in Table VI. all but two are greater than the corresponding current ratios, showing that $\delta V_c/\delta A$ is *negative* for normal changes of current though it is positive for non-normal changes with these carbons, currents, and length of arc.

To sum up the change in the value of $\delta V_c/\delta A$ produced by coring one or both of the carbons, we find that while coring the positive carbon alone makes very little difference in either the normal or non-normal change of cross-section that accompanies a given change of current, coring the negative carbon *diminishes* the change of cross-section, both for normal and non-normal changes of current, but more for the second than for the first, and more when both carbons are cored than when the negative alone is cored. Thus, coring the negative carbon both *diminishes* and *retards* the change in the cross-sections of the arc that accompany a change of current. This retardation of the change of cross-section is quite sufficient to account for the fact already mentioned on p. 311, viz., that if I quickly altered the resistance in the circuit outside the arc, when both carbons were *cored*, I could sometimes see the first quick swing of the voltmeter needle in the same direction as that of the ammeter, but never when both were *solid.* For as the resistance did not alter *directly* after the current, with the cored carbons, the new current would be flowing through the old resistance for an appreciable time after the change, and so the accompanying change of P.D. in the same direction as the change of current would be able to influence the voltmeter needle.

The Change in the Specific Resistance of the Arc produced by a Change of Current when Either or Both Carbons are Cored.

We have next to consider $\delta V_s/\delta A$, the part of $\delta V/\delta A$ that depends on the changes in the specific resistances of the mist and the vapour that occur with each change of current, when either or both carbons are cored.

As it is the positive carbon only that *volatilises,* while the negative simply burns, coring the negative carbon alone must have a very different effect on the specific resistance of the arc from coring the positive alone. For when the negative carbon alone is cored, the whole of the vapour and almost the whole of the mist must issue from the *uncored* carbon, the core in the negative carbon only contributing a little metallic vapour to the mist in contact with it; when, on the other hand, it is the positive alone that is cored, the whole comes from the *cored* carbon. Thus, while, with the cored *negative,* the vapour is always *solid-carbon* vapour, and the mist is practically *solid-carbon* mist, with the cored *positive* the vapour and mist are both *core* vapour and mist alone, until the current is large enough for the volatilising surface to cover the whole core, and they only begin to have an admixture of solid-carbon vapour and mist when the current is larger than this. When, therefore, the *negative* carbon alone is cored, the specific resistance of the vapour is constant, and that of the mist increases with each small increase of current, but more and more slowly, with the *same* addition of current, the larger the original current before the addition is made. The curve connecting $\delta V_s/\delta A$ with the normal current in this case must, therefore, be of the form A B C (fig. 13), for the *change* of specific resistance must be greatest when the current is just large enough for the mist to cover the whole core, and must steadily diminish as the direct current increases after that, till it becomes practically zero with very large currents, so that the curve becomes asymptotic to the axis of current.

When the positive carbon alone is cored, the curve is quite different. If the arc always remained perfectly central, it would be of the form D E F G (fig. 13). The specific resistances of the vapour and mist would remain constant till the volatilising surface was large enough to cover the core, so that until then $\delta V_s/\delta A$ would be zero, and D E would be the first part of the curve. The first increment of current that was added after this would increase the specific resistances by the largest possible amount, because this would be the point at which the specific resistances of the existing vapour and mist and of those added would be most different. Therefore the curve would rise suddenly at E. After this, each addition to the normal current would make the change of specific resistance due to the same added small non-normal increment of current smaller and smaller, so that the curve would fall towards the axis of current as shown in F G (fig. 13). Finally, there would already be so much solid-carbon vapour and mist in the arc that the addition of a little more would make practically no change, so that this curve also is asymptotic to the axis of current. The fact that the arc is never really quite central, and that the volatilising surface must therefore cover a little solid carbon long before it is larger than the core, must introduce some modifications into the first part of the curve, shortening D E, and making E F rise less abruptly, something like D E′ F′ G, but these modifications are unimportant.

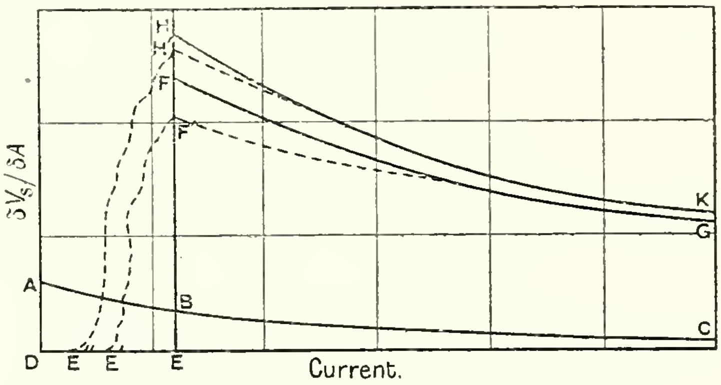

Fig. 13. Suggested curves connecting the part of $\delta V/\delta A$ that depends on the change in the specific resistance of the arc with the direct current for a constant length of arc.

When both carbons are cored, the curve must be like D E H K, or rather D E″ H′ K, because the effect of the metallic vapour from the negative core will be added to that of the positive core, and the change of specific resistance, when solid-carbon mist begins to be added, will, therefore, be greater.

How the Whole Value of $\delta V/\delta A$ *is Affected by Coring Either or Both Carbons.*

By combining the two changes in the resistance of the arc introduced by the core, viz., that due to the changes in the cross-sections of the arc, and that produced by the alterations in its specific resistance, we can see how the complete value of $\delta V/\delta A$ is affected by the core.

From what has been said on p. 329 it is clear that, if the cross-section ratios in Tables V. and VI. can be considered typical, $\delta V_c/\delta A$ never has a greater negative value when the positive carbon alone is cored than when both are solid; never a greater negative value when the negative alone than when the positive alone is cored, and never a greater negative value when both are cored than when the negative alone is cored, the conditions as to current length of arc, &c., being the same in all cases. But $\delta V_s/\delta A$ is zero when both carbons are solid, is greatest when both are cored, and has always some positive value, however small, when either carbon alone is cored. Consequently, when the superimposed alternating current alters the resistance of the arc, if all other things are equal, the sum of these two, *i.e.*, $\delta V/\delta A$, is more positive when either carbon is cored than when both are solid, and most positive when both are cored.

The general effect on $\delta V/\delta A$ of coring either or both carbons is given in the preceding paragraph, but with a given root mean square value of the alternating current $\delta V/\delta A$ depends not only on the nature of the carbons, but also on the frequency of the alternating current, the magnitude of the direct current, and the length of the arc. To complete our knowledge of the influence of cores on the value of $\delta V/\delta A$ therefore, we must examine the effect they produce on the curves connecting each of these variables with $\delta V/\delta A$ when the others are constant. Take first the curves connecting $\delta V/\delta A$ with the frequency of the alternating current.

The Change Produced in the Curve Connecting $\delta V/\delta A$ with the Frequency of the Alternating Current, by Coring Either or Both Carbons.

A B C (fig. 14), which is copied from fig. 10, is the curve, connecting $\delta V/\delta A$ with the current-frequency for solid carbons. Since for moderate frequencies $\delta V/\delta A$ is always most positive when both carbons are cored, and more positive when one is cored than when both are solid, the curve when both carbons are cored must resemble D E F, and the curves for one carbon cored and the other solid must lie between A B C, and D E F, but we have no means of knowing which of the two will start the higher. It follows, therefore, that the frequency with which $\delta V/\delta A$ becomes positive, if it is not already positive, for normal changes of current (*i.e.*, for frequency 0), must be lower when one carbon is cored than when both are solid and lowest when both are cored. Thus, with the same direct current and length of arc, $\delta V/\delta A$ may be positive for all four sets of carbons, as at the points C, P, K, and F, or positive for some and negative for others as at B N H and E, or negative for all. Moreover, since the *true* resistance of the arc is greatest when both carbons are solid and least when both are cored, and smaller when the positive alone than when the negative alone is cored, the *horizontal* part of the curve, which shows the true resistance of the arc, must be highest when both carbons are solid, next highest for + solid − cored carbons, lower for + cored − solid carbons, and lowest of all when both are cored. Hence, since the curve for two solid carbons starts lowest, it must cut all the others at some fairly high frequencies, and that for two cored carbons, which starts highest, must also cut the other two, so that the curves will be like I (fig. 14), if the curve starts lower when the positive alone is cored, than when the negative alone is cored; and like II (fig. 14) if it starts higher.

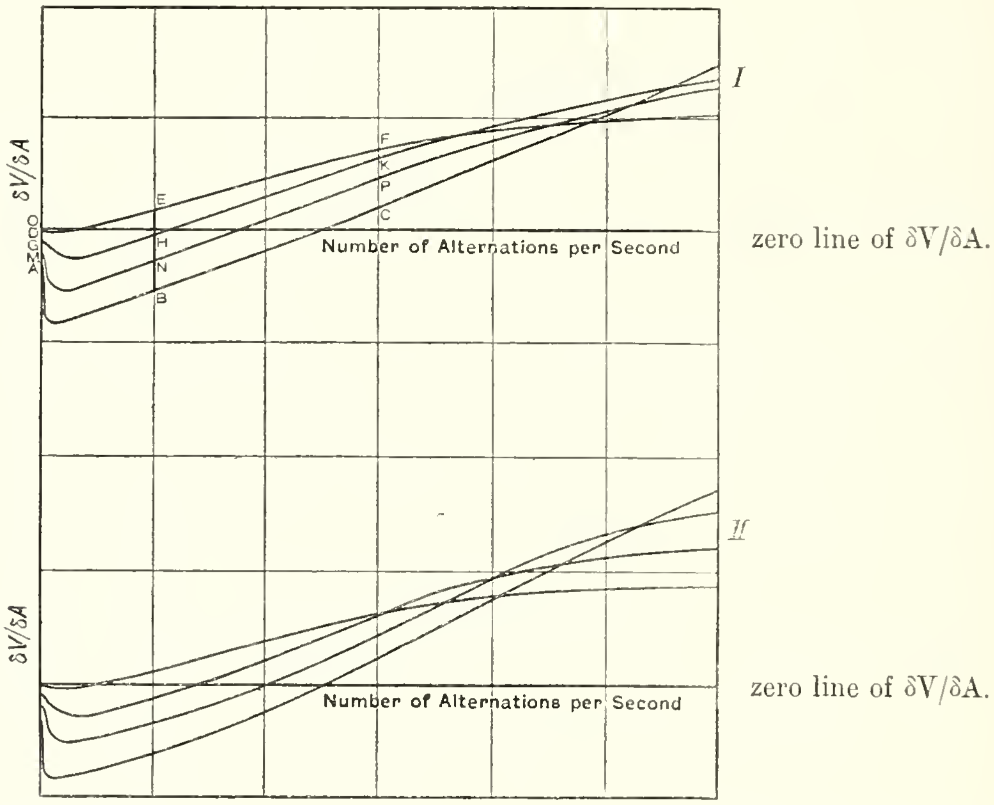

Fig. 14. Suggested curves connecting δV/δA with the frequency of the superimposed alternating current for a constant direct current and length of arc.

The Effect Produced by Coring Either or Both Carbons on the Curve Connecting the Non-Normal Value of δV/δA *with* A, *when the Length of the Arc is Constant.*

Take next the curves connecting δV/δA with the normal direct current, when the length of the arc and the frequency of the alternating current are constant.

In Tables V. and VI., pp. 327, 328, the cross-section ratios for solid carbons differ less, on the whole, from the corresponding current ratios the larger the current on which the increase of 2 amperes has been superimposed. This shows that with solid carbons, when the length of the arc is constant, δV/δA diminishes as the current increases. Consequently the curve connecting δV/δA with A for solid carbons is of the form A B C (fig. 15). With cored carbons the curves depend not only on $\delta V_c/A$, which is obtained from Tables V. and VI., but also on $\delta V_s/\delta A$, the curves connecting which with A are given in fig. 13. The curves connecting $\delta V_c/\delta A$ with A cannot be obtained straight from Tables V. and VI., because the values are too irregular, but we can deduce them from what we already know. For instance, when the positive carbon alone is cored, it must have the same form A B C, as when both are solid, since the change of cross-section due to a given change of current is not materially altered by coring the positive carbon alone. Coring the negative carbon alone *diminishes* the negative value of $\delta V_c/\delta A$, and must diminish it most when the current is least, for it is then that the metallic vapour from the core will be expended on the smallest quantity of hard carbon mist, and will consequently have most effect. Hence the curve for a cored negative and solid positive carbon must resemble D E F (fig. 15), and the current for which $\delta V_c/\delta A$ becomes positive, if any, will depend upon the length of the arc and the frequency for which the curve is drawn. Finally, with both carbons cored, $\delta V_c/\delta A$ is even more positive than when the negative only is cored, so that the curve must resemble G H K (fig. 15), since the same reasoning as before shows that the cores have least effect when the current is largest.

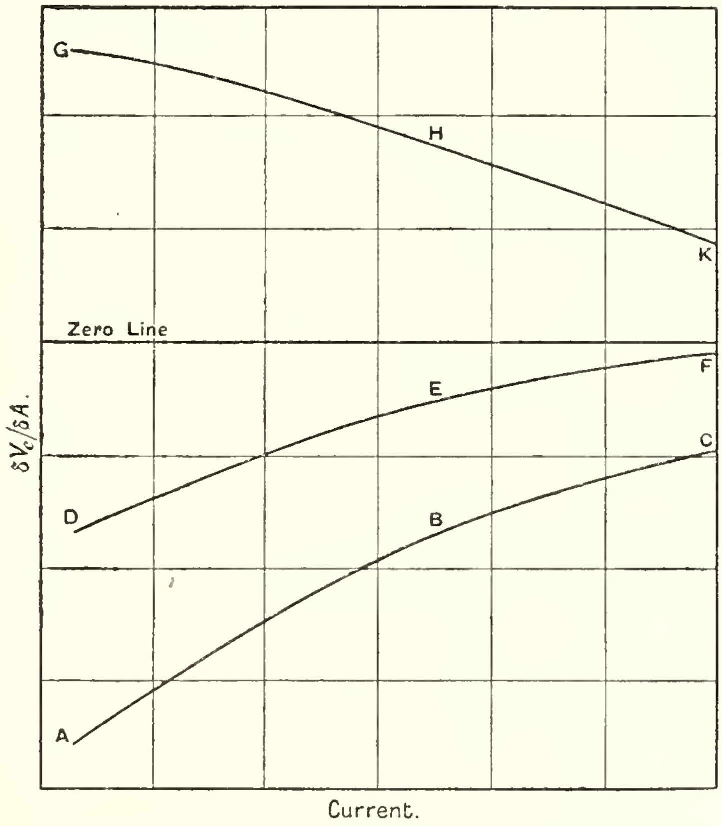

Fig. 15. Suggested curve connecting the part of $\delta V/\delta A$ that depends on changes in the cross-section of the arc with the direct current for a constant length of arc.

To find the full curves connecting $\delta V/\delta A$ with A, for each pair of carbons, we have only to add each ordinate of each curve in fig. 13 to the corresponding ordinate of the curve for the same carbons in fig. 15. Curves resembling those that would be thus obtained for one length of arc and frequency of alternating current are given in fig. 16. The exact distance of each above or below the zero line, and the exact points where it cuts that line must, of course, depend upon the length of arc and frequency of alternating current for which the curves are drawn, but their relative shapes and positions must be similar to those in fig. 16 whatever the length of the arc and the frequency.

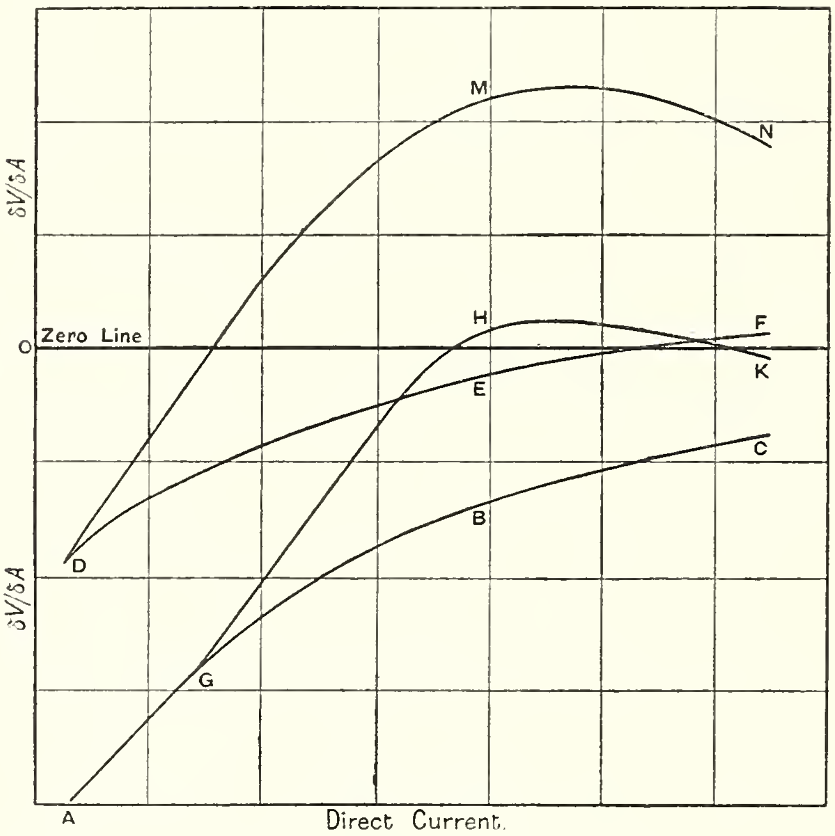

Fig. 16. Suggested curves connecting δV/δA with the direct current for a constant length of arc.

The Effect Produced by Coring Either or Both Carbons on the Curve connecting the Non-Normal Value of δV/δA *with the Length of the Arc when* A *is Constant.*

Finally, we come to the curve connecting δV/δA with l, the length of the arc, when the frequency of the alternating current and the value of the direct current are both constant.

We must refer first of all to the connection between δV/δA and l when both carbons are solid, in order to see how this connection is varied by the cores. P Q (fig. 17) is the rise of P.D. that would accompany the increase of current δA, with an arc of l millims., if the resistance of the arc did not alter with the current. Q R is the fall of P.D. due to the enlargement of the vapour film and the mist (the frequency of the superimposed alternating current is taken too great for the carbons to be able to change their forms). When the current increases from A to A + δA, therefore, the P.D. actually falls from P to R. Now the rise P Q depends only on the amount by which the current is increased, and the resistance through which that increased current has to flow, *i.e.*, on δA, A, and l; or, since A and δA are supposed to be the same for each length of arc, P Q depends simply on l, and increases when l increases.

The *fall* of P.D.—Q R—is more complex. It depends principally on how much of the extra carbon volatilised by the larger current remains between the carbons, and how much escapes along them. When the carbons have short thick ends more will remain than when they have long pointed ones, and as the ends of the carbons are thicker, with the same current, the longer the arc, a small increase of current will diminish the resistance of the arc more, the longer the arc. But the blunting of the carbons, which is a rapid affair when the arc is short, takes place more and more slowly as it is lengthened, till at last the addition of a millimetre or so to the length of the arc makes practically no difference in the shapes of the carbons. Hence the diminution of resistance due to the addition of δA to the current increases rapidly at first, when the arc is short, and more and more slowly as the arc lengthens, till finally it becomes practically constant; and hence also, Q R—the fall of P.D. accompanying this diminution—increases more and more slowly as the arc is lengthened. Thus, while the rise of P.D.—P Q—increases at a *constant* rate as the arc is lengthened, the fall, Q R, increases at a *diminishing* rate. While the arc is so short, therefore, that Q R increases more rapidly than P Q when l is increased, the whole fall of P.D.—P S—will *increase*, with the length of the arc, or, since P S is $-\delta V$ and δA is the same for all the lengths of arc, $-\delta V/\delta A$ *increases* as the arc is lengthened. When the arc is so long that P Q increases faster than Q R, P S, and, therefore, $-\delta V/\delta A$ will *diminish* as the arc is lengthened. Between the two stages there must be a length of arc for which $-\delta V/\delta A$ is a maximum. The curve connecting $-\delta V/\delta A$ with l for a constant current, with solid carbons, must, therefore, be of the form A B C (fig. 18), and *there seems to be no reason why, with very long arcs,* $\delta V/\delta A$ *should not actually become positive, with superimposed alternating currents of comparatively low frequency, even with solid carbons.*

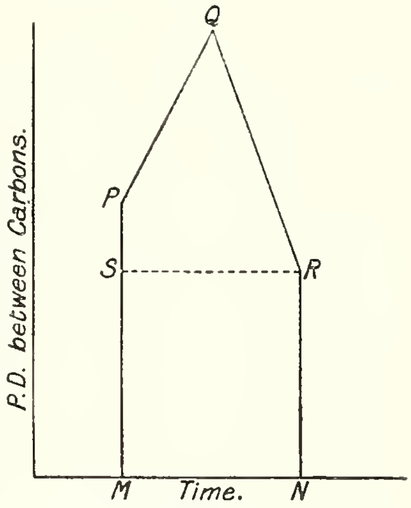

Fig. 17.

The curves connecting $\delta V/\delta A$ with l, when cored carbons are used, must resemble the curve for solid carbons, A B C (fig. 18), but must be higher up the figure (D E F, G H K) when one carbon is cored, and still higher up (M N P) when both are cored. Also, since a change in the specific resistance of the arc must have more effect on the value of $\delta V/\delta A$ the longer the arc, the distance between the curves for cored carbons and the curve for solid carbons must increase as the arc is lengthened, as it is made to do in fig. 18.

Curves very similar to those in figs. 16 and 18 were obtained by Messrs. FRITH and RODGERS, in 1896, by actual measurements of $\delta V/\delta A$. Other measurements that they carried out at the same time coincide with some of the other deductions I have made concerning the influence of cores on the value of $\delta V/\delta A$. Hence, experience, as far as it goes, confirms the conclusions to which I have been led by a theoretical consideration of the conditions. Since, therefore, all the principal phenomena of the arc but one,* with cored and with solid carbons alike, may be readily accounted for without recourse to any such unusual attributes as a negative resistance, or even a large back E.M.F., it seems superfluous to imagine their existence without stronger proof of it than has yet been obtained.

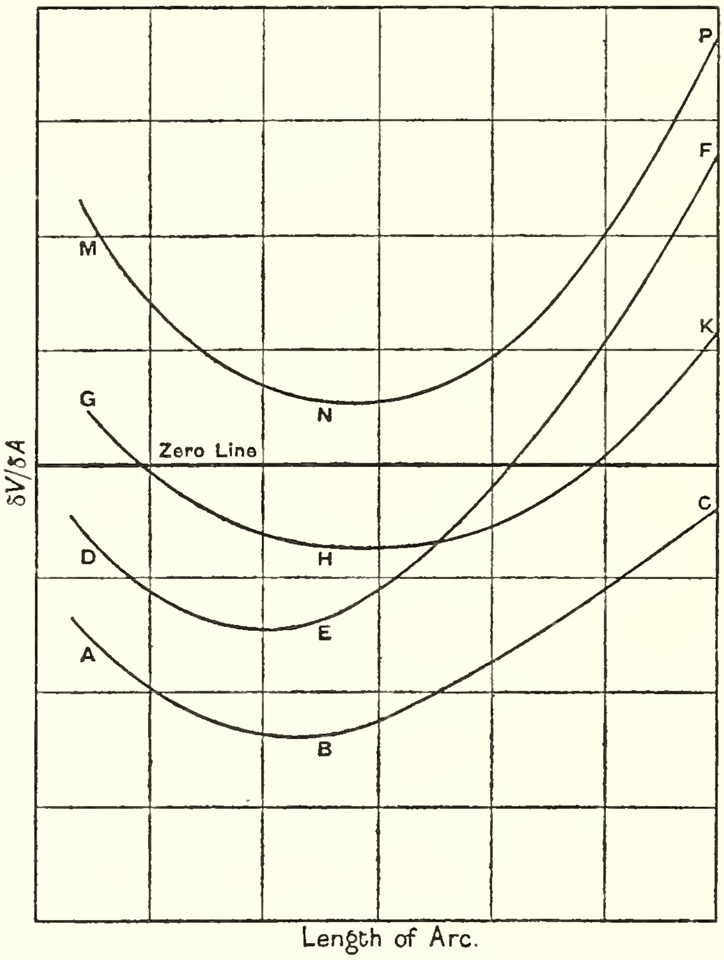

Fig. 18. Suggested curves connecting δV/δA with the length of the arc for a constant direct current

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* The one exception is the fall of potential of some 8 to 11 volts at the junction of the negative carbon with the arc. This may be a true back E.M.F.

INDEX SLIP.

VI. *On Chemical Dynamics and Statics under the Influence of Light.*

By MEYER WILDERMAN, *Ph.D., B.Sc. (Oxon.).*

Communicated by Dr. LUDWIG MOND, *F.R.S.*

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CONTENTS.

INTRODUCTION.

THE nature of the forces which come into play when substances react one upon another chemically, is a problem which has specially engaged scientific minds during the last century. During the second half of that period chemical statics and dynamics have developed into a veritable science. The general law governing the velocity of chemical reaction and chemical equilibrium in homogeneous systems is now known as the law of mass action, and was to a great extent foreseen by BERTHOLLET.[*] In heterogeneous systems the law concerning the velocity of physical

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[*] C. L. BERTHOLLET, 'Essai de Statique Chimique,' 1803; WILHELMY, 1850; HARCOURT and ESSON, 1866; GULDBERG and WAAGE, 1867; VAN'T HOFF, 1878.

or molecular transformation also proves to be of a general and simple nature; the velocity being directly proportional to the surface of contact of the reacting parts of the heterogeneous systems and to the remoteness of the system from the point of equilibrium.* The velocity of chemical reaction and chemical equilibrium in heterogeneous systems represent no phenomena *sui generis*, the laws concerning them being only combinations of the above two laws.† The laws relating to equilibrium found their rational explanation and foundation in the thermodynamic researches of HORSTMANN, and more fully in those of W. GIBBS and VAN'T HOFF, whilst the laws applying to the velocity of reaction in homogeneous systems are the result of VAN'T HOFF'S thermodynamic considerations.

In all the above researches the phenomena of the velocity of chemical reaction and of chemical equilibrium are the outcome of those intrinsic properties of matter, always existent in and inseparable from it, which we usually call chemical affinity or chemical potential. It is known, however, that a system can be brought into a state of reaction, and that new systems and new equilibria can be formed, when energy from an external source, such as light or electricity, is introduced into it. The effect of an electric current upon a chemical system, *e.g.*, is determined by FARADAY'S law of electrolysis, whilst the thermodynamic connexion between chemical and electrical (and gravitation) energy has been developed by W. GIBBS.

The object of this investigation was to ascertain, if possible, the laws governing the velocity of chemical reaction and chemical equilibrium when this is caused by the introduction of light energy into the system. Is the velocity directly proportional to the amount of the light energy introduced or absorbed by the system in the unit of time, independent of the reacting masses or concentrations, *i.e.*, is the law here analogous to that of FARADAY for electrolysis, or is the velocity of reaction some function of the reacting masses? What are the laws governing chemical equilibrium as affected by light? It is evident that to furnish an answer to the above problems careful experiments bearing directly on the fundamental issues in question and a careful theoretical consideration of the results so obtained are absolutely needed. This is the more imperative as from the hundreds of reactions known to be caused or influenced by light‡ not half a dozen can be found suitable for quantitative measurements.

It soon appeared that the chemical reaction chosen for the study of the laws of chemical kinetics must be very simple and as far as possible uncomplicated by secondary phenomena. The chemical action observed must be caused by light alone, and stop when light is removed. BUNSEN and ROSCOE'S reaction ($H_2 + Cl_2 = 2HCl$) seems to fulfil these conditions, but inasmuch as no change of volume takes place, no

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[*] See M. WILDERMAN, 'Zeits. Physik. Chem.,' 1899, 30, p. 341, and especially 'Phil. Mag.,' 1901, July, p. 50.

[†] See 'Zeits.,' *loc. cit.*, pp. 363–382.

[‡] See EDER'S 'Handbuch der Photographie.'

answer could be afforded to the question whether the velocity of reaction is a function of the varying masses or concentrations of the combining substances or not, unless the hydrochloric acid formed is as rapidly removed as it is formed during the reaction. A secondary reaction would thus take place which would complicate the principal reaction. For these and similar reasons* DAVY'S reaction ($CO + Cl_2 = COCl_2$) was chosen for study. The reaction occurs only in light, the gases can be used in a dry state, and the volume of the mixed gases changes, two volumes of the original mixture producing one volume of the compound.

Since highly dried gases combine very slowly, it was obvious that an artificial source of light must be employed, which should be at the same time of great actinic power and susceptible of being maintained constant in its intensity for long periods. At the suggestion of Dr. LUDWIG MOND the acetylene light was finally decided on, as it is rich in actinic rays and its spectrum closely resembles that of sunlight. Apparatus was devised for producing a flame constant in intensity and composition. Arrangements were made for measuring the intensity of the light with an accuracy to 0·1 per cent., and suitable methods chosen for the preparation of pure chlorine and carbon monoxide. A preliminary study extending over two and a half years was made of the conditions under which the experiments must be conducted so as to give not only concordant but accurate results, *i.e.*, results free from constant errors. The general arrangement of an experiment was as follows :—

Pure, dry chlorine and carbon monoxide were freshly prepared in the dark, and there introduced into a reaction vessel, connected with a manometer to indicate the variation of pressure during the reaction. The reaction vessel was placed behind a quartz window, in a water bath kept at a constant temperature, and exposed to a powerful acetylene light. The acetylene light was kept of constant intensity and free from smoke by means of a special generator, balance governor, regulating tap, purifier and burner. The intensity of the acetylene light was measured by means of a Rubens' thermopile and the deflections of a galvanometer, and the observed values standardized by means of a Clark cell and manganin resistances. The variations of the pressure in the reaction vessel were read on the scale of the manometer by means of a cathetometer. After applying corrections for the variation of temperature of the bath, atmospheric pressure, &c., the experimental results representing the rate of formation of carbonyl chloride from chlorine and carbon monoxide were subjected to a theoretical investigation.

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* See MELLOR, 'Journal of the Chemical Society,' 1901, p. 227.

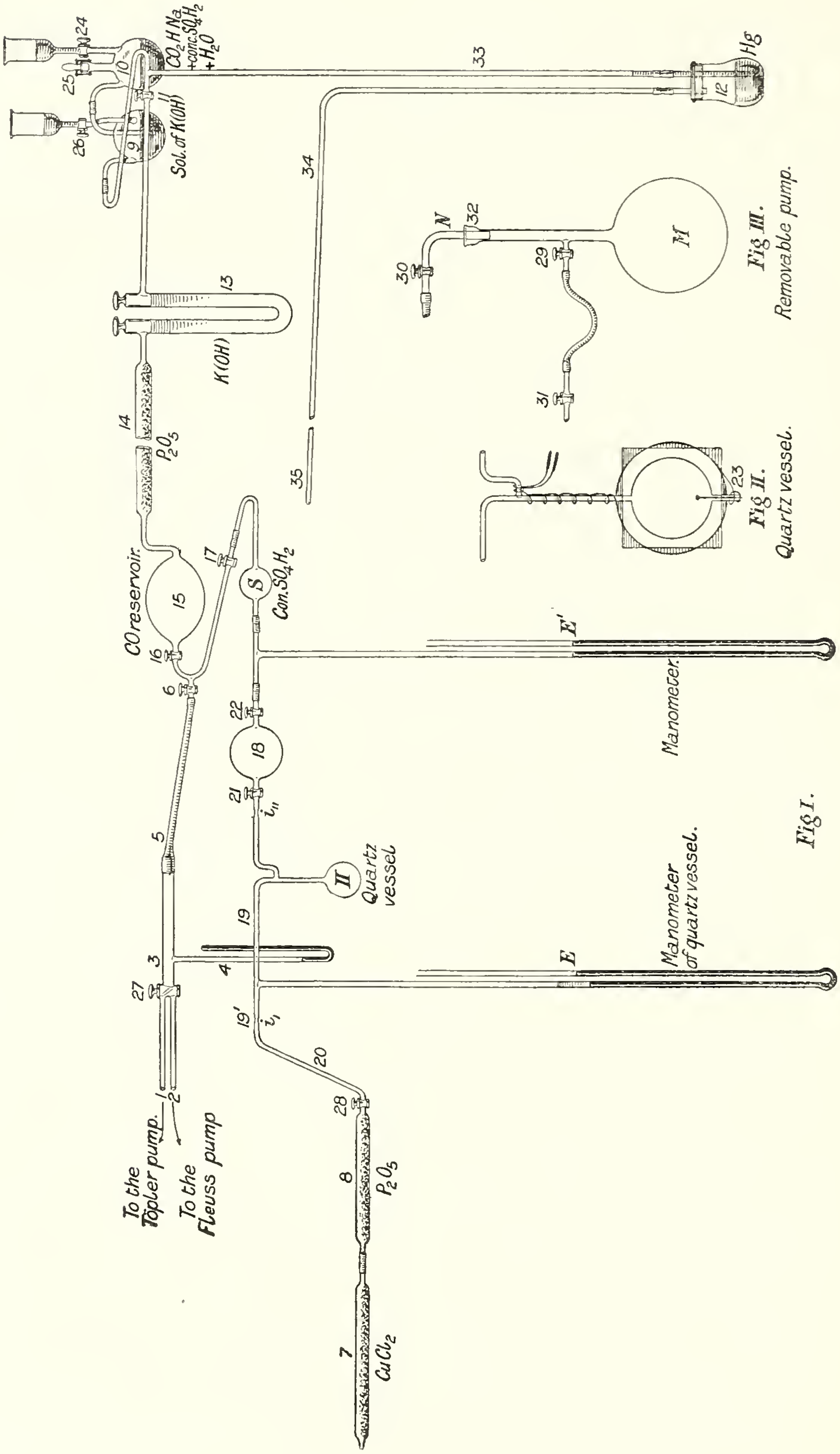

Fig I.

Fig II. Quartz vessel.

Fig III. Removable pump.

PART I.

General Arrangements for the Preparation of Pure Cl_2 and CO, and for Filling the Reaction Vessel. (See Diagram 1.)

A Töpler pump is connected with one arm (1) of the T-tube, and a double-cylinder Fleuss pump with the second (2), the third (3) carries the manometer (4), and is connected with the rest of the apparatus by tube (5). A 3-way tap connects either (1) or (2) with (6).

On the left of the diagram the apparatus for producing pure chlorine is shown. Tube (7) containing cupric chloride was heated by one small flame; the chlorine formed passes through tube (8) containing phosphorus pentoxide which is connected with the reaction vessel whenever it is to be filled with chlorine. Before filling the reaction vessel with chlorine, the cupric chloride and phosphorus pentoxide tubes were exhausted and heated till a vacuum of ·01 millim. was obtained. Chlorine was produced by heating the cupric chloride tube, the chlorine then removed, and a further supply prepared and directly used for the experiment.

On the right of the diagram the apparatus for producing pure carbon monoxide is shown. Vessel (10) contains sodium formate and concentrated sulphuric acid, vessel (9) contains a concentrated solution of potassium hydroxide. When the mercury tap (11) is closed, the carbon monoxide formed bubbles through the mercury in vessel (12). When the tap is opened it passes through the U-tube (13) containing pieces of caustic potash, then through the long tube (14) containing phosphorous pentoxide to the receiver (15), which was chosen of a large size so that the gas should be as little contaminated with air as possible. This vessel (15) was closed by the mercury taps (16), (17) and (6), and was further protected from contamination with air by the tube between the taps (16), (6) and (17) being filled with pure carbon monoxide. Special precautions were taken to keep the carbon monoxide in (15), (14) and (13) pure; while the carbon monoxide from the tube between (16), (6) and (17) was from time to time completely removed by pumping and heating, and the tube again filled with pure carbon monoxide from (15). Before filling the glass bulb (18) with carbon monoxide, every vessel containing the gas was first evacuated to about ·01 millim., fresh gas was again prepared and immediately used for the experiment.

In the middle of the diagram the reaction vessel (II) is shown, into which carbon monoxide and chlorine are brought together for exposure to light. This consists of a glass cylinder with ground flanges on which two parallel quartz plates are fixed, one in front and the other at the back. A capillary tube (19) connects the manometer E with the reaction vessel, and with the tube (20) through which the chlorine gas is passed from the cupric chloride tube into the quartz vessel. The latter is also connected with the bulb (18), (21) and (22) being mercury taps. The bulb (18) is connected with a manometer (E′) and is filled first with carbon monoxide. The pressure of carbon monoxide in (18) should be greater than the pressure of chlorine in the quartz vessel (11). By opening the tap (21) the carbon monoxide is allowed to pass into the quartz vessel (II). No chlorine, as direct careful tests showed, passes under such circumstances into the bulb (18).

I now pass to a more detailed description of the apparatus used.

The Reaction Vessel (fig. II.), was a glass cylinder of 3·65 centims. diameter, 3·6 centims. long (capacity = 41·26 cub. centims.), with flanges 6 millims. wide at each end (as in fig. II.). The flanges were very carefully ground so that the two perfectly smooth quartz plates, when placed on them, fitted perfectly, and an excellent vacuum could be obtained. The quartz plates, with parallel surfaces, 45 sq. millims., and about 2 millims. thick, were cut out perpendicularly to the optical axis, and were optically pure. The front plate turned the plane of polarisation to the left, the back to the right.

Since chlorine acts on any cement which could be used for the purpose of keeping a vacuum, the quartz plates were placed directly on the well-ground flanges of the glass cylinder, and melted Crookes' cement, consisting of beeswax and resin (proportions, 5 parts beeswax to 8 parts resin) put on outside where the outer edges of the quartz plates met the glass flanges, care being taken that the cement was properly melted and free from air. The corners of the quartz plates projecting over the flanges and those parts of the glass flanges which remain uncovered by the quartz plates were then covered up with melted Crookes' cement, the whole being heated and made smooth and firm by a very small flame. In this condition the vessel can preserve a very high vacuum for a very long time. The cement was then covered with a varnish of pitch in benzine to protect the cement from the action of water, and allowed to become thoroughly dry The outside of the cylinder was also covered with pitch so that light might only enter through the quartz plates.

In the capillary tube (23), at the bottom of the glass cylinder, an iron-nickel couple was fixed to measure the temperature of the gas in the inside of the cylinder during the reaction. Two very fine iron-and-nickel wires (about 0·1 millim. diameter) were made considerably thinner at their ends (0·05 to 0·02 millim.) by repeated alternate immersions in nitric acid and in water. About 1 centim. of the two very fine ends were twisted together and a trace of melted soft solder put on the extreme ends. On bringing it near a flame, the solder melted and ran down the twisted wires and was quickly shaken off, forming only a very thin film of solder between the wires. The soldered ends were then washed and all but 2 millims. of the connected ends were removed. The two wires were then covered with shellac and a thin layer of pitch. The very thin double wire (perhaps 0·2 millim.) was then passed through the very narrow capillary tube (23) projecting about $\frac{1}{2}$ millim. into the cylinder, and fixed at the bottom in the capillary tube by a trace first of pitch, then of Crookes' cement, and then again of pitch. This thermopile was very sensitive to variations of temperature, and does not interrupt any essential portion of the light on its passage through the quartz vessel to the back plate. The second iron-nickel thermocouple was wound outside the tube as near as possible to the first couple in the glass cylinder, the two iron-and-nickel wires being drawn up round the cylinder, and then wound up round the capillary tube. These wires were first covered with shellac and then with pitch varnish. The thermopile assumed the temperature of the air or gas, owing to its extreme thinness, with very great rapidity. Subsequently a thin, glass bulb of similar volume was used instead of the quartz vessel.

The capillary tubes used were of a very narrow diameter. The capillary tube E of the manometer was necessarily somewhat wider, so that the mercury might move easily, and rapidly assume equal levels in both arms of the U-tube. A length of 155·7 centims. of the capillary of one of the manometers contained 9·476 grams of mercury = 0·701 centim. The total volume of the capillary tubes in the manometer over the mercury during the experiments (20 to 50 centims., &c.) is very small in comparison with the volume of the cylinder of the quartz vessel, which is over 40 cub. centims., amounting to only a few tenths of 1 per cent. The manometer contained a layer of concentrated sulphuric acid (about 10 centims. long), enough to protect the mercury from the chlorine. The concentrated sulphuric acid freed the capillary tube from any specks of dust, thus enabling the mercury to move in it much more easily. The acid must be heated *in vacuo* after it is brought into the capillary to remove air and sulphurous acid. Only after the sulphuric acid has been heated *in vacuo* can a very high vacuum be obtained which will remain constant for any length of time. In filling the capillary tubes with the sulphuric acid and mercury, the part of the apparatus between (22) and (19′), which can be separated from the other parts, is kept almost in a horizontal position, the open tube of the manometer being connected with a tube dipping into a small beaker of mercury covered by concentrated sulphuric acid. Tap (22) being closed, tube (19′) is held over the mercury in the concentrated sulphuric acid till a few centims. of sulphuric acid rise in the tube, and then dipped into the mercury, allowing it to follow the sulphuric acid. If the mercury column is broken by sulphuric acid, the column is driven out from the capillary by forcing air into the vessel at (19′) until most of the acid is expelled from the capillary, when the tube is refilled. The capillary U-tube of the manometer was calibrated in the usual way. Since concentrated sulphuric acid adheres to the glass, the sulphuric acid column is shorter when the mercury is low and longer when it is high, especially if the mercury is moving rapidly up and down. During the experiment upon the velocity of reaction the movement of the mercury is so slow that uniform results are obtained; but a reading must be made of the levels of both mercury and sulphuric acid.

The density of the sulphuric acid used was easily found from the heights of the sulphuric acid and of the mercury in both arms of the manometer when exposed to the pressure of the atmosphere. The U-tube of the manometer was fixed on a glass scale silvered on the back to avoid parallax, the readings of the scale were easily made by means of a cathetometer to 0·05 millim.* As the experiments proceeded, it was found that there was no possibility of protecting, by means of mercury taps, the gas mixture in the quartz vessel from contamination with air for more than a few hours, even when to the mercury taps capillary tubes were added containing the same reacting gases as the quartz vessel, with a second mercury tap at each end. The tubes of the quartz vessel on both sides were sealed for this reason by means of a hand blow-pipe as soon as the quartz vessel was filled with the gas mixture. Later on the quartz vessel had to be abandoned altogether, chiefly for the reason that it could not be heated before filling the reaction vessel with the gases; more reliable results were then obtained with a thin bulb of very pure glass than with the quartz vessel.

Filling the Reaction Vessel with Carbon Monoxide and Chlorine.

Having read the position of the meniscus of the sulphuric acid and of the mercury on both arms of the manometer, the apparatus was exhausted, every part of it being heated to expel the air which persistently sticks to the glass walls of the apparatus. Since, however, the quartz vessel (owing to the Crookes' cement and pitch) could not be heated, the complete removal of the air was effected as follows:—Having connected the pumps through (1) and (2) with (6), the taps (6), (17), (22), (21) and (28) being open and the taps (16) and (11) closed, all the vessels (7), (8), (E), (II), (18), (E′), (S), (R), (19), (3), (2), (1) and (4) were exhausted first by the Fleuss and then Töpler pump, and all, except the quartz vessel (II), were heated. The concentrated sulphuric acid in (S) and over the mercury in (E) was also heated until no more gas was given off. In this way a high vacuum was obtained. The taps (6) and (28) were then closed and carbon monoxide passed from its reservoir (15) into the bulbs (S) and (18) and to the quartz vessel (II) until the pressure was about 10 centims. The carbon monoxide was then removed by exhaustion, (16) and (28) being closed until a good vacuum was indicated by the Töpler pump, when the vessels were again filled with carbon monoxide. This was repeated several times till the air was completely removed from the walls of the quartz vessel. Better results, however, were obtained when a thin bulb of pure glass was used and the bulb heated during the evacuation. But even in this case, after the first evacuation the bulb was filled with carbon monoxide

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* The mercury meniscus in the short arm always remains as clear as a mirror. From its position and an ordinary calibration of the capillary tube of the manometer, the variation in the mercury column can be determined with even greater accuracy than 0·05 millim. The readings of the mercury meniscus in the long arm of the manometer, together with the upper ends of the sulphuric acid columns in the two arms, enables the length of the sulphuric acid columns to be measured with an accuracy much exceeding 0·05 millim. mercury, considering that the specific gravity of the sulphuric acid is only about 1·85.

and evacuated to a high vacuum of about 0·01 millim. Taps (16), (17) and (21) were then closed, and chlorine prepared in (7) till the pressure in the reaction vessel became equal to about 10 centims. Tap (6) was connected with the removable pump (M), and (M) and (R) heated and evacuated, carbon monoxide sent into it from (15), again evacuated, and then (17) and (21) opened and the chlorine removed. The taps (17) and (16) were then turned off, (6) connected with the pumps, (R) evacuated, all vessels (13), (14), (15), (R), (S), (E′) and (18) evacuated, and carbon monoxide from (9) and (10) removed as far as possible, partly by opening tap (11) and then removing the same from (15), &c., partly by allowing the freshly-prepared carbon monoxide to bubble for some time in (12). The bulbs (15), (S) and (18) were then finally repeatedly filled, at one atmosphere pressure or more, with fresh carbon monoxide from (10) (prepared in the dark, only one incandescent lamp at a distance being used). The quantity and pressure of the carbon monoxide introduced into the glass bulb (18) is known from the volume of the bulb and from the indications of the manometer connected with it. The tap (17) was then turned off; the reaction vessel was next completely protected from light. The tap (28) was now turned on, and 1 or 2 centims. of the tube containing cupric chloride was then slowly and cautiously heated (in the dark), so as to evolve chlorine and to allow it to pass to the reaction vessel at a slow rate. From the indications of the manometer the amount of chlorine introduced into the quartz vessel was known, and the production of chlorine was stopped by removing the burner from the tube as soon as the desired quantity of chlorine, which is very small, had been introduced into the quartz vessel. The capillary tube was immediately sealed up with a hand blow-pipe at $i_{,}$—where it had been previously drawn out. After the heated parts had cooled down, the position of the meniscus of the mercury and of the concentrated sulphuric acid was read in both arms of the manometer by means of a faint light, as well as the temperature of the room and the barometric pressure. The manometer (E′) was again read, the tap (22) closed, the tap (21) opened, and the carbon monoxide, which is at a greater pressure in (18) than the chlorine in the reaction vessel, was slowly allowed to pass through the drawn-out capillary tube (at $i_{,,}$) to the quartz vessel, so as to keep the SO_4H_2 column over the mercury the whole time long enough, and when the mercury no longer moved in the manometer (E), the tap (21) was closed and the capillary tube sealed at $i_{,,}$—where it was previously drawn out. The vessel was again allowed to cool and the temperature and pressure readings again noted.

From the variation in the height of the manometer the quantity of carbon monoxide introduced into the quartz vessel was known. The volume of the bulb (18) is immaterial, if it is of sufficiently large size to allow of the introduction of any desired quantity of carbon monoxide into the reaction vessel. The bulb (18) was then taken off, the end with the tap (21) immersed in a beaker containing a solution of potassium iodide, and the tap opened. It was found that with the above arrangements, *i.e.*, with a thin capillary tube drawn out at ($i_{//}$) and with an overpressure of carbon monoxide in (18), not a trace of iodine (*i.e.*, of chlorine) can be detected in the bulb (18), even with such a sensitive reagent as freshly-prepared starch solution. By leaving the tap (21) intentionally open for half an hour, only small traces of chlorine could be detected in the bulb (18). This shows that the diffusion of the heavy chlorine gas to the top through a very thin capillary into the vessel containing carbon monoxide, which is a vacuum for chlorine,* is extraordinarily slow. For this reason the method of filling the vessels must not be reversed, *i.e.*, we must not fill the quartz vessels first with carbon monoxide and then with chlorine from the bulb, nor can we uniformly mix the two gases in the two vessels by opening the tap (21), even when the capillary tube is large, a method adopted in many similar investigations, but which was found, at any rate in this case, to be wrong.

The Removal of Chlorine from Tubes (7) *and* (8) *and from the Quartz Vessel. Removable Pump.* (See fig. 3, Table I.)

Before passing to the description of the methods of preparation of pure chlorine and carbon monoxide, a few words must be added as to the mode in which chlorine can be completely removed from the vessels before a new experiment is proceeded with. The removal of carbon monoxide is a simple matter—this being done by the Töpler pump, but chlorine cannot be removed by the Töpler pump, because even small quantities of chlorine instantly attack the mercury. All attempts to protect the mercury pump by inserting tubes with precipitated copper or mercury for the absorption of the passing chlorine completely failed. This, however, was effected in the following manner :—The vessel (M) was connected through (30) with the vessels containing chlorine and was heated and evacuated through the taps (29) and (31), connected with (15) by means of a Töpler and Fleuss pump, and while the tap (30) was turned off, the taps (29) and (31) were then turned off and the tap (30) turned on. A great part of the chlorine passes from the vessels containing it into the

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* In this research the velocity of combination of chlorine and carbon monoxide, as a function of the reacting masses, had to be studied. A horizontal gauge, as used by BUNSEN and ROSCOE, could not be employed, because very great variations in the reacting concentrations or masses of the gases, amounting to 70–80 per cent., had to be studied. Thus a mercury manometer had to be employed. To be able to carry out this research, in view of the chlorine attacking the mercury, advantage was taken of the extremely slow diffusion of chlorine, which in concentrated SO_4H_2 is still smaller than into a vessel of carbon monoxide, which is a vacuum for chlorine. If the column of the concentrated SO_4H_2 over the mercury in the manometer is taken long enough (10 centims.), and care is taken that the filling of the quartz vessel with chlorine or carbon monoxide is very slow, so that the concentrated SO_4H_2 should not remain on the walls of the capillary tubes, but have time enough to run down, then we find that the dry chlorine will not attack the mercury for days, and even weeks. Sometimes we find after a longer time that the mercury meniscus becomes a little dull, without, however, losing its shape, and without the mercury losing its mobility, and without interfering with accurate reading.

vessel (M). The tap (30) was again shut and the india-rubber tube removed from the tap (31). After opening tap (29) and carefully allowing air to pass into (M), the vessel (M) was detached from the rest of the apparatus at (32), where the ground tube (N) perfectly fitted into the neck of (M). The chlorine was then removed from (M) by blowing through a tube introduced into it through its neck; (M) was now replaced on the tube (N) and evacuated. Chlorine was aspirated into (M) and blown out until a pretty high vacuum was obtained in all the apparatus. Air was then allowed to pass into the vessels which contained the chlorine and the whole again evacuated directly by the Fleuss pump, and finally to a high vacuum by the Töpler pump, in the ordinary way. Chlorine can now be again prepared from the copper chloride in (7).

Experience has shown that the only and perfectly reliable way of getting pure gases free from any contamination with air is to remove, before each experiment, the chlorine and carbon monoxide (though they are apparently perfectly pure) from all the heated vessels as completely as possible, and to immediately prepare perfectly fresh chlorine and carbon monoxide. As soon as they are prepared they are sealed up in the quartz vessel (or the glass bulb used instead of it) as quickly as possible.

THE PREPARATION OF PURE GASES.

A. *Preparation of Pure Chlorine.* (See (7) and (8) in fig. 1, Table I.)

In order to get chlorine free from any admixture of air and water vapour, which prove to be most fatal to the gas mixture, and also of any other gas, the ordinary simple methods could not be employed. It was therefore prepared either from platinous chloride or cupric chloride in a vacuum. Cupric chloride, suggested by Dr. LUDWIG MOND, has great advantages in comparison with platinous chloride; it is very much cheaper, water can be easily removed from it, and there is no danger that oxygen or hydrogen from the air will be absorbed by the residue, as is the case with platinum. Besides this, occluded gases cannot be completely removed from the platinum unless by exhaustion at a temperature higher than that at which platinous chloride gives off chlorine. Cupric chloride, so called "purissima," always contains hydrochloric acid. This, it was found, cannot be completely removed. The cupric chloride was, therefore, prepared from precipitated copper and chlorine, taking all precautions to avoid conditions which might contaminate the product with hydrochloric acid. Finely divided copper, precipitated from a solution of copper sulphate by means of zinc, was placed in a long combustion tube drawn out at both ends. The hydrogen current, first washed and dried, was passed over the copper (heated to a dull red heat) for several hours to remove the film of oxide. The tube was next sealed at one end and exhausted, and air was then allowed to pass into the tube, which was again exhausted and heated. The hydrogen was thus completely removed.

The end of the tube was then opened and a current of chlorine, prepared from manganese dioxide (freed from carbonates) and concentrated hydrochloric acid, passed through two wash-bottles of water and two bottles of concentrated sulphuric acid, was passed over the reduced copper.

Chlorine combines with copper in the cold, but as the reaction progresses the copper and tube become heated from one end to the other. The heat developed is usually so great that the cuprous chloride formed melts to a cake. When the contents of the tube have become green, the tube is broken, the mixture of cuprous and cupric chlorides is powdered and placed in a Jena tube drawn out at both ends. The tube is now heated for its whole length to about 250–300°, and chlorine is allowed to pass over it for a long time, the tube being shaken from time to time, when more chlorine is absorbed. The whole mass is then allowed to cool in the current of dry chlorine. From the increase in the weight of the tube and the weight of the copper taken, the amount of the cupric chloride formed can be calculated, and, if necessary, the operation of passing chlorine over the heated mixture of cupric and cuprous chlorides is repeated. There is no necessity for the whole mass to be transformed into cupric chloride. A current of air is then drawn through the tube to remove the chlorine, for the reason stated above, and then one end of the tube is sealed up.

Tube (7) with cupric chloride and cuprous chloride thus prepared is now ready to be used for the experiment; it is placed on a combustion furnace, one end of it being connected by means of a piece of india-rubber tube used for vacua to tube (8), containing phosphorus pentoxide, and the india-rubber covered with Crookes' cement.*

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* It was found that no tube of soft glass could be used, the atmospheric pressure outside pressing the glass in at the places where the tube was heated. Thus a tube of hard glass had to be used. This, as known, cannot be joined with the soft glass of which the glass cylinder of the quartz vessel and the capillary tubes are of necessity made. Since it was found that air (oxygen) and water vapour are just the gases which are most fatal for the gas mixture, the heating of cupric chloride in a vacuum was inevitable, and no other method could be employed instead. Luckily, the amount of chlorine gas required for each experiment was exceedingly small, and only about $\frac{1}{200}$ gram. mol. of cupric chloride had to be decomposed for each experiment, *i.e.*, only 1 or 2 centims. of the tube (7) had to be heated, and, since the filling of the quartz vessel with chlorine and carbon monoxide had to be carried out (for reasons given above) slowly, and cupric chloride decomposes at a comparatively low temperature, this centimetre or two of the tube had to be heated slowly and cautiously with only a comparatively small flame. Tube (7) was heated at the sealed end, which is more removed from tube (8), and the glass of (7) is made to meet the glass of (8). Under these conditions not only is the glass of (7) and (8), where they meet, quite cool, but the tube (7) is so already, being 30 or 40 centims. removed from (8). The gas passed the drawn-out cold tubes (7) and (8), where they meet, with the india-rubber collar on the top, for only about 10 minutes. Under these conditions no traces of the action of chlorine upon the india-rubber collar can be found on cutting the same, or by chemical analysis. Chemical analysis, however, can give us little information about small impurities when the quantities of gas are so small as those which I had at my disposal. There, however, still remains a superior analysis for impurities, when no chemical or physical method can be of any more use, viz., the possibility of getting regular curves and a velocity constant. This analysis showed that either the chlorine is absolutely free from any impurities, or that they are so small and of such a kind as not to interfere with the phenomena under consideration.

Before the chlorine was prepared for the experiment the tube containing cupric chloride, (7), and the tube (8), with phosphorus pentoxide, were connected with the tube (20) leading to the quartz vessel (II), and heated and exhausted till the pressure was reduced to not more than 0·01 millim. In this way the air was first expelled from all vessels and from the cupric chloride. The tap connecting all these parts with the mercury pump was then shut, and 1 or 2 centims. of the tube (7) gradually heated nearly to red heat and chlorine slowly evolved. When the manometer indicated that the pressure of the chlorine was about 10 centims., the heating of (7), and with it the formation of chlorine, was stopped. After removing the chlorine by means of the removable pump, fresh chlorine gas was admitted. This process was repeated to expel the last trace of air, when chlorine was again introduced and sealed up in the tube.

B. *Preparation of Pure Carbon Monoxide.* (See (9), (10), (13), (14) and (15) of figure (1), Table I.)

Carbon monoxide gas was prepared from sodium formate (35 gr.), and a mixture of concentrated sulphuric acid (200 gr.) and water (100 gr.), the proportions given by Lord Rayleigh. Carbon monoxide is produced when the mixture is heated, and its formation is stopped when the mixture is cooled down to the ordinary temperature, so that the same solution can be repeatedly used for the production of carbon monoxide.

The experiment was so arranged that neither the vessels nor the liquids used for the reaction contained any air. The sodium formate was introduced into (10) through the neck (25), the stopper of which was so well ground that when covered with vaseline it could stand a vacuum for any length of time when the pressure of the carbon monoxide in the vessel was one atmosphere. Vessels (9) and (10) had the U-tube (13) containing pieces of caustic potash, the long and wide tube (14) containing phosphorus pentoxide and the carbon monoxide reservoir (15), as well as the tube (R) between (16), (6) and (17), the purpose of which was to protect the carbon monoxide in (15) from contamination with air, were all heated and completely exhausted. During this taps (11) and (16) were open, and taps (24), (26) and (17) were turned off.

The air had next to be removed from the channels of the taps (24) and (26). This was affected in the way shown in figure (4). After all the vessels (9), (10), (13), (14), (15), &c., were evacuated to a high degree, a capillary tube (t') with the tap (T) at one end and a piece of india-rubber tubing (R) at the other drawn-out end, was pressed tightly into the tube of the funnel of (10), and another similar one into the funnel of (9). (T) was turned off, (24) opened. After this the same was done with tap (26). Since the volume of the channels in the taps (24) and (26) and the space above them is perhaps only 0·3 cub. centim., while the volume of all the vessels is about 1500 cub. centims., the pressure in all the vessels is only about 0·15 millim. The taps (24) and (26) were then closed and tap (T) opened to allow the removal of the tube (t'). A little water was brought over the taps at (24) and (26). Vessels (9), (10), (13), (14) and (15) were then again brought to a high vacuum, and it is evident that the air still contained in the channels of the taps (24) and (26) (the pressure in them being 0·15 millim., and the volume about 0·02 centim.) could later on introduce, when opened to allow liquid to pass through them to (9) or (10), a contamination with air into the vessels of only about $\frac{0\cdot15 \times 0\cdot02}{1500} = 0\cdot0000002$ millim. Taps (16), (6), (17) and (11) were now closed and a concentrated solution of caustic potash in water, first boiled in a vacuum and freed from air, and kept in an evacuated flask, poured into the funnel of (24). Some of the caustic potash solution was forced into (9) through tap (24), but not so as to reach the tube leading from (9) to (10), to prevent the vapour pressure in (9) from pressing the solution into (10). Into the funnel of (24) a mixture of two parts of concentrated sulphuric acid and of one part of water boiled out *in vacuo* was quickly introduced. About 250 cub. centims. of the sulphuric acid solution was rapidly passed into (10), and a burner placed under it; more caustic potash solution was again passed into (9) until tube (32) in (9) was covered about 2 centims., when the vessel (10) was rapidly heated by passing a flame round it. In this way the caustic potash solution may be prevented from passing into (10) through tube connecting (9) and (10), and if a trace of it does pass into (10) it is subsequently neutralised by the sulphuric acid and does not affect the result in any way. Vessel (10) must be heated on all sides to avoid bumping. Tap (11) is turned off during the formation of carbon monoxide to prevent the distillation of water into vessels (13) and (14) containing solid caustic potash and phosphorus pentoxide. The carbon monoxide formed in (10) passes through a solution of caustic potash in (9), leaving there any traces of carbonic acid or of sulphurous acid, and it presses the mercury in (33) down until it begins to bubble through the mercury seal in (12), passing from there through tube (34) to the open air. The carbon monoxide is then pumped up at the end (35) till the pressure in (8) and (10) becomes about 150 millims., the carbon monoxide which is still being formed bringing the mercury in tube (33) down again till it begins to bubble through the seal in (12). Repeating this several times, we expel the last traces of air from the vessels and liquids. The vessels (13), (14), (15), (5) and (18) were then filled with carbon monoxide. Tap (11) is partially opened, so that the carbon monoxide should not bubble too rapidly through the solution of caustic potash and only slowly

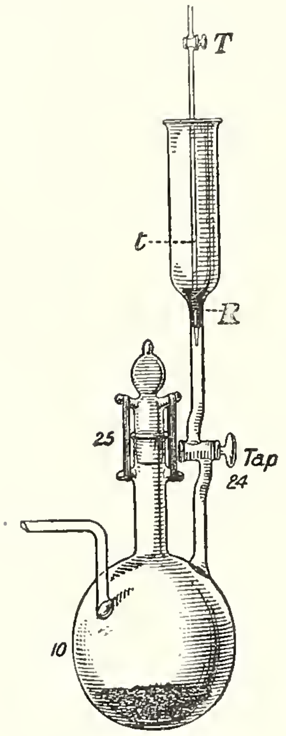

Fig. 4.

through the concentrated sulphuric acid in the tilted vessel (S). After a short time, when the mercury had risen in tube (33) about 10 centims., tap (11) was turned off again. This is done because the formation of carbon monoxide goes on more quickly and regularly as the pressure of carbon monoxide increases. When the newly formed carbon monoxide again begins to bubble through the mercury, the tap (11) is again opened and shut as before; this is repeated until the pressure of carbon monoxide becomes everywhere a little over one atmosphere, *i.e.*, the mercury column in (33) does not rise again when the tap (11) is opened, and carbon monoxide continues to bubble through the mercury (if a still higher pressure is desired the tube at (35) is closed). The taps (11) and (16) are now closed (open at 35), allowing the carbon monoxide gas to bubble through the mercury and escape to the air. After removing the burner from (10) it is rapidly and uniformly cooled on all sides by means of a wet cloth, until the formation and bubbling of carbon monoxide through the caustic potash ceases. The tube (4) is also filled with carbon monoxide at the same time in order to protect, subsequently, the carbon monoxide in (15) from contamination with air. The glass tubes of the different parts of the apparatus are directly joined together without the use of india-rubber tubes, and all the taps have mercury seals.

In the funnels of (9) and (10) sufficient caustic potash solution and of sulphuric acid solution is always left, and taps (24), (26), and (25) should be so exceptionally well ground that even after many weeks (when covered with vaseline) the taps remain quite transparent. The object of these precautions was that pure and fresh gas might be prepared quickly for each experiment. Carbon monoxide gas, which had been kept in the vessels for even small lengths of time, was never used. When an experiment was made, vessels R, S, (18), E, (15), (14), (13), &c., containing pure carbon monoxide, were always first evacuated, heated, and the freshly-prepared carbon monoxide passed directly into the bulb (18), allowing it to bubble slowly through the concentrated sulphuric acid in (S) as described. The tap (22) was then turned off, (21) turned on, and then the capillary tube (19) at $i_{\prime\prime}$ was immediately sealed up with a hand blow-pipe.

PART II.

ARRANGEMENTS FOR AN ACETYLENE LIGHT OF ABOUT 250 CANDLE-POWER OF CONSTANT INTENSITY.

Generator. (Arrangement for Constant Pressure.)

Acetylene generators, although they have some advantages over the ordinary gas-holder, have also some disadvantages; firstly, because every time a fresh container of carbide is used, a fresh portion of air from the container is mixed with the gas, and though the volume of the container is very small in comparison with the volume of the acetylene gas in the gas-holder, still the mixture is undoubtedly a source of error, and special precautions have to be taken to remove the first portion of the acetylene formed from the container, so as to keep the composition of the gas during the experiments as constant as possible. Secondly, the pressure of the gas from such a

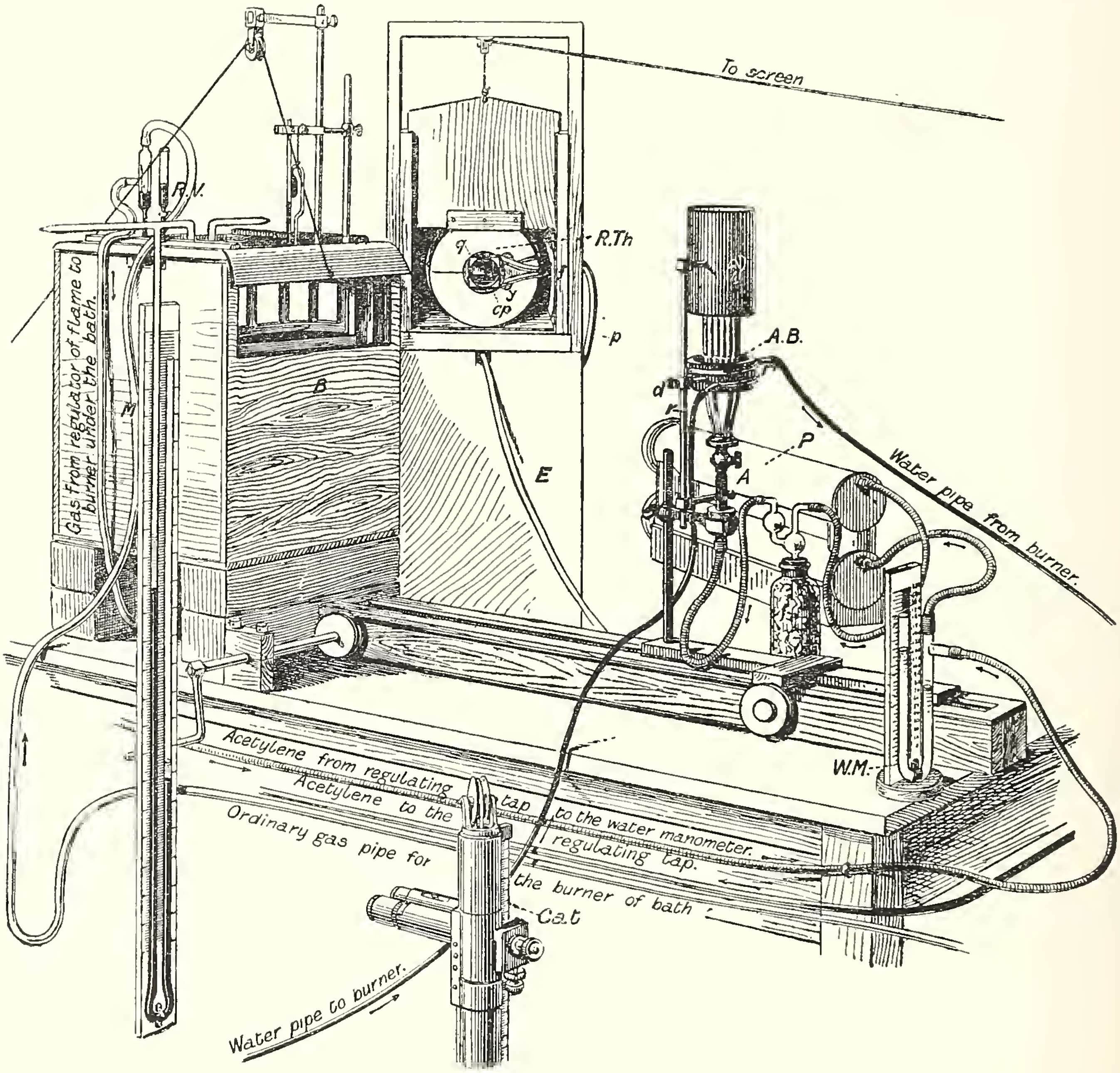

Fig. 5.

Sketch of Acetylene Burner and Purifier, Thermopile, Reaction Vessel, Bath, Water Manometer, and Cathetometer.—A.B., acetylene burner; P, purifier; R.Th., Rubens thermopile; B, bath; R.V., reaction vessel; M, mercury manometer of reaction vessel; Cat., cathetometer; W.M., water manometer.

generator varies very considerably in comparison with that supplied from large gas-holders. The generator used was the so-called "Incanto," by Messrs. Thorn and Hoddle, with variations of 10 per cent. in the pressure of the gas delivered. This variation in pressure was found to be due to the strain of the floating balls on the chain of the generator, but a modification reduced the variations to about $1\frac{1}{2}$ per cent. The axis x (fig. 6) on which the ball L turns, was filed up till the movement of the ball in the axis was easy, and β, which guides the balls, as well as the stem of L at α, were then filed and clamped to give the ball a perfectly free movement up and down, but not much side play. Sheets of lead (s) were then fixed round the stem as near to the balls as possible, and the weight carefully adjusted so that a small additional weight of about 10–15 grammes placed near the balls should draw them quite down and open the valve, and that the removal of this weight should bring the balls up again, closing the valve. The modified generator gives, without a balance governor, for the heights of the bell out of the tank, between 16·5 centims. and 5 centims. (these are the limits within which the bell of the gas-holder chiefly varies in its height during the production and consumption of gas), a variation of only 1·5 millim. for 100 millims., *i.e.*, of $1\frac{1}{2}$ per cent. These variations of the pressure were further reduced by the balance governor.

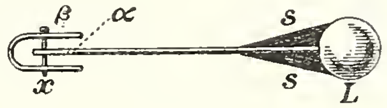

Fig. 6.

It was found that with a burner of such a candle power as I had to use (about $12 \times 20 = 240$ candles), a pressure of about 4 inches is necessary (instead of the usual 2). For this the upper chamber of the gas-holder had to be almost filled with water, leaving only space sufficient for the expansion of the water (in the winter care must be taken that the water does not freeze when the gas-holder is in the open air; more free space or a salt solution must be used). The gas generator was placed on the roof of the laboratory; from the generator a lead pipe brought the gas to the room; first to the balance governor, from the balance governor to the regulating tap, from the regulating tap to the water manometer WM, and then to the purifier; here it passed over the purifying substance of the lower cylinder, then of the higher cylinder, and thence to the burner.

The Regulating Tap to counteract the different sources of error was of the ordinary type. One tap, α, must always be quite open, when acetylene is consumed during the experiments. By turning another tap, the quantity of gas passing per unit of time to the burner is regulated, and the adjustment is indicated by the pointer on a fixed scale of 90 degrees. The purpose of this tap was to adjust the supply of gas to the burner so that the intensity of the acetylene light should, under varying conditions, always be kept the same. A series of conditions affect the intensity of the acetylene flame and necessitate the use of a regulating tap, such as the variation in the diameter of the outflow tubes in the nipples of the burner or the variation of the atmospheric pressure, which though in one and the same day hardly ever varying more than 1 or 2 millims., changes during a longer period considerably. There is another source of error of an irregular but temporary nature which also necessitates its use: the admixture of air when a new container is used. Everything was done to remove this source of error at its source. When a new container was introduced, the tap supplying water to the same was opened, and the cross-bar of the container pressing a metal plate on the india-rubber ring somewhat loosened. Water entered the container, the tap was turned off, and the acetylene with the admixed air allowed to escape between the metal plate and the india-rubber ring. This was repeated two or three times. In this way the air was expelled from the carbide containers so that when the cross-bar was tightened up and the tap opened again, no appreciable effect of the new container upon the acetylene ought to have taken place. With such precautions this source of error quickly disappears, owing to the gas-holder, leading pipes, balance governor, purifier, and burner containing a great quantity of pure acetylene—as can be seen from the observed intensity of light read from the deflection of the galvanometer. Variations, however, still existed, and sometimes required to be adjusted by the regulating tap. Another possible source of error was the variation in the composition of the gas, arising from the carbide used not being always of the same quality (it is not certain that such a source of error does exist). This was counteracted by the adjustment of the regulating tap.

These adjustments were always guided by the indications of the deflection of the galvanometer.

Water Manometer. (See fig. 5.)

Since it was necessary to work with a pressure of about 4 inches when the tap of the burner was shut, and of about $2\frac{1}{2}$ inches when it was open, 0·1 millim. variation in the height of the upper and lower side of the water manometer would indicate 0·2 millim. in 25 millim., *i.e.*, 0·8 per cent. variation in the pressure of the gas. Its chief purpose is to indicate in a quick manner, whether all the apparatus connected with the supply of the acetylene gas to the burner is in good working order.

The Acetylene Burner. (See fig. 5.)

All attempts to get a light of a great candle power, which would remain of a constant intensity and composition have been, as far as I know, unsuccessful up to the present. We have now standard lights of 1 or 10 candle power, but we have none of 200 or 1000 candle power, since the light of the arc varies considerably both in intensity and composition. The object here was to obtain a light of, say, 200 or 500 candle power, or of any other intensity desired, which would remain constant in its intensity and composition for any length of time, which could at any time be easily adjusted with great accuracy to the desired intensity, and which could be used with ease in the ordinary work of a laboratory. With the burners on the market which were tried, the gas is always passed either through a very thin slit giving a flat flame, or through two thin pinholes—the two gas streams meeting in one point, and giving again a thin flat flame (24–30 candle power). This is done in order to get the surface of the flame in contact with the air as large as possible, to obtain complete combustion and as white a flame as possible. It was found that after

24 hours' use—often even after much less—the candle power of the burner, either with the slits or pinholes, was no longer the same, and very often the slit or pinhole was already so much carbonised that the flame began to smoke; on the contrary, pinholes with a larger diameter, giving 40–50 candle power the pair, require a very much longer time before they become carbonised and begin to smoke, though even their candle power also diminishes with time. Since the form and even the thickness of the flat flame changes continuously, we can only get a constant light by cutting out a piece from the middle of the flame for a certain time, screening all the rest of it. Since we cannot get one flat white flame, by means of several gas streams directed to the same point, of more than 60 or 70 candle power, the increase of thickness or of the size of the flame beyond the 70 candle power being always accompanied by the formation of smoke, we could thus, in the best circumstances, not get a constant flame of more than 20 candle power, a candle power not very different from standards already existing. On the other hand, it was impossible with several flat flames to get one light of great intensity in a small space, since the flames cannot be placed very near to one another (owing to the form of the burner), and a flame of 200 or 250 candle power (12–15 nipples) necessarily occupies a very large area. If we further consider that each of the flames is different from the others in size and form, and that the flame of any one burner soon changes in form and size, and that only a small part of each could be cut off securely by a screen so as to give a constant light for some time, it is evident that the number of lights or nipples which would be required for a 200–250 candle power light to remain constant would be about 40 or 50. Assuming that even the greatest care be taken in placing the burners and screens on as small an area as possible, still the burner would occupy too much space, and no point or line could be calculated from the different lights which could theoretically be assumed to be the point or line from which the total light was coming.

The burner which was ultimately constructed free from these difficulties is that shown in the drawing (fig. 5).

The wide tube A of the burner is divided into four narrower tubes as shown, leading at intervals of 90° into the channel of a hollow ring cut in the brass ring. In the hollow brass ring (AB) 12 small brass pieces containing capillary tubes were fixed, and in the end of the brass pieces nipples were fixed. Each nipple has one round pinhole of about 15 or 20 candle power; the holes are parallel to each other, and each gives a flame in the form of a straight thick line of a few millimetres diameter and of a few centimetres in height. Round the brass ring a brass jacket is fixed, forming a hollow ring connected with the tubes r and r'. Water runs continuously through the hollow ring of the burner, which thus remains cool, in spite of the fact that flames of about 200–250 candle power are concentrated in a very small area. Using this arrangement of the burner, we find that the acetylene flame becomes perfectly pure and clear, and remains so for any length of time, even when the nipples have pinholes of only 15 or 20 candle power each. The clear circular flame so obtained consists of lines interrupted by narrow air spaces. Having all twelve lines in a narrow circle of only 1 or $1\frac{1}{4}$ inch diameter, at equal distances from one another, the direction of all the flames perpendicular, and the flames of equal length, though, perhaps, of not quite the same thickness, we can safely assume that the light comes from a perpendicular line drawn through a point near the centre of the narrow circle.

Since the error arising from small variations in the thickness of the lines cannot possibly in this case be greater than 1–2 millims. in the distance, this can, for the distance we have to use ($\frac{1}{2}$ to 2 metres), be completely neglected. The variations in intensity in the line of the flame proved to be due chiefly to variations in its top; by means of the chimney γ, all the top parts of the line-flames are cut off. Owing to the draught the lines are straightened and the air supply increased, while the products of combustion are removed and a clear white flame, remarkable for its constancy and brilliancy, is obtained. The screen and chimney γ can be moved higher or lower by means of the screw d, so as to get not only a constant flame with the photometer, but a flame of the desired intensity, the rest of the adjustment of the intensity being produced by means of the regulating tap. Besides the upper part of the flame, the lower part was also cut out by means of an adjustable short cylinder, which was also water-jacketed and connected with the water jacket of the burner.

Thus, with the simple arrangements described (generator, balance governor and burner), a source of light of 200–250 candle power (or 500 candle power and more, according to the number of nipples employed) can be obtained, which will remain constant, within 1 or 2 per cent., for a considerable time without regulation or adjustment.* By means of the regulating tap and measuring instruments, the intensity of the light can be adjusted with an accuracy to 0·1 per cent., and even much less.

THE GENERAL ARRANGEMENTS USED FOR THE MEASUREMENT AND ADJUSTMENT OF THE INTENSITY OF THE ACETYLENE LIGHT.

The Principle of the Method. Acetylene as a Universal Standard from 0·1 or 1 to 500 or 1000 Candle Power.

The light of the acetylene burner, which is placed at a certain distance from the thermopile, is allowed to fall on the exposed junctions of the Rubens thermopile (with 40 iron-constantan junctions), which is connected with galvanometer. A second measurement is made directly after by means of a Clark cell and standard

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* It should be noted that with the increase of the candle power of the burner, a greater pressure of the gas (in the gas-holder, &c.) is necessary for getting the best conditions for the flame.

manganin resistances (manganin 100,000 ohms, 6 ohms in the shunt were used, as shown in the diagram ; the coil of the galvanometer, also of manganin, is 3 ohms). These resistances give, under the conditions of experiment, a sufficient deflection (about + 15 centims. to − 15 centims.), so that the value of the deflection caused by the acetylene light is always measured in standard units, independent of the sensitiveness of the galvanometer, &c. (the diagram also shows that the difference between the temperature in the quartz vessel immersed in the bath, owing to the reaction which takes place in it, and that in the bath is also measured with the same galvanometer by means of iron-nickel thermocouples ; this, however, has nothing to do with the photometer itself).

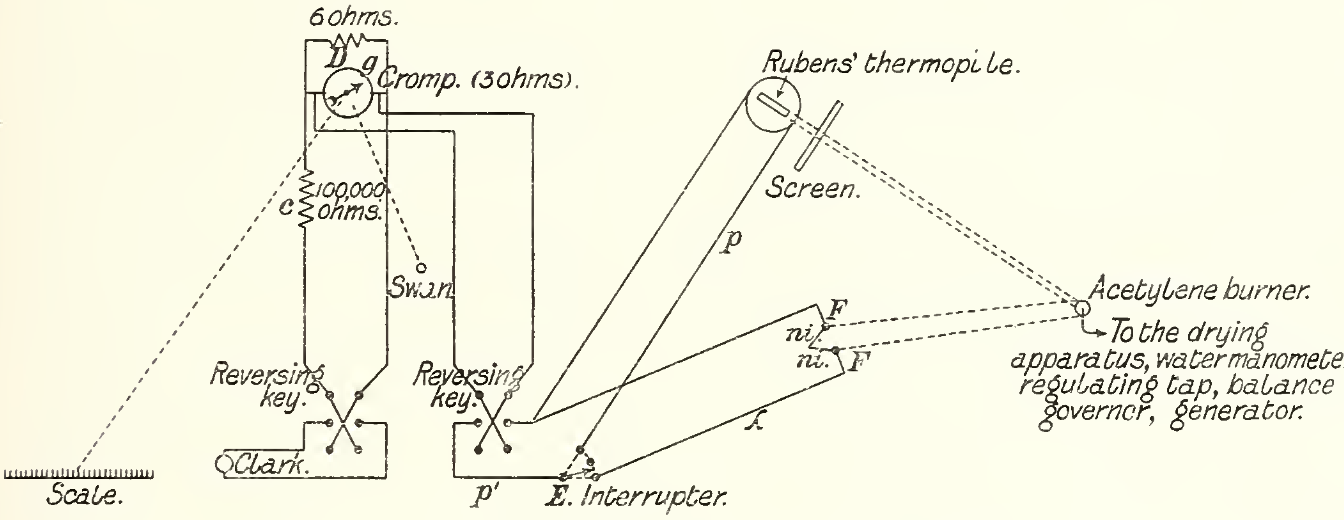

Fig. 7. Diagram to show arrangement of apparatus.

The principle of the measurement of the light intensity consists in its determination objectively by means of the deflection of the galvanometer and standard units (Clark, manganin resistances). We believe that if two sources of light (say acetylene gas) at a fixed distance, say 1 metre from the plane containing a given thermopile (with a given number of iron-constantan junctions), in the same relative position to the thermopile (the lines of the flames being parallel to the line of the exposed junctions and seen in the same position from the narrow tube in the double copper cylinder of the thermopile), give, or are made to give, the same deflection in standard units, then the intensity of the lights must be the same, provided they are quite pure and free from smoke and that the burner is cool. We assume that the heat effects of any source of light upon the exposed junctions of the thermopile, *i.e.*, the rise of their temperature, will be directly proportional to the amount of light falling upon them, *i.e.*, to the intensity of the light. This point is of primary importance. A careful theoretical investigation of it was absolutely necessary, and the investigation confirmed the conceptions. The electromotive force of the thermopile being thus directly proportional to the difference of temperature of the thermo-junctions exposed to the light, and of those which are left in the dark, the intensity of the light of a given source of light must be directly proportional to the corrected deflection of the galvanometer (or to the tangent of the angle), and can be measured by it.

It should be remarked that this objective method of measuring the intensity of light by means of a thermopile (or bolometer), and of checking it by means of a Clark cell and known standard resistances, measures the total heat energy produced by the given source of light in the thermopile, and thus differs from the other methods of measuring the intensity of light, the ordinary photometers, based upon the physiological effect of the light upon the eye. No doubt there is a distinct difference between the two; an acetylene light which we physiologically perceive, say of 16 candle power, is very much cooler than a 16 candle-power coal-gas light. The temperature to which the exposed junctions of the thermopile will be raised by the rays of flames of the same candle power, but from different sources of light, will therefore be different, the more so as the colour and composition of different lights are also different. Properly speaking two lights from two different sources (say acetylene and coal gas, or arc light) can neither be compared physiologically on account of their different compositions, nor in the objective way by means of a thermopile or bolometer, as given above, and no light can be compared except with a light of the same nature. For comparison of two lights of the same kind there can be no doubt that the objective method by means of a thermopile or bolometer is by far more accurate and reliable than measurement in the physiological way. As, however, for many practical purposes, the intensity of different lights has almost always to be expressed in candle units, different sources have to be compared and measured in this physiological way as far as it is practicable. In this photometric work, at any rate, all the standard units for comparison, the small as well as the large ones, ought to be correct multiples of one another, *i.e.*, ought to be all from the same source of light and of the same composition. Acetylene, as far as we know, is the only source of light which gives reliable standards from very small units, such as 0·1 or 1 candle power (when only a part of the line is used) up to very great units, such as 500–1000 candle power (when many lines on a space of about 2 inches in diameter should be used), and, except the burners, the same arrangements can be easily manipulated for fixing and adjusting all the standards in an absolutely correct and objective manner, as described here.

The author now passes to the description of the thermopile and of the other parts of the arrangements, indicated by the above diagram, which were used for measuring the intensity of the acetylene light.

The Thermopile (*or Bolometer*). See fig. 5.

A detailed description of the thermopile used is given by RUBENS in the 'Zeitschrift für Instrumentenkunde,' 1898, pp. 65–69, but a few data with regard to it must be given here.

The thermopile has 40 thermo-junctions[*] of iron and constantan, on an area of 2 centims., 20 of them in one line being exposed to the light, and 20 (10 in one line on each side of the line of the junction exposed to the light) remaining in the dark. The wires used are very thin (0·1 to 0·15 millim.), and the places of the junctions (those exposed to the light as well as those remaining in the dark, are hammered to little thin round plates (0·5 to 0·8 millim. diameter) so as to increase their sensitiveness to variation of temperature, and are made dead black. Before the line of junctions exposed to the light there is a small and then a larger cone of polished nickel, placed opposite and near the line of junctions, which causes a greater quantity of light to fall upon the junctions. The electromotive force of the thermopile is 0·00106 volt per 1° C.

In connection with the Rubens' thermopile a Crompton's dead-beat galvanometer was used, in order to avoid the numerous disturbances experienced by galvanometers other than that of the D'Arsonval type, and its sensitiveness was adjusted to get a sufficiently great deflection of the spot of light—not to get the greatest possible deflection, but to arrange the measurements of intensity so that after they were brought to a great accuracy, say of 0·1 per cent., the measurement should be made in an easy, steady, and reliable manner, and independent of numerous obstructive influences lying beyond the thermopile itself. This meant that special precautions had to be taken with both the thermopile and the galvanometer.

Whatever form is given to the thermopile, the next precaution, especially when a sensitive thermopile (or bolometer) is used, is to protect it from the influence of the surrounding medium, so as to secure concordant results. The junctions which are exposed to light are necessarily much more exposed to all sorts of air currents than those protected and covered from the light, and are also more subjected to the influence of the variation of the temperature of the room. The unavoidable continuous use of the acetylene flame to be measured by the thermopile from time to time, produces air currents, set up by local differences in the temperature of the room. The sensitiveness of the whole arrangement was necessarily so great that if the hand was put before the thermopile at the distance of 1 or 2 decimetres, the deflection of the galvanometer was considerable. This difficulty was evaded in the following manner :—

The thermopile was enclosed in a cylinder of thin copper (about 1 millim. thick ; the two circular sides of the front and back being made of the same thin copper. In the centre of the front side a circular opening of about 4½ centims. was cut and in this a copper tube of the same diameter (for the quartz plate) was fixed. In the centre of the circular copper plate behind, a thick but very narrow tube (of about 3 or 4 millims. internal diameter) was fixed for the purpose of seeing and directing the thermopile upon the light of the burner. The thermopile was fixed on a piece of

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[*] Through an accident our thermopile had only 38 junctions.

ebonite in the middle of the air space of the inner cylinder, so that the larger cone should be fully exposed to the light (except a little of the four corners, the whole cone was exposed) and the thermopile everywhere equally removed from the cylinder. To protect the thermopile from moisture, which is especially fatal to its iron wires, a cylinder with calcium chloride was put into the inner cylinder. By means of the tubes in front and behind, the copper cylinder was fixed in another larger copper cylinder, and the space between was filled with 6 or 7 litres of water. Except the small space of the larger tube in the front side, the narrow tube behind and two narrow tubes on the top, filled with Faraday wax, through which the insulated leads from the thermopile were drawn, the inner cylinder was thus enveloped on all sides by a thick layer of water. The outer copper cylinder was entirely covered by very thick sheets of asbestos. In this way any variation of temperature in the inner cylinder was counteracted by the conductivity of the copper sides, surrounded by water, while the thick sheets of asbestos and the large quantity of water between the cylinders made any rapid change of the temperature of the water due to alteration in the temperature of the room impossible.

It was found that if a continuous water current from the main was passed between the two cylinders (even if the current was passed simultaneously in different places between the cylinders as well as between the front and back sides of the cylinder, and the water from the main was used only after half an hour or an hour, when the temperature of the water from the main ought to be constant), very large deflections of the galvanometer, as much as several centimetres, were observed, and these varied continuously though the thermopile was closed to light and should have given no deflection at all. Obviously the temperature of the water from the main is never quite constant, continually varying by several thousandths or even hundredths of a degree Besides this, layers of different temperature may exist in the bulk of the surrounding water owing to the fact that the temperature of water from the main is lower than that of the room, and that it must take a long time before the 6 or 7 litres of water in the cylinders are replaced by fresh water from the main, *i.e.*, the bulk of the water is exposed to the influence of the warmer temperature of the room for a longer time, and this warmer water is being continually mixed with the cold water from the main. This difficulty was finally overcome by leaving the 6 or 7 litres in the cylinders to assume the temperature of the room, giving up the stirring altogether and replacing the same by the water current from the main. Through this the difference between the temperature of the water and that of the room was made very small, *i.e.*, the warming of the water between the cylinders by the surrounding temperature of the room was made exceedingly slow. It should be observed that it is not the constancy of the temperature of the air space of the inner cylinder which we require, but that the variation of its temperature should be the same everywhere, and so slow that it should be in comparison with the velocity of cooling or warming of the thermopile by the surrounding air in the inner cylinder.

exceedingly small, while all the junctions should be at the same temperature in the dark.

There still remained other sources of error. In the first instance, there was the quartz plate fixed in front of the larger tube closing up and protecting the inner air space from the air currents of the room. The quartz plate is exposed on the inside to the temperature of the air in the inner cylinder, on the outside to that of the room. There was additional reason why the temperature of the water between the cylinders and of the air space in the inner cylinder had to be brought to the temperature of the room; because it is evidently necessary that the thermopile should be exposed to the same temperature on all sides. In the second instance, the quartz plate and the inner air space between the same, the cone and the copper ring upon which the quartz plate is fixed, are being heated by the rays of light while measurements of the intensity of light are carried out, the rest of the inner cylinder remaining unexposed.

To counteract these sources of error the air space exposed to the light was made very small in comparison with the total air space of the inner cylinder. The narrow circular copper plate (*cp*, fig. 5), on which the quartz plate (*q*) was fixed, was also water-jacketed by means of the india-rubber tube (*y*), so that the four ends of the quartz plate, equal to about one-third of the total surface of the plate, were directly cooled by the narrow circular plate. In front of the quartz plate a large wooden screen was placed, and to its back (not to be seen in this drawing) a copper cylinder was fixed of about 1 inch in thickness and of the same diameter as the outside copper cylinder of the thermopile, filled with water of the same temperature as that contained between the two copper cylinders of the thermopile.

In filling all the apparatus with water from the main, the space between the two copper cylinders was first filled with water through E. From the top of the outer cylinder the water passes through the india-rubber tube (*y*) behind the quartz plates and through the india-rubber tube (*f*) to the lower part of the cylinder which forms the water screen. From the top of the water screen the water passes through an india-rubber tube and pewter pipe (*p*) back to the tank, and then the run of water is stopped. The india-rubber tubes *f* and *y* allow the screen to move up and down, and when it is down the water screen quite covers the whole front surface of the copper cylinder of the thermopile, being removed from it by only about half a centimetre. Direct tests of these arrangements showed them to be successful; after the light has been used and the quartz plates again screened, the deflection returns to the same zero quickly (the thermo-electromotive force in the dark never exceeding about 2 millims.), and remains so for any length of time, and the same deflection is obtained every time the screen is opened again. It takes only a fraction of a minute for the spot of light to attain its maximum deflection or return to zero.

The Galvanometer, &c. (See fig. 7.)

With an acetylene flame of about 250 candle power it was possible to use a Crompton's dead-beat galvanometer instead of the more sensitive one made by Nalder Brothers.

One of the conducting leads p from the Rubens thermopile leads to the interrupter E (see diagram p. 357), the purpose of which is either to interrupt the current, or to bring the lead (p) from the thermopile into connexion with the lead (p') conducting to the galvanometer (g), or to connect the lead (λ) from the nickel-iron thermocouple of the quartz vessel with the lead (p') conducting to the galvanometer. From E the wire passes to the reversing key, which is enclosed in an asbestos box, and from here to the galvanometer (g).

The spot of light from an electric incandescent lamp, after passing through a lens, was reflected from the galvanometer mirror upon a transparent celluloid scale.

Great difficulty was experienced in steadying the galvanometer; the suspension of the galvanometer in a box on an india-rubber band, and the placing of the box on a very heavy stone, which again was placed in its turn on thick pieces of india-rubber, gave vibrations of 1 to 2 millims., owing to the fact that the dark room the author had to use was near machinery at work. It was ultimately steadied in the following manner:—A soft thick copper wire was drawn from one wall of the room to the other, and the wire was first stretched and shortened until it stood the weight of the box containing the galvanometer suspended on two very thick and flexible rubber rings. Inside the box the galvanometer (with the wooden plate on which it was standing on pieces of copper) was suspended from one rubber ring on the hook of a screw, which was passed through a hollow wooden cylinder on the top of the wooden box and held by a nut, placed on a metal plate on the top of the wooden cylinder. By raising the screw outside and turning the nut the galvanometer could be brought to any height desired, and by carefully turning the screw it could be placed at any angle, so as to get the spot of light at any required place on the scale. The screws of the galvanometer were resting upon metal pieces on the wooden plate, and adjusted so as to get the required sensitiveness by weakening the magnetic field, *i.e.*, by bringing the circular coil partially out of the central iron core. It was further necessary that the whole arrangement of the suspension of the galvanometer should not be upset by the necessity of fixing the leads to the galvanometer, since it was impossible to ensure that greater vibrations of the leads outside the box would never take place. For this reason the galvanometer was not connected directly with the heavy leads; these were fixed to the wooden box, then for each lead three or four pieces of very thin galvanometer suspension wire (each about 2 inches in length) were soldered to two pieces of thick copper wire; one of them was fixed to the lead and the other to the terminal of the galvanometer. Thus the galvanometer became for the first time quite freely suspended in the box, the fine suspension wires on the one hand allowing free movement to the galvanometer wherever and whenever it may be required, and, on the other hand, exerting no directing influence whatever on its mass.

The small vibrations of the walls of the room were thus allowed to affect the copper wire at the ends, and were weakened almost to zero before they were transmitted to the middle part of the wire. These vibrations in the middle part of the wire were further weakened by the two rubber rings upon which the box with the galvanometer was suspended, and, lastly, the galvanometer itself was made independent both of the vibrations of the box and of the leads. In this way excellent results were obtained, the movements of the spot of light when the scale was removed from the galvanometer 1 or 1·2 metres not exceeding 0·1 millim. Having now, from the acetylene flame, a deflection of the spot of light of about 10 to 15 centims., each reading was brought (and with it the possibility of adjustment of the intensity of light to the right or left) to an accuracy of about 0·1 per cent., an accuracy far greater than that required for the research.

Determination of the Value of the Observed Deflection of the Galvanometer or of the Intensity of Light in Standard Units. (Fig. 7.)

With the arrangement described above, the deflection of the spot of light depends upon conditions which may easily vary according to the circumstance and time. Assuming that the distance of the source of light from the thermopile is fixed, that the flame is in the correct position, that the distance of the scale from the mirror is fixed, still, if the india-rubber rings should become a little stretched in time, or any similar accident happen, the sensitiveness of the galvanometer would vary. It is, therefore, necessary that measurements of the intensity of light should be made independent of variations in the sensitiveness of the galvanometer. It is further desirable to be able to express at once the intensity of light in standard units independently of any given arrangements of the photometer, &c. For this reason, directly after the measurement of the light by means of the thermopile was made, a second measurement was made with a Clark cell and manganin resistances, as given in the above diagram, thus determining the value of the deflection, as caused by the light, in units given by the Clark and manganin resistances.

THE REMAINING PARTS OF THE APPARATUS, &C.

The Bath. (Fig. 5, p. 352.)

The reaction vessel with the mixture of chlorine and hydrogen was immersed in a water-bath and there exposed to light. The bath contained quartz windows, and the reaction vessel was placed behind one of them, the manometer M (E in fig. 1) remaning outside the bath. The volume of the gas in the capillary tubes and in the capillary of the manometer was only a few tenths per cent. of the volume of the gas in the reaction vessel immersed in the bath, so that if the differences between the temperature of the room and that of the bath were very great a small correction was necessary.

Two mercury thermometers were immersed in the bath, one divided into degrees centigrade which could be read to 0°·1, and the other a 0°·1 thermometer of Beckmann's type, with divisions about 3 millims. apart from one another, allowing the temperature of the bath to be read to 0°·01. The thermometers were kept very near to the reaction vessel; the temperature of the gaseous mixture in the reaction vessel with the quartz windows was indicated by the iron-nickel thermocouple inside the same. Later on the temperature was calculated, no thermocouple being employed, to ensure the gaseous mixture not being contaminated with any traces of other substances during the reaction. Near the capillary tube of the manometer was a thermometer, divided into degrees centigrade to indicate the temperature of the room.

To keep the temperature of the bath constant at any desired temperature, the copper bath was large, containing about 70 litres of water. It was covered with very thick sheets of asbestos, placed in a wooden box with an air space between it and the sides of the box, which was placed in another wooden box with another air space between them, while the top of the bath was covered with a wooden lid. At the bottom a small circle was cut out of the wood and asbestos for a rose burner 2 centims. distant from the exposed circle of the copper bottom. The temperature of the bath itself regulated the supply of gas to the burner. The liquid was thoroughly stirred at frequent intervals. Since with all these arrangements the temperature of the bath could not be kept sufficiently constant, owing to the heat absorbed from the powerful acetylene light, the temperature of the bath was adjusted to the desired degree by melting ice, especially when the temperatures required were below 25° or 30°, and by thorough stirring. In this manner the variations of temperature of the bath were kept within as narrow limits as possible during the whole time of the experiment. Each time the readings of the manometer and of the temperature of the bath and of the reaction vessel had to be made, the bath was effectually stirred, readings being taken two minutes later. During this period of two minutes the temperature of the bath near the quartz vessel does not rise under the action of the light more than 0°·01. Since for our purpose it is important to know the difference of the temperature of the gas mixture at two different times, so as to be able to apply the necessary correction, the above manner of making the readings each time two minutes after the bath was well stirred, eliminated the error in the determined differences of temperature almost completely. An investigation of the velocity with which the mercury of the manometer assumes its maximum when the glass bulb or quartz vessel is immersed in the bath showed that after two minutes the temperature of the gas in the bulb is much less than 0°·01 removed from the convergence temperature, the amount of our reading error. This convergence temperature of the gaseous mixture is higher than the temperature of the bath, but always remains constant for the same intensity of the same source of light falling upon the gaseous mixture, provided that the reaction goes on so slowly that the heating of the system by the heat of reaction can be neglected. We are also able from the temperature of the bath to calculate the temperature of the gas mixture. Having once determined the necessary elements for such a calculation (in a manner given by the author on several other occasions)* from the velocity of cooling of the gaseous mixture by the bath and from the velocity of heating of the gaseous mixture by the given source of light (at the beginning of the induction period), a thermocouple was not introduced into the thin glass bulb used instead of the quartz vessel, as it was better to make sure that during the reaction no vapour of any kind could enter into the gaseous mixture from the cement with which the thermocouple has to be fixed in the capillary of the vessel, or from the shellac and pitch with which the wires of the thermocouple have to be covered in order that they may be protected against the action of chlorine. Indeed, the best results, as far as experience goes, were obtained when none of these precautions were neglected.

PART III.

Experimental Results. (Tables I.–V.)

In the following tables the experimental data are given:—

No. is the number of the observation made.

τ is the time at which the observation was made.

$\tau'-\tau''$ is the time between two successive operations.

π is the reading of the manometer E of the quartz vessel at the time τ, read with the cathetometer (38 divisions of the cathetometer scale = 1 millim. of the manometer scale).

$\pi'-\pi''$ is the rise of the manometer E during the time $\tau''-\tau'$.

is the intensity of the acetylene light, *i.e.*, the integral intensity of the light of all wave-lengths contained in the same, expressed in millimetre deflection of the galvanometer read on the scale at the time τ, including the thermo-electromotive force of the Rubens thermopile in the dark; Th.E.M.F. gives the thermo-electromotive force of the Rubens thermopile in the dark, read on the scale at the time τ.

$i'-th.e.m.f'.$ gives the intensity of light at the time τ'. A correction for the deviation of this value from the average intensity of the light during the whole time of the reaction can be applied to the velocity constant K, given in Tables (II., III., IV. and V.), putting K directly proportional to the

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* See "On Real and Apparent Freezing-Points," by M. Wilderman, 'Phil. Mag.,' December, 1897, pp. 474, 475.

intensity of light. I omit, however, this correction, because the variations in the values of K, especially when taken, as in our case, at small intervals, are too considerable for the application of very small corrections to be of any essential use.

Std. gives the sensitiveness of the galvanometer used for the measurement of the intensity of light, measured with standard units (manganin resistances and Clark), and expressed in millimetre deflection of the galvanometer on the same scale. From this the value of (i) is also known in standard units.

t_B is the actual temperature of the bath on 1° thermometer at the time τ.

t_r is the temperature t_B read on the 0°·1 Beckmann thermometer at the same time τ.

$t_{man.}$ is the temperature of the room near the manometer.

Since the volume of the gas in the capillary tubes changes during the reaction, owing to the rise of the mercury in the same, its value is during the reaction from 0·2 per cent. to 0·5 per cent. of the volume of the gas in the quartz vessel or the bulb.

A variation in the temperature of the room = 1° produced a change in the height of the manometer from $\frac{0{\cdot}2 \text{ per cent.}}{273}$ to $\frac{0{\cdot}5 \text{ per cent.}}{273}$ of the total pressure of the gas. When the pressure of the gas = 760 millims., this amounts to $\frac{0{\cdot}2 \times 760}{273 \times 100} = 0{\cdot}005$ millim. to 0·012 millim. per 1° variation in the temperature of the room. So long as we investigate only small intervals of the curve, *i.e.*, when the temperature of the room could not change by 1°, no correction need appear in the tables, and $t_{man.}$ need not enter into the equation. When, however, the curve is investigated at greater time intervals, a correction for $t_{man.}$ can be usefully applied.

$t'_r - t''_r$ is the difference in the temperature of the bath (and gas mixture) at the time τ' and τ'', read to 0°·01 on Beckmann's thermometer.

$t'_r - t''_{r\,corr.}$ is the correction in millimetre pressure, which is to be added to the observed $\pi' - \pi''$ for the variation of the temperature of the bath. This value, when the expansion of the glass bulb is simultaneously accounted for, equals 1·8 millim. for each 1° variation of temperature of the bath. The value of the correction was found from direct observations on the manometer, by bringing the bulb successively to higher temperatures. This correction is especially important when small parts of the curve are investigated, and becomes of smaller importance the greater $\pi' - \pi''$ is, since the variations of t remain almost constant during the whole time of the experiment.

h is the barometric pressure at the time τ, read with the vernier; the temperature of the mercury is given in brackets.

$h'-h''$ is the variation of the barometer on passing from τ' to τ'', when the correction for the temperature of the mercury is also made. This correction must be added to the observed $\pi'-\pi''$; it is for the same day, when the barometer changes very little, of little importance; on the contrary, it becomes important for the ordinary changes of the barometer.

$\pi'-\pi''_{corr.}$ is the true variation in the height of the manometer, if the atmospheric pressure and the temperature of the bath (or of the gas mixture) should have remained constant the whole time, *i.e.*, after the corrections for the variations of the temperature of the bath and for the atmospheric pressure were made. Results were not reduced to normal atmospheric pressure, since this would not serve any purpose (see Table I.).

TABLE I.—CO and Cl_2 (in the glass bulb).

The glass bulb was filled with the gases in the dark. The gases freshly prepared mercury and of the conc. SO_4H_2 (sp.gr. 1·84)) on the manometer was 505·4 millims., temperature of the room 24°·5. On leaving the glass bulb in the dark from Friday, temperature of the room to 22°·3. The manometer rose from 510 to 513·5, *i.e.*, by of barometer and temperature of the room. Thus during three days no combination Barometer, 763·2 (21°·7), temperature of room, 22°·3. Manometer fell to 51·17, *i.e.*, variation of temperature of the room and of the atmospheric pressure. The vessel over the bulb and the temperature of the bath brought the light of the manometer che centre of glass bulb = 62·5 centims.

No.	Time of observation, τ.		$\tau'' - \tau$ in minutes.	Indication of the manometer at the time τ, π.	$\pi' - \pi''$ in millimetres.	The intensity of light in millimetre deflection of galvanometer, i (+th.e.m.f.).	i − th. e.m.f.	Sensitiveness of galvanometer measured with standard units in millimetre deflection, *std.* (right & left).
1st curve.	h.	m.	minutes.		millims.	millims.	millims.	millims.
1	11	50		512·8		—	—	266
			15		0			
2	12	5		512·8		195*	195	—
			45		−0·1 × 2	(th.e.m.f. = 0)		
3	12	50		512·7		—	—	—
			110		−0·3 × 2			
4	2	40		512·4		—	—	—
			80		−0·5 × 2			
5	4	0		511·9		—	—	—
			35		0			
6	4	35		511·9		206	201·5	—
			70		2·6 × 2	(th.e.m.f. = 4·5)		
7	5	45		514·5		—	—	266
Next day	—		—	—	1·3 × 2	—	—	—
2nd curve.								
8	10	33		515·8–364·9		—	—	267
			19		2·3			
9	10	52		517·0–363·8		197	197	—
			10		2·4			
10	11	2		518·3–362·7		—	—	—
			10·5		2·4			

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* At the beginning, during the induction period, when no reaction is visible, no special

Experiment started 5th July, 1901.

in the dark. The partial pressure of Cl_2 (from the variation of the height of the
and of CO was 110 millims., when the barometer was 764·6 millims. (21°·7) and the
12 A.M., till Monday, 11 A.M., the barometer changed to 766·85 (21°·4), the
(513·5–510·0) 2 = 7 millims. instead of 7·2 millims., which corresponds to the variation
whatever took place in the dark. From Monday it was left till Tuesday, 11 A.M.
by (51·35–51·17) 2 = 3·6 millims. instead of 3·65 millims., corresponding to the
was then placed in the dark of 20°·8. The pressure of the water column in the bath
to 512·8. Distance of acetylene light from Rubens' thermopile = 105 centims.; from

The temperature of bath on 1° thermometer, t_B.	The *read* temperature of bath on the $\frac{1}{10}$° Beckmann thermometer, t_r.	Variation of the temperature of the bath and of the gas mixture, $t'_r - t''_r$.	Calculated correction for $t'_r - t''_r$ in millimetres, which is to be added to $\pi' - \pi''$.	Height of barometer, h at the time τ (and temperature).	Calculated variation of the barometer in millimetres, $h' - h''$ (corrected for temperature).	$\pi' - \pi''_{corr.}$, the variation of the manometer when corrections for temperature of the bath and for atmospheric pressure were made.	No.
°	°	°	millims.	millims. °	millims.	millims.	1st curve.
20·8	3·47			763·2 (21·4)			1
		0·05*	1·8 × 0·05 = 0·09		0·06	0·15	
—	3·52			—			2
		0·04	1·8 × 0·04 = 0·07		0·17	0·04	
—	3·56			—			3
		0·36	0·65		0·41	0·46 ?	
—	3·92			—			4
		0·43	0·77		0·29	0·06	
—	4·35			—			5
		0·15	0·27		0·13	0·40	
—	4·50			—			6
		0·38	0·68		0·28	6·16	
—	4·88			761·95 (20·8)			7
—	—	− 0·48	− 0·86	—	− 1·8	− 0·06	Next day
							2nd curve.
21·7	4·40			763·75 (20·8)			8
		0·03	1·8 × 0·03 = 00·5		0·06	2·41	
—	4·43			—			9
		0·05	0·09		0·03	2·52	
—	4·48			—			10
		0·05	0·09		0·03	2·52	

care was taken to keep the temperature of the bath and the intensity of light constant.

TABLE I.—CO and Cl_2 (in the glass bulb).

No.	Time of observation, τ.		$\tau'' - \tau'$ in minutes.	Indication of the manometer at the time τ, π.	$\pi' - \pi''$ in millimetres.	The intensity of light in millimetre deflection of galvanometer, i (+ th.e.m.f.).	i − th.e.m.f.	Sensitiveness of galvanometer measured with standard units in millimetre deflection, *std.* (right & left).
2nd curve.	h.	m.	minutes.		millims.	millims.	millims.	millims.
11	11	12½		519·5–361·5		204	202	—
			9·5		2·2	(th.e.m.f. = 2)		
12	11	22		520·6–360·4		—	—	—
			10·5		2·3			
13	11	32½		521·8–359·3		203	201	—
			10		2·0	(th.e.m.f. = 2)		
14	11	42		522·8–358·3		204	202	—
			10		1·9	(th.e.m.f. = 2)		
15	11	52		523·8–357·4		203·5	201·5	—
			10		1·9	(th.e.m.f. = 2)		
16	12	2		524·7–356·4		—	—	—
			10		1·7			
17	12	12		525·6–355·6		—	—	—
			10		2·3			
18	12	22		526·8–354·5		202	200	—
			10		1·5	(th.e.m.f. = 2)		
19	12	32		527·5–353·7		—	—	—
			10		1·6			
20	12	42		528·3–352·9		—	—	—
			9		1·7			
21	12	51		529·2–352·1		—	—	—
			9·5		1·5			
22	1	2½		530·0–351·4		204	201·5	—
			9·5		1·4	(th.e.m.f. = 2)		
23	1	12		530·7–350·7		—	—	—
			10		1·4			
24	1	22		531·4–350·0		—	—	—
			11·5		2·1			
25	1	33½		532·5–349·0		—	—	—
			8·5		1·1			
26	1	42		533·0–348·4		202	198·5	—
			10		1·2	(th.e.m.f. = 3·5)		
27	1	52		533·6–347·8		—	—	267
			10		1·0			
28	2	2		534·1–347·3		—	—	—
			10		1·4			
29	2	12		534·8–346·6		202	198·5	—
			10·5		1·3	(th.e.m.f. = 3·5)		
30	2	22½		535·5–346·0		202·2	198·5	—
			11		1·0	(th.e.m.f. = 3·5)		
31	2	33½		536·0–345·5		—	—	—
			9		1·2			
32	2	42½		536·6–344·9		—	—	—
			9·5		1·0			

Experiment started 5th July, 1901—(continued).

The temperature of bath on 1° thermometer, t_B.	The *read* temperature of bath on the $\frac{1}{10}$° Beckmann thermometer, t_r.	Variation of the temperature of the bath and of the gas mixture, $t'_r - t''_r$.	Calculated correction for $t'_r - t''_r$ in millimetres, which is to be added to $\pi' - \pi''$.	Height of barometer, h at the time τ (and temperature).	Calculated variation of the barometer in millimetres, $h' - h''$ (corrected for temperature).	$\pi' - \pi''_{corr.}$, the variation of the manometer when corrections for temperature of the bath and for atmospheric pressure were made.	No.
°	°	°	millims.	millims. °	millims.	millims.	2nd curve.
—	4·53			—			11
		−0·06	−0·11		0·03	2·12	
—	4·47			—			12
		0·05	0·09		0·03	2·42	
—	4·52			—			13
		0·04	0·07		0·03	2·10	
—	4·56			—			14
		−0·03	−0·05		0·03	1·88	
—	4·53			—			15
		0·06	0·11		0·03	2·04	
—	4·59			—			16
		−0·01	−0·02		0·03	1·71	
—	4·58			—			17
		−0·26	−0·47		0·03	1·86	
—	4·32			—			18
		0·04	0·07		0·03	1·60	
—	4·36			—			19
		0·07	0·13		0·03	1·76	
—	4·43			—			20
		−0·15	−0·27		0·03	1·46	
—	4·28			—			21
		0·09	0·16		0·03	1·69	
—	4·37			—			22
		0·05	0·09		0·03	1·52	
—	4·42			763·3 (21·8)			23
		0·06	0·11		0·01	1·52	
—	4·48			—			24
		−0·22	−0·40		0·01	1·71	
—	4·26			—			25
		0·08	0·14		0·01	1·26	
—	4·34			—			26
		0·06	0·11		0·01	1·32	
21·7	4·40			—			27
		0·08	0·14		0·01	1·15	
—	4·48			—			28
		−0·15	−0·27		0·01	1·14	
—	4·33			—			29
		0·05	0·09		0·01	1·40	
—	4·38			—			30
		0·09	1·8 × 0·09 = 0·16		0·01	1·17	
—	4·47			—			31
		−0·14	−0·25		0·01	0·96	
—	4·33			—			32
		0·05	0·09		0·01	1·10	

TABLE I.—CO and Cl_2 (in the glass bulb).

No.	Time of observation, τ.		$\tau'' - \tau'$ in minutes.	Indication of the manometer at the time τ, π.	$\pi' - \pi''$ in millimetres.	The intensity of light in millimetre deflection of galvanometer, i (+th.e.m.f.).	i − th. e.m.f.	Sensitiveness of galvanometer measured with standard units in millimetre deflection *std.* (right & left).
2nd curve.	h.	m.	minutes.		millims.	millims.	millims.	millims.
33	2	52		537·1–344·4		—	—	—
			11		1·1			
34	3	3		537·7–343·9		—	—	—
			10·5		1·2			
35	3	13½		538·3–343·3		202 (th.e.m.f. = 3·5)	198·5	—
			11		1·0			
36	3	24½		538·8–342·8		—	—	—
			12		1·3			
37	3	36½		539·5–342·2		202 (th.e.m.f. = 3·5)	198·5	—
			13·5		1·1			
38	3	50		540·0–341·6		201 (th.e.m.f. = 3·5)	197·5	—
			16·5		1·6			
39	4	6½		540·8–340·8		202 (th.e.m.f. = 3·5)	198·5	—
			13·5		1·2			
40	4	20		541·4–340·2		204 (th.e.m.f. = 5)	199	—
			15·5		1·1			
41	4	35½		542·0–339·7		—	—	—
			17·0		1·4			
42	4	52½		542·7–339·0		202 (th.e.m.f. = 3·5)	198·5	—
			15		1·0			
43	5	7½		543·3–338·6		203 (th.e.m.f. = 3·5)	199·5	267
			13		1·4			
44	5	20½		544·0–337·9		—	—	—
3rd curve.			11		0·5			
45	5	31½		544·2–337·6		—	—	—
			15		0			
46	5	46½		544·2–337·6		—	—	—
			10		0			
47	5	56½		544·2–337·6		—	—	267
Next day	—		—	—	1·8	—	—	—
4th curve.								
48	10	56		545·0–366·6		202 (th.e.m.f. = 2)	200	265
			10		0			
49	11	6		545·0–336·6		—	—	—
			10		0·4			
50	11	16		545·2–336·4		201 (th.e.m.f. = 1·5)	199·5	—
			10		0·6			

Experiment started 5th July, 1901 (continued).

The temperature of bath on 1° thermometer, t_B.	The *read* temperature of bath on the $\frac{1}{10}$° Beckmann thermometer, t_r.	Variation of the temperature of the bath and of the gas mixture, $t'_r - t''_r$.	Calculated correction for $t'_r - t''_r$ in millimetres, which is to be added to $\pi' - \pi''$.	Height of barometer, h at the time τ (and temperature).	Calculated variation of the barometer in millimetres, $h' - h''$ (corrected for temperature).	$\pi' - \pi''_{corr.}$, the variation of the manometer when corrections for temperature of the bath and for atmospheric pressure were made.	No.
°	°	°	millims.	millims. °	millims.	millims.	2nd curve.
—	4·38			—			33
		0·09	0·16		0·01	1·27	
—	4·47			—			34
		−0·10	−0·18		0·01	1·03	
—	4·37			—			35
		0·09	0·16		0·01	1·17	
—	4·46			—			36
		−0·11	−0·20		0·02	1·21	
—	4·35			—			37
		0·11	0·20		0·02	1·32	
—	4·46			—			38
		−0·09	−0·16		0·02	1·46	
—	4·37			—			39
		−0·03	−0·05		0·02	1·17	
—	4·34			—			40
		0·12	0·22		0·02	1·34	
—	4·46			—			41
		−0·05	−0·09		0·02	1·33	
—	4·41			—			42
		0·12	0·22		0·02	1·24	
—	4·53			—			43
		−0·16	−0·29		0·02	1·13	
—	4·37			—			44
		0·02	0·04		0·01	0·55	3rd curve.
—	4·39			—			45
		0·07	0·13		0·02	0·15	
—	4·46			—			46
		0·07	0·13		0·01	0·14	
—	4·53			762·85 (21·4)			47
—	—	−0·21	−0·38	—	−1·7	−0·28	Next day
							4th curve.
—	4·32			764·55 (21·4)			48
		0·01	0·02		0·06	0·08	
—	4·33			—			49
		0·03	0·05		0·06	0·51	
—	4·36			—			50
		0·06	0·11		0·06	0·77	

TABLE I.—CO and Cl_2 (in the glass bulb).

No.	Time of observation, τ.		$\tau'' - \tau'$ in minutes.	Indication of the manometer at the time τ, π.	$\pi' - \pi''$ in millimetres.	The intensity of light in millimetre deflection of galvanometer, i (+th.e.m f.).	i − th.e.m.f.	Sensitiveness of galvanometer measured with standard units in millimetre deflection *std.* (right & left).
4th curve.	h.	m.	minutes.		millims.	millims.	millims.	millims.
51	11	26		545·5–336·1		—	—	—
			13		1·0			
52	11	39		546·0–335·6		203 (th.e.m.f. = 3)	200	—
			21		2·3			
53	12	0		547·2–334·5		—	—	—
			18·5		1·3			
54	12	18½		547·9–333·9		202 (th.e.m.f. = 2)	200	—
			16		1·2			
55	12	34½		548·5–333·3		203·5 (th.e.m.f. = 2)	201·5	--
			15·5		1·0			
56	12	50		549·0–332·8		201·5 (th.e.m.f. = 2)	199·5	—
			15		1·0			
57	1	5		549·5–332·3		—	—	—
			15		1·0			
58	1	20		550·0–331·8		203·5 (th.e.m.f. = 3)	200·5	—
			20		1·2			
59	1	40		550·6–331·2		202·0 (th.e.m.f. = 3·5)	198·5	—
			20		1·4			
60	2	0		551·3–330·5		203·5 (th.e.m.f. = 3)	200·5	—
			21·5		1·1			
61	2	21½		551·9–330·0		204 (th.e.m.f. = 3)	201	—
			21·0		1·2			
62	2	42½		552·5–329·4		—	—	—
			23·5		0·9			
63	3	6		553·0–329·0		202 (th.e.m.f. = 3)	199	—
			44	—	2·1	—	—	—
5th curve.								
64	3	55		554·0–327·9		199·0	199	—
			22		0·8			
65	4	17		554·4–327·5		202 (th.e.m.f. = 2)	200	—
			23		1·0			
66	4	40		554·9–327·0		—	—	—
			20		0·6			
67	5	0		552·2–326·7		203 (th e.m.f. = 2·5)	200·5	—
			23		1·2			
68	5	23		555·8–326·1		202·5 (th e.m.f. = 2·5)	200	—
			22		0·8			
69	5	45		556·2–325·7		202·5 (th.e.m.f. = 2·5)	200	265

Experiment started 5th July, 1901 (continued).

The temperature of bath on 1° thermometer, t_B.	The *real* temperature of bath on the $\frac{1}{10}$° Beekmann thermometer, t_r.	Variation of the temperature of the bath and of the gas mixture, $t'_r - t''_r$.	Calculated correction for $t'_r - t''_r$ in millimetres, which is to be added to $\pi' - \pi''$.	Height of barometer, h at the time τ (and temperature).	Calculated variation of the barometer in millimetres, $h' - h''$ (corrected for temperature).	$\pi' - \pi''_{corr.}$, the variation of the manometer when corrections for temperature of the bath and for atmospheric pressure were made.	No.
°	°	°	millims.	millims. °	millims.	millims.	4th curve.
—	4·42			—			51
		0·06	0·11		0·08	1·19	
—	4·48			—			52
		−0·26	−0·47		0·12	1·95	
—	4·22			—			53
		0·13	0·23		0·11	1·64	
—	4·35			—			54
		0	0		0·09	1·29	
—	4·35			—			55
		0·05	0·09		0·09	1·18	
21·7	4·40			—			56
		0·06	0·11		0·09	1·20	
—	4·46			763·9 (22·4)			57
		−0·10	−0·18		0·04	0·86	
—	4·36			—			58
		0·11	0·20		0·06	1·46	
—	4·47			—			59
		−0·10	−0·18		0·06	1·28	
—	4·37			—			60
		0·06	0·11		0·06	1·27	
—	4·43			—			61
		−0·07	−0·13		0·06	1·13	
—	4·36			—			62
		0·20	0·36		0·06	1·32	
—	4·56			—			63
—	—	−0·06	−0·11	—	0·13	2·12	
							5th curve.
—	4·50			—			64
		0·13	0·23		0·06	1·09	
—	4·37			—			65
		0	0		0·06	1·06	
—	4·37			—			66
		0·18	0·33		0·06	0·99	
—	4·55			—			67
		−0·13	−0·23		0·06	1·03	
—	4·42			763·1 (22·12)			68
		0·03	0·05		0·06	0·91	
—	4·45			—			69

If we now draw curves, taking the times τ's as abscissæ and the corresponding amount of carbonyl chloride formed (*i.e.*, the π's) as ordinates, then the $\frac{\pi' - \pi''}{\tau_2 - \tau_1}$'s or $\frac{d\pi}{d\tau}$'s give the rate of formation of carbonyl chloride, or the rate of combination of chlorine and carbon monoxide. The curves appear to be remarkably regular, especially those obtained with the glass bulb. The total number of direct observations is in Table I. about 70. To trace the nature of the curve through its whole length observations were made at small intervals, thus dispensing with interpolating results. Errors arising from the variations of the temperature of the bath, from the variations of the barometric pressure, &c., can never be completely eliminated by the application of corrections. For this reason they are greater in the results obtained for small intervals than when greater ones are taken. By this method the phenomenon is nevertheless more thoroughly known and its nature more evident, since such an investigation of the curve does not permit of phenomena characteristic of only one part of the curve obscuring the true nature of other parts of the curve. As will be seen from the tables given below this course proved to be necessary in our case, since at the beginning of the curves we always met with a peculiar phenomenon, called "induction," not characteristic of the rest of the curve.

When the $\frac{\pi' - \pi''}{\tau_2 - \tau_1}$'s or $\frac{d\pi}{d\tau}$'s are successively taken on the curve and compared with one another, we find that they start with very small values approaching zero (the curve starts asymptotically to the abscissa), and gradually increase till they reach a maximum, after which they gradually decrease. If we consider curves (1), (2), (3), (4) and (5) of Table I. as parts of the same curve, belonging all to one system, we find that the $\frac{d\pi}{d\tau}$'s gradually diminish, approaching the value of zero, *i.e.*, when no more reaction takes place. This takes place when one of the combining substances completely disappears from the gas mixture.

An investigation of the curves, after the $\frac{d\pi}{d\tau}$'s arrived almost at their maximum, shows with absolute certainty that the equation

$$[\log_e(A - x_1) - \log_e(A - x_2) + \log_e(B - x_2) - \log_e(B - x_1)] : (\tau_2 - \tau_1) = C \quad (1)$$

(a constant) holds good, where A and B are the quantities or volumes or partial pressures of chlorine and carbon monoxide before the reaction was first started, expressed in millimetre pressure of the manometer. $A - x_1$, $A - x_2$, $B - x_1$, $B - x_2$, are the quantities of chlorine and of carbon monoxide present in the system at the times τ_1 and τ_2 (see Table II. below).

It is thus evident that our integral equation must be

$$\frac{1}{A - B}[\log_e(A - x_1) - \log_e(A - x_2) + \log_e(B - x_2) - \log_e(B - x_1)] : (\tau_2 - \tau_1) = K \quad (2).$$

The differential equation giving the law of velocity of reaction is thus

$$\frac{dx}{d\tau} = \mathrm{K}\,(\mathrm{A} - x)\,(\mathrm{B} - x) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

i.e., the velocity of combination of chlorine and carbon monoxide in light, or the velocity of the formation of carbonyl chloride, is at the time τ directly proportional to the product of the reacting masses at the time τ. Since the chemical equation for the reaction is $Cl_2 + CO = COCl_2$, this equation in light has the form which it ought to have according to the law of mass action in homogeneous systems, if the chemical reaction were to go on in the dark as the outcome of those intrinsic properties of matter only, which we call chemical affinity or chemical potential. In the above equations K is the velocity constant, which gives the velocity of combination of chlorine and carbon monoxide under given conditions of experiment, when $\mathrm{A} - x$ for chlorine is 1 and $\mathrm{B} - x$ for carbon monoxide is 1. K in the above equations is evidently also an integral velocity constant for all wave lengths of the acetylene light, the value of (K) being different for each wave length. Since, however, each wave length has an equation of the same form $\frac{dx}{d\tau} = (\mathrm{K})\,(\mathrm{A} - x)\,(\mathrm{B} - x)$, the equation for light consisting of more than one wave length remains the same; K or (K) is besides a function of the intensity of light, of the temperature, and of the surrounding medium.

In the following tables (II., III., IV. and V.):

No. is the number of the observation.

$\pi' - \pi'' = dx$ is the amount of carbonyl chloride formed, or of chlorine or of carbon monoxide which has disappeared during the times $\tau_2 - \tau_1$.

$\mathrm{A} - x$ is the quantity of chlorine present in the system at the time τ.

$\mathrm{B} - x$ is the quantity of carbon monoxide present in the system at the time τ.

$\tau_2 - \tau_1$ is the time between two successive observations.

Equation (2) should be true if the law of mass action holds good.

$\frac{dx}{d\tau}$ gives the rate of formation of carbonyl chloride at the successive times; this ought to be constant, if the rate of formation of carbonyl chloride in a unit of time were independent of the reacting masses and were directly proportional to the intensity of the light introduced only.

$\frac{dx}{d\tau} : (\mathrm{A} - x)$ gives the rate of formation of carbonyl chloride at the time τ, divided by the quantity of chlorine present in the system at the time τ. This ought to be constant if the rate of formation of carbonyl chloride at a given intensity of light were directly proportional to the amount of light absorbed by the system (*i.e.*, by chlorine) in the unit of time during the reaction.

TABLE II.—Cl_2 and CO (in the Glass Bulb). Experiment started 5th July, 1901. Temperature ca. 21°·7.

No.	$\pi' - \pi'' = dx$.	$A - x$ (Cl_2).	log $(A - x)$.	log $(A - x_1)$ $-$ log $(A - x_2)$.	$B - x$ (CO).	log $(B - x)$.	log $(B - x_1)$ $-$ log $(B - x_2)$.	Σ log $=$ [log $(A - x_1)$ $-$ log $(A - x_2)$] $-$ [log $(B - x_1)$ $-$ log $(B - x_2)$].	$\tau_2 - \tau_1$.	$\frac{\Sigma \log}{\tau_2 - \tau_1} . 10^4$ $= (A - B) K \times 10^4 : 2{\cdot}3026$.	$\frac{dx}{d\tau} . 100$.	$\frac{dx}{d\tau} : \frac{A - x}{10^5}$.	K . 10^7 : 2·3026.
1st curve. 1		502·4	2·70105		109·4	2·03902			minutes.				
	0·15			·00013			·00060	·00047	15	0·31	1·0	20	0·79
2		502·25	2·70092		109·25	2·03842							
	0·04			·00003			·00016	·00013	45	0·029	0·1	2	0·07
3		502·21	2·70089		109·21	2·03826							
	0·46 ?			·00041 ?			·00183 ?	·00142 ?	110	0·13 ?	0·4	8	0·33
4		501·75	2·70048		108·75	2·03643							
	0·06			·00004			·00024	·00020	80	0·025	0·07	14	0·06
5		501·69	2·70044		108·69	2·03619							
	0·40			·00035			·00160	·00125	35	0·357	1·1	22	0·91
6		501·29	2·70009		108·29	2·03459							
	6·16			·00537			·02543	·02006	70	2·87	8·8	177	7·30
7		495·13	2·69472		102·13	2·00916							
Next day.	− 0·06												
2nd curve. 8		495·19	2·69477		102·19	2·00941							
	2·41			·00212			·01037	·00825	19	4·34	12·7	256	11·04
9		492·78	2·69265		99·78	1·99904							
	2·52			·00223			·01111	·00888	10	8·88	25·2	509	22·59
10		490·26	2·69042		97·26	1·98793							
	2·52			·00223			·01140	·00917	10·5	8·73	24·0	492	22·21
11		487·74	2·68819		94·74	1·97653							
	2·12			·00189			·00983	·00794	9·5	8·36	22·3	459	21·27
12		485·62	2·68630		92·62	1·96670							
	2·42			·00217			·01149	·00932	10·5	8·87	23·0	476	22·56
13		483·20	2·68413		90·20	1·95521							
	2·10			·00189			·01023	·00834	10	8·34	21·0	437	21·22
14		481·10	2·68224		88·10	1·94498							
	1·88			·00170			·00937	·00767	10	7·67	18·8	392	19·51
15		479·22	2·68054		86·22	1·93561							
	2·04			·00186			·01040	·00854	10	8·54	20·4	427	21·72

16		477·18	2·67868		84·18	1·92521							
	1·71			·00156			·00891	·00735	10	7·35	17·1	360	18·70
17		475·47	2·67712		82·47	1·91630							
	1·86			·00170			·00991	·00821	10	8·21	18·6	393	20·88
18		473·61	2·67542		80·61	1·90639							
	1·60			·00147			·00871	·00724	10	7·24	16·0	339	18·42
19		472·01	2·67395		79·01	1·89768							
	1·76			·00162			·00978	·00816	10	8·16	17·6	374	20·76
20		470·25	2·67233		77·25	1·88790							
	1·46			·00135			·00829	·00694	9	7·77	16·2	345	19·76
21		468·79	2·67098		75·79	1·87961							
	1·69			·00157			·00979	·00822	9·5	8·65	17·8	381	22·00
22		467·10	2·66941		74·10	1·86982							
	1·52			·00142			·00900	·00758	9·5	7·98	16·0	344	20·30
23		465·58	2·66799		72·58	1·86082							
	1·52			·00142			·00919	·00777	10	7·77	15·2	327	19·77
24		464·06	2·66657		71·06	1·85163							
	1·71			·00160			·01058	·00898	11·5	7·81	14·9	322	19·87
25		462·35	2·66497		69·35	1·84105							
	1·26			·00118			·00797	·00679	8·5	7·99	14·8	320	20·33
26		461·09	2·66379		68·09	1·83308							
	1·32			·00125			·00850	·00725	10	7·25	13·2	287	18·45
27		459·77	2·66254		66·77	1·82458							
	1·15			·00109			·00754	·00645	10	6·45	11·5	251	16·41
28		458·62	2·66145		65·62	1·81704							
	1·14			·00108			·00761	·00653	10	6·53	11·4	249	16·61
29		457·48	2·66037		64 48	1·80943							
	1·40			·00133			·00954	·00821	10·5	7·82	13·3	291	19·90
30		456·08	2·65904		63·08	1·79989							
	1·17			·00111			·00813	·00702	11	6·38	10·6	233	16·23
31		454·91	2·65793		61·91	1·79176							
	0·96			·00092			·00679	·00587	9	6·52	10·7	235	16·59
32		453·95	2·65701		60·95	1·78497							
	1·10			·00106			·00791	·00685	9·5	7·21	11·5	255	18·34
33		452·85	2·65595		59·85	1·77706							
	1·27			·00122			·00931	·00809	11	7·35	11·5	254	18·70
34		451·58	2·65473		58·58	1·76775							
	1·03			·00099			·00770	·00671	10·5	6·41	9·8	217	16·30
35		450·55	2·65374		57·55	1·76005							
	1·17			·00113			·00892	·00779	11	7·08	10·6	236	18·01
36		449·38	2·65261		56·38	1·75113							
	1·11			·00107			·00864	·00757	12	6 31	9·2	205	16·05
37		448·27	2·65154		55·27	1·74249							
	1·32			·00128			·01050	·00922	13·5	6·83	9·8	219	17·38

TABLE II.—Cl_2 and CO (in the Glass Bulb). Experiment started 5th July, 1901. Temperature ca. 21°·7 (continued).

No.	$\pi' - \pi'' = dx$.	$A - x$ (Cl_2).	log $(A - x)$.	log $(A - x_1)$ − log $(A - x_2)$.	$B - x$ (CO).	log $(B - x)$.	log $(B - x_1)$ − log $(B - x_2)$.	$\Sigma \log = [\log(A - x_1) - \log(A - x_2)] - [\log(B - x_1) - \log(B - x_2)]$.	$\tau_2 - \tau_1$.	$\frac{\Sigma \log}{\tau_2 - \tau_1} . 10^4 = (A - B) K \times 10^4 : 2{\cdot}3026$.	$\frac{dx}{d\tau} . 100$.	$\frac{dx}{d\tau} : \frac{A - x}{10^6}$.	$K . 10^7 : 2{\cdot}3026$.
									minutes.				
38		446·95	2·65026		53·95	1·73199							
	1·46			·00142			·01191	·01049	16·5	6·36	8·8	197	16·18
39		445·49	2·64884		52·49	1·72008							
	1·17			·00114			·00979	·00865	13·5	6·48	8·7	191	16·49
40		444·32	2·64770		51·32	1·71029							
	1·34			·00132			·01149	·01017	15·5	6·56	8·9	201	16·69
41		442·98	2·64638		49·98	1·69880							
	1·33			·00130			·01172	·01042	17	6·13?	7·6	172	15·60
42		441·65	2·64508		48·65	1·68708							
	1·24			·00122			·01121	·00999	15	6·66	8·3	188	16·95
43		440·41	2·64386		47·41	1·67587							
	1·13			·00112			·01048	·00936	13	7·20	8·7	198	18·32
44		439·28	2·64274		46·28	1·66539							
	0·55			·00054			·00519	·00465	11	7·23	5·0	114	10·75
3rd curve. 45		438·73	2·64220		45·73	1·66020							
	0·15			·00015			·00143	·00128	15	0·85	1·0	23	2·16
46		438·58	2·64205		45·58	1·65877							
	0·14			·00014			·00133	·00119	10	1·19	1·4	32	3·03
47		438·44	2·64191		45·44	1·65744							
Next day.	−0·28												
4th curve. 48		438·72	2·64219		45·72	1·66011							
	0·08			·00008			·00076	·00068	10	0·68	0·8	18	1·73
49		438·64	2·64211		45·64	1·65935							
	0·51			·00051			·00488	·00437	10	4·37	5·1	116	11·10
50		438·13	2·64160		45·13	1·65447							
	0·77			·00076			·00748	·00672	10	6·72	7·7	176	17·10
51		437·36	2·64084		44·36	1·64699							
	1·19			·00118			·01181	·01063	13	8·58	9·1	208	21·83

52		436·17	2·63966		43·17	1·63518						
	1·95			·00195			·02007	·01812	21	8·63	9·3	214	21·93
53		434·22	2·63771		41·22	1·61511						
	1·64			·00164			·01763	·01599	18·5	8·64	8·8	203	21·98
54		432·58	2·63607		39·58	1·59748						
	1·29			·00130			·01439	·01309	16	8·18	8·1	188	20·80
55		431·29	2·63477		38·29	1·58309						
	1·18			·00119			·01360	·01241	15·5	8·00	7·6	176	20·35
56		430·11	2·63358		37·11	1·56949						
	1·20			·00121			·01427	·01306	15	8·70	8·0	186	22·14
57		428·91	2·63237		35·91	1·55522						
	0·86			·00088			·01053	·00965	15	6·43	5·7	133	16·44
58		428·05	2·63149		35·05	1·54469						
	1·46			·00148			·01848	·01700	20	8·50	7·3	171	21·62
59		426·59	2·63001		33·59	1·52621						
	1·28			·00130			·01687	·01557	20	7·78	6·4	151	19·80
60		425·31	2·62871		32·31	1·50934						
	1·27			·00130			·01742	·01612	21·5	7·50	5·9	139	19·08
61		424·04	2·62741		31·04	1·49192						
	1·13			·00116			·01610	·01494	21·0	7·11	5·4	128	18·09
62		422·91	2·62625		29·91	1·47582						
	1·32			·00136			·01961	·01825	23·5	7·76	5·6	133	19·74
63		421·59	2·62489		28·59	1·45621						
	2·34			·00242			·03708	·02466	44	5·60	5·3	126	14·25
5th curve. 64		419·25	2·62247		26·25	1·41913						
	1·09			·00113			·01842	·01729	22	7·86	5·0	120	20·00
65		418·16	2·62134		25·16	1·40071						
	1·06			·00110			·01869	·01759	23	7·65	4·6	110	19·46
66		417·10	2·62024		24·10	1·38202						
	0·99			·00103			·01822	·01719	20	8·59	4·9	118	21·85
67		416·11	2·61921		23·11	1·36380						
	1·03			·00108			·01988	·01880	23	8·17	4·7	113	20·79
68		415·08	2·61813		22·08	1·34400						
	0·91			·00095			·01828	·01733	22	7·88	4·1	99	20·05
69		414·17	2·61718		21·17	1·32572						

The amount transformed into $CO.Cl_2 = \frac{88 \cdot 23}{109 \cdot 40} = 80 \cdot 65$ per cent.

TABLE III.—CO and Cl_2 (Quartz Vessel). Started 13th December, 1900. Temperature of Bath 43°·7 C.

Distance of acetylene light from Rubens thermopile = 105 centims., from the centre of quartz vessel = 66·5 centims The quantity of Cl_2 taken was 224·7 millims. (at 43°·7); of CO, 343·6 millims. (at 43°·7).

The resistance D connected with the galvanometer of diagram (fig. 7, p. 357) was in this case 1 ohm instead of 6 ohms; the sensitiveness of the galvanometer was then right and left = 461 millims. The intensity of the light, removed by the same distance of 105 centims. from the thermopile, was right and left: (1)–(2) 190·4, (2)–(3) 194·5, (3)–(4) 194·5, (4)–(5) 192·5, (5)–(6) 192·5, (6)–(7) 195, (7)–(8) 195. The light intensity was kept more carefully constant on the second day: (9)–(10) 193·5, (10)–(11) 193·5, (11)–(12) 194·5, (12)–(13) 193·5, (13)–(14) 193·5, (14)–(15) 193·5. The temperature of the bath was, except (3), when it was 43°·95, always 43°·7. It was easier to keep the bath constant at this temperature. The variation of the barometer (759 millims.) was very small and could be neglected.

No.	$\pi' - \pi'' = dx$.	A − x (Cl_2).	log (A − x).	log (A − x_1) − log (A − x_2).	B − x (CO).	log (B − x).	log (B − x_1) − log (B − x_2).	− Σ log = − − [log (A − x_1) − log (A − x_2)] + [log (B − x_1) − log (B − x_2)].	$\tau_2 - \tau_1$.	$\frac{-\Sigma \log}{\tau_2 - \tau_1} . 10^5 = (B - A) K \times 10^5 : 2{\cdot}3026$.	$\frac{dx}{d\tau} . 100$.	$\frac{dx}{d\tau} : \frac{A - x}{10^5}$.	K . 10^7 : 2·3026.
									minutes.				
1		224·7	2·35160		343·6	2·53605							
	0			0			0	0	85	0	0		0
2		224·7	2·35160		343·6	2·53605							
	3·0 × 2			·01175			·00765	·00410	25	16·4	24·0	110	13·8
3		218·7	2·33985		337·6	2·52840							
	2·0 × 2			·00802			·00517	·00285	17	16·7	23·5	110	14·0
4		214·7	2·33183		333·6	2·52323							
	3·5 × 2			·01439			·00921	·00518	18	28·8	38·9	187	24·2
5		207·7	2·31744		326·6	2·51402							
	2·5 × 2			·01059			·00670	·00389	15	25·8	33·3	164	21·7
6		202·7	2·30685		321·6	2·50732							
	4·0 × 2			·01748			·01094	·00654	20	32·7	40·0	205	27·5

7		194·7	2·28937		313·6	2·49638							
	1·0 × 2			·00449			·00278	·00171	6	28·5	33·3	173	24·0
8		192·7	2·28488		311·6	2·49360							
Next day	(barometer 766 millims.).												
9		185·7	2·26881		304·6	2·48373							
	7·5 × 2			·03658			·02193	·01465	83	17·6	18·0	105	14·8
10		170·7	2·23223		289·6	2·46180							
	4·0 × 2			·02084			·01217	·00867	30	28·9	26·6	163	24·3
11		162·7	2·21139		281·6	2·44963							
	4·1 × 2			·02246			·01283	·00963	30	30·8	27·3	177	25·9
12		154·5	2·18893		273·4	2·43680							
	3·1 × 2			·01779			·00996	·00783	30	26·1	20·6	139	22·0
13		148·3	2·17114		267·2	2·42684							
	3·0 × 2			·01794			·00987	·00807	30	26·9	20·0	140	22·6
14		142·3	2·15320		261·2	2·41697							
	2·8 × 2			·01743			·00941	·00802	30	26·7	18·6	136	22·5
15		136·7	2·13577		255·6	2·40756							

The total amount transformed into $CO.Cl_2$ is $\frac{88}{224 \cdot 7} = 39 \cdot 16$ per cent.

TABLE IV.—CO and Cl_2 (Quartz Vessel). Started 13th December, 1900. Temperature of Bath 43°·7.

Distance of the acetylene light from thermopile = 105 centims., from the centre of the quartz vessel = 62·5 centims. The quantity of Cl_2 taken was 287·8 millims. (43°·7); of CO, was 359·4 millims. (at 43°·7). Barometer, 759 millims. The sensitiveness of the galvanometer, temperature of bath, atmospheric pressure, &c., were here the same as in Table (III.).

The Cl_2 and CO are absolutely the same as in Table III.; only exceedingly small traces of air could enter the gas mixture from the conc. SO_4H_2, with which the Cl_2 gas was pressed into the quartz vessel.

No.	$\pi' - \pi'' = dx$.	$A - x$ (Cl_2).	log $(A - x)$.	$\log(A - x_1) - \log(A - x_2)$.	$B - x$ (CO).	log $(B - x)$.	$\log(B - x_1) - \log(B - x_2)$.	$-\Sigma\log = -[\log(A - x_1) - \log(A - x_2)] + [\log(B - x_1) - \log(B - x_2)]$.	$\tau_2 - \tau_1$. minutes.	$\frac{-\Sigma\log}{\tau_2 - \tau_1} . 10^5 = (B - A) K \times 10^5 : 2·3026$.	$\frac{dx}{d\tau} . 100$.	$\frac{dx}{d\tau} : \frac{A - x}{10^5}$.	$K . 10^7 : 2·3026$.
1		287·8	2·45909		359·4	2·55558							
	0			0			0	0	85	*	*	*	*
2		287·8	2·45909		359·4	2·55558							
	2·0 ?			·00303			·00243	·00060	25	2·4 ?	8·00 ?	28·0 ?	3·35 ?
3		285·8	2·45606		357·4	2·55315							
4	1·6			·00244			·00194	·00050	35	1·43	4·57	16·1	2·00
5		284·2	2·45362		355·8	2·55121							
	1·0			·00153			·00123	·00030	15	2·00	6·66	23·5	2·79
6		283·2	2·45209		354·8	2·54998							
	1·0			·00153			·00122	·00031	20	1·55	5·00	17·7	2·17
7		282·2	2·45056		353·8	2·54876							
Next day.													
8		282·2	2·45056		353·8	2·54876							
	1·0			·00154			·00123	·00031	83	·37	1·20	4·27	·52
9		281·2	2·44902		352·8	2·54753							
	2·0			·00310			·00247	·00063	30	2·10	6·66	23·9	2·98
10		279·2	2·44592		350·8	2·54506							
	3·0			·00470			·00363	·00107	30	3·56	10·00	36·2	4·97
11		276·2	2·44122		347·8	2·54133							
	3·0			·00474			·00376	·00098	30	3·27	10·00	36·6	4·57
12		273·2	2·43648		344·8	2·53757							
	3·0			·00479			·00380	·00099	30	3·30	10·00	37·0	4·61
13		270·2	2·43169		341·8	2·53377							

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* The total amount transformed into $CO.Cl_2$ is $\frac{17·6}{287·8} = 6·11$ per cent. It is evident that with such small variations in the masses of the reacting substances, none of the last four columns can show in preference to the others which is the fundamental law underlying the phenomena of velocity of reaction.

TABLE V.—CO and Cl_2 (in the Glass Bulb), 21st July, 1901.

Distance of the acetylene light from Rubens thermopile = 105 centim., from the centre of the glass bulb = 62·5 centims.

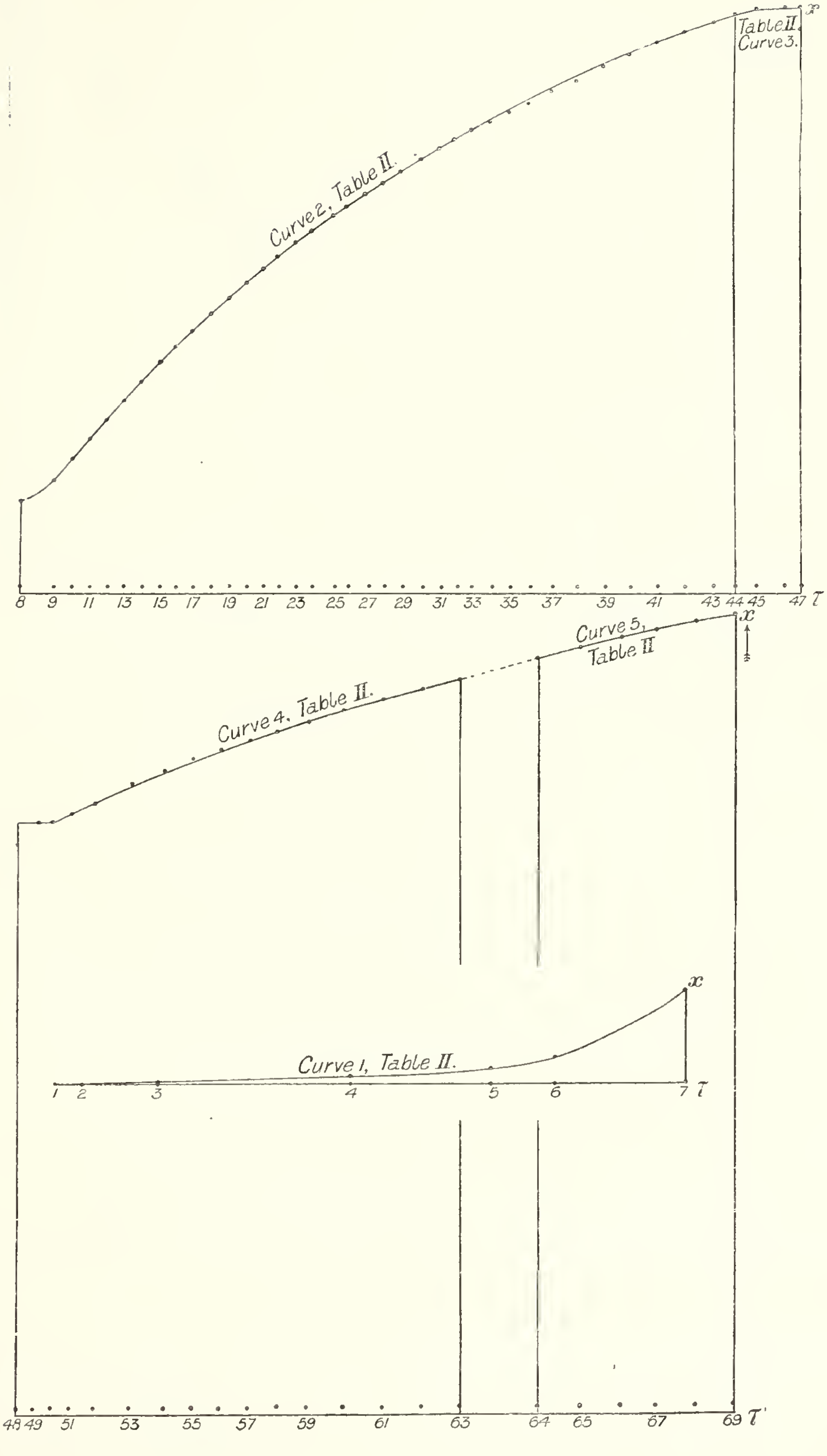
The quantity of Cl_2 = 388·27 millims. (at 21°·3 and 757·85 (22°·9) barometer pressure), the quantity of CO = 350·68 millims. The gases the same as in curves 1, 2, 3, 4, 5, only the CO dried by a longer column of conc. SO_4H_2. The intensity of light was: (1)–(2) 202·5, (2)–(3) 202·0, (3)–(4) 201 to 202, (4)–(5) 201–202, (5)–(6) 201–202, (7)–(8) 202, (8)–(9) 202–202·5, (9)–(10) 202, (10)–(11) 202, (11)–(12) 202, (12)–(13) 201, (13)–(14) 201, (14)–(15) 201, (15)–(16) 201, (16)–(17) 201, (17)–(18) 201. Calibration, as in curves 1, 2, 3, 4, 5 = 263 millims. (r and l). Barometer, 757·85 (22°·9), fell to 756·35 (22°·7).

No.	$\pi' - \pi'' = dx$.	$A - x$ (Cl_2).	log ($A - x$).	log ($A - x_1$) − log ($A - x_2$).	$B - x$ (CO).	log ($B - x$).	log ($B - x_1$) − log ($B - x_2$).	Σ log = [log ($A - x_1$) − log ($A - x_2$)] − [log ($B - x_1$) − log ($B - x_2$)].	$\tau_2 - \tau_1$. minutes.	$\frac{\Sigma \log}{\tau_2 - \tau_1} . 10^6 = (A - B) K \times 10^6 : 2·3026$.	$\frac{dx}{d\tau} . 100$.	$\frac{dx}{d\tau} : \frac{A - x}{10^5}$.	K . 10^7 : 2·3026.
1		388·27	2·58915		350·68	2·54491							
	0			0			0	0	47	0	0	0	0
2		388·27	2·58915		350·68	2·54491							
	−0·02			0			0	0	48	0	0	0	0
3		388·29	2·58916		350·70	2·54494							
	0·17			·00020			·00021	·00001	149	·07	·011	0·03	·02
4		388·12	2·58896		350·53	2·54473							
	0·51			·00057			·00063	·00006	69	·87	0·74	1·91	·20
5		387·61	2·58839		350·02	2·54410							
	1·02			·00114			·00127	·00013	24	5·42	4·25	11·0	1·44
6		386·59	2·58725		349·00	2·54283							
Next day, 750·40 (21°·7), barometer fell to 748·55 (21°·85) at 18); risen after the interruption of light by 0·8 millim. (calculated).													
7		385·79	2·58635		348·20	2·54183							
	12			·00013			·00015	·00002	12	1·67	1·00	2·59	·44
8		385·67	2·58622		348·08	2·54168							
	3·03			·00344			·00380	·00036	47	7·66	6·45	16·86	2·04

TABLE V.—CO and Cl_2 (in the Glass Bulb), 21st July, 1901—continued.

No.	$\pi'-\pi''$ $=dx$.	$A-x$ (Cl_2).	log $(A-x)$.	log $(A-x_1)$ $-\log(A-x_2)$.	$B-x$ (CO).	log $(B-x)$.	log $(B-x_1)$ $-\log$ $(B-x_2)$.	$\Sigma\log =$ $[\log(A-x_1)$ $-\log(A-x_2)]$ $-[\log(B-x_1)$ $-\log(B-x_2)]$.	$\tau_2-\tau_1$.	$\frac{\Sigma\log}{\tau_2-\tau_1}\cdot 10^6$ $=(A-B)K\times$ $10^6:2\cdot3026$.	$\frac{dx}{d\tau}\cdot 100$.	$\frac{dx}{d\tau}:\frac{A-x}{10^5}$.	$K\cdot10^7:$ $2\cdot3026$.
									minutes.				
9		382·64	2·58278		345·05	2·53788							
	3·48			·00396			·00440	·00044	40·5	10·87	8·59	22·66	2·89
10		379·16	2·57882		341·57	2·53348							
	2·38			·00272			·00303	·00031	19·5	15·90	12·20	32·40	4·23
11		376·78	2·57610		339·19	2·53045							
	3·19			·00371			·00411	·00040	28	14·29	11·40	30·50	3·80
12		373·59	2·57239		336·00	2·52634							
	3·55			·00414			·00461	·00047	30	15·67	11·84	31·96	4·17
13		370·04	2·56825		332·45	2·52173							
	3·45			·00408			·00453	·00045	30	15·00	11·50	31·42	4·00
14		366·59	2·56417		329·00	2·51720							
	1·99			·00235			·00264	·00029	16	18·13	12·44	34·10	4·82
15		364·60	2·56182		327·01	2·51456							
	3·13			·00375			·00418	·00043	25	17·20	12·52	34·60	4·57
16		361·47	2·55807		323·88	2·51038							
	1·79			·00215			·00240	·00025	15	16·67	11·94	33·20	4·43
17		359·68	2·55592		322·09	2·50798							
	1·64			·00199			·00222	·00023	15	15·33	10·94	30·56	4·08
18		358·04	2·55393		320·45	2·50576							

The total amount transformed into $CO.Cl_2 = \frac{29\cdot51}{350\cdot68} = 8\cdot41$ per cent.


x
Table II. Curve 3.
Curve 2, Table II.
8
9
11
13
15
17
19
21
23
25
27
29
31
33
35
37
39
41
43
44
45
47
τ
x
Curve 5, Table II
Curve 4, Table II.
x
Curve 1, Table II.
1
2
3
4
5
6
7
τ
48
49
51
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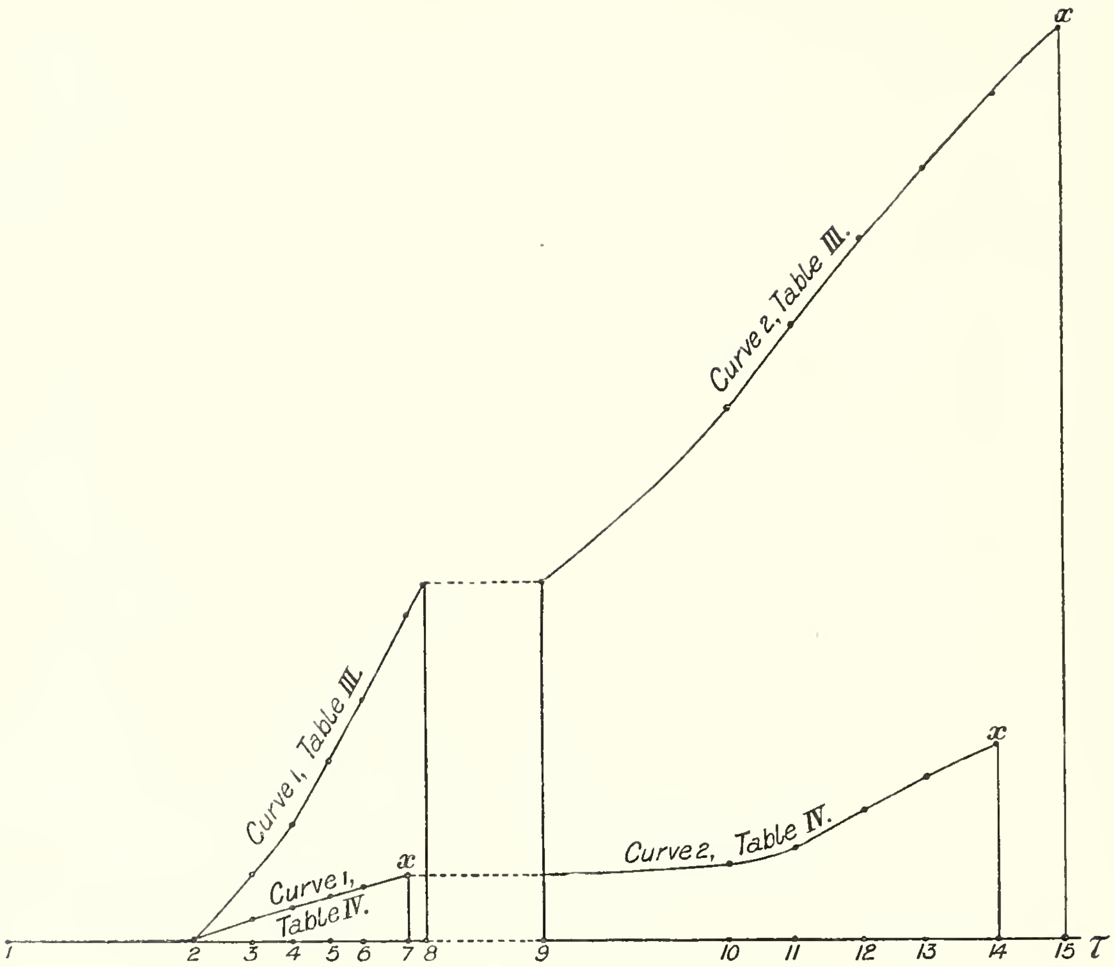

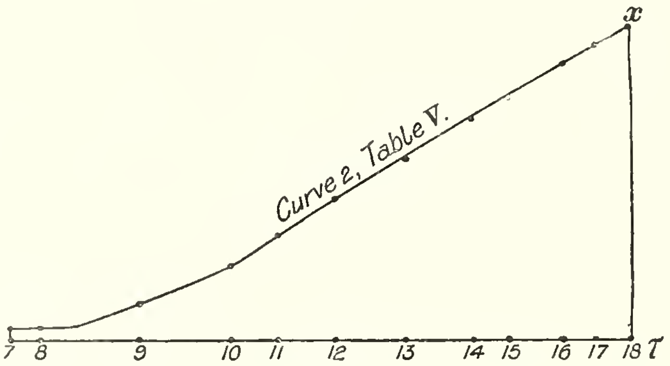

In the above tables curves (1), (2), (3), (4), and (5), all belong to one system at 21°·7.

The values of K in the above tables, calculated from equation (1), show, that as the system is brought from the dark to the light the reaction at first does not appear to be going on, then it goes on very slowly giving very small values for K, gradually the values for K, and with it the speed of reaction, increase until the values obtained for K remain constant, the speed diminishing at the same time according to the law of mass action. If after the values of K remain constant for a sufficient time, the light is removed for some hours, and the system again exposed to the light, we again find the same phenomenon; the velocity constant K is not obtained at once but only after the reaction has gone on for some time. Further, it is found that in every case the same velocity constant is obtained after a time. It follows from this that the combining chlorine and carbon monoxide when exposed to light of a certain intensity and composition, always acquire after a certain time the same constant properties, the same chemical affinity to one another. The fact that the same constant was found in all curves of the same system, and that the investigation was carried on as far as 80·66 per cent. (in Tables I. and II.) and 39·16 per cent. (in Table III.) of the total amount of possible combination, shows that the above equation (3), p. 377, which is a true expression of the law of mass action, truly represents the fundamental law underlying chemical kinetics in light. At the same time the last two columns of the above tables illustrate beyond any doubt that it is no longer possible to assume that a law analogous to FARADAY'S for electrolysis governs the phenomena of chemical kinetics in light.

Instead of getting a constant in the last columns, the values of $dx/d\tau \cdot 100$ fall from 25·2 to 4·1 (in Table II.), and from 40 to 18·6 (in Table III.), and the values of $\frac{dx}{d\tau} : \frac{(A-x)}{10^5}$ (in Table II.) fall from 50·9 to 9·9, and (in Table III.) from 205 to 136. Special attention should be given to the curves (1), (2), (3), (4), and (5), of Table II. Here a large quantity of chlorine and a small quantity of carbon monoxide were employed; in this way the variations in the quantity of carbon monoxide were increased, and in that of chlorine made small, *i.e.*, it is the variation in the quantity of the carbon monoxide which absorbs but little light, and not in the quantity of the chlorine, which absorbs much, which in this case proves to be the main cause of the velocity of reaction decreasing so rapidly. It is thus evident that it is not the quantity of light absorbed by the molecules in the unit of time, but the quantity of the reacting substances present, which determines the velocity of the reaction, no matter what quantity of light the molecules absorb, provided that under the action of light the atoms and molecules acquire that quantity of energy which is characteristic of them after the period of "induction" has passed. In other words a system containing two molecules chlorine and one molecule carbon monoxide will combine at the same rate as a system containing one molecule chlorine and two molecules carbon monoxide, though the first system absorbs almost twice as much light as the second.

The "Induction" and "Deduction" Periods of Energy of the System and the Chemical Periods of "Induction" and "Deduction" in Light.

Having considered those parts of the curves where the velocity constant can be traced, we now consider the parts before the velocity constant is reached. We find that, starting with a system such as chlorine and carbon monoxide, at first it seems for some time that no combination takes place at all. Combination, however, becomes gradually more and more apparent, the velocity becomes greater and greater, till a constant value for K is obtained. This is a peculiar phenomenon, which BUNSEN and ROSCOE first observed in the case of chlorine and hydrogen, and which they appropriately called the "induction period." If now, after the velocity constant has been observed for some time, the light is removed from the system, the reaction at once becomes very slow and soon stops. If the system is, after a time, again exposed to light, we find at first an "induction period," after which the same velocity constant is obtained. This shows that as the light is removed from the system the reacting molecules lose the properties which they had acquired in the light, gradually returning to their old state; and that when the system is again exposed to the light the molecules and atoms each time gradually acquire the same new properties. Besides the "induction period" we thus have to deal also with a "deduction period." The "induction period" is evidently not due to the absence of some product of the reaction, but is a period during which the molecules and atoms of the systems continuously change their state of energy from that in the dark to that in the light; and the "deduction period" is a period during which the molecules and atoms gradually return from their state of energy in the light to the state of energy they possess in the dark. The properties of the "induction" and "deduction" periods require, however, still further consideration. On removing the light from the system, that state of energy of the atoms and molecules which makes them capable of entering into reaction rapidly passes away, with the energy stored in the molecules and atoms under the action of light, and is transformed partly into heat and partly in chemical action as long as this goes on after the removal of the light.

The curves given above show, however, that while chemical action ceases, or apparently ceases, after a short time, it takes a considerable time before the atoms and molecules again completely acquire the properties which they previously had in the dark. Thus, between the first curve and the second (between 7 and 8) the light was removed for 16 hours and 48 minutes, between the third and fourth (between 47 and 48) for 17 hours, between the fourth and fifth (63 and 64) the light was interrupted only for 5 minutes, and the rest of the time (39 minutes) it was again exposed to the light. We nevertheless find that, after 17 hours, the "induction period" of the second curve did not again become as slow as it was in the first curve; after the third interruption of the light, for about the same 17 hours, the "induction period" was almost quite the same—starting with almost the same values of K; again, during the fourth interruption of the light for only a few minutes, the chlorine and carbon monoxide of the system returned only so little to the properties which they had at first in the dark that no marked variation in the value of the velocity constant K could be established. Thus we find a remarkable analogy (though not a reversible identity) between the period of "deduction" and "induction." On exposing the system for the first time to light, the energy of the light is absorbed by the system for a considerable time before the atoms and molecules acquire the state of energy when the reaction becomes apparent, *i.e.*, the energy of the system first continuously increases and changes though no chemical effect can be perceived in the system. When the chemical reaction becomes evident the chemical "induction period" then continues till the new constant state of energy characterised by K is reached. On removing the light, the chemical "deduction period" continues only a short time, when the reaction ceases to take place, but it takes a long time for the atoms and molecules to lose those properties which they acquired in the light before chemical reaction started, and this gradual diminution of the energy of the system is again not to be discovered from the chemical reactions of the systems. The chemical "deduction period," however, lasts much less time than the chemical "induction period." It is evident that the curves of the "induction" and "deduction periods" given above only represent the amount of chemical transformation, *i.e.*, are curves of chemical "induction" and "deduction," and are not the curves which represent the gradual increase and decrease, the "induction" and "deduction" periods, of the whole energy of the system, when it is exposed to light or when light is removed from the same. There are other methods by which the variation of energy during the "induction" and "deduction" periods may be determined. The author is now engaged in the elucidation of the laws concerning the induction and deduction periods of energy which up to the present have only the character of qualitative observations.*

The Influence of Small Traces of Air and Water upon the Mixture of Pure Chlorine and Carbon Monoxide (and other Gaseous Systems).

The admixture of small traces of air with the reacting gases produces a most remarkable retarding effect upon the velocity of the reaction. Bunsen and Roscoe found that this held for a mixture of chlorine and hydrogen, so that it appears to be a general rule for all gaseous systems.

Two "quartz vessels" were placed one behind the other, both vessels were evacuated and treated in exactly the same way, and finally filled with carbon monoxide from the same sample at the same time. Chlorine from the same sample was driven by means of the same concentrated sulphuric acid (which, for reasons mentioned before, it was impossible to keep for any length of time quite free from

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* As to the chemical induction and deduction periods it is evident that, since velocity of reaction follows the law of action of mass, when the molecules taking part in the reaction have attained, under the influence of light, a constant value of their chemical potentials, the same law of mass action must also be the governing principle for the velocity of reaction at any given moment of the chemical induction and deduction periods, only the velocity constant, K in equation (3), will vary in time as the chemical potentials of the reacting substances change.

air) first into the vessel behind, and then, about a quarter of an hour later, into the vessel in front. Both vessels were simultaneously exposed in the bath to the same acetylene light, but the velocity of combination of chlorine and carbon monoxide was considerably slower in the front vessel than in the vessel placed behind it. (The opposite would have been expected.) (See Curves 1 and 2 of Tables III. and IV.)

The accelerating influence of water vapour upon the velocity of reaction is very great. The same glass bulb was filled with the chlorine and carbon monoxide, both freshly prepared in the dark. The chlorine was in both cases absolutely the same, *i.e.*, equally dry; the freshly prepared carbon monoxide on the contrary was allowed to bubble in the two experiments through different heights of sulphuric acid in the bulb S (fig. 1, p. 340) by tilting the bulb more in the second experiment than in the first. The sulphuric acid was the same in both cases, and each time was first heated in the bulb in a vacuum till it was perfectly freed from any gas. The freshly-prepared carbon monoxide was thus most probably in one case a little drier than in the other, and the difference in the quantity of water still retained by the carbon monoxide evidently could only be exceedingly very small. The difference in the speed of combination of carbon monoxide and chlorine on the contrary proved to be very great. (See curves of Table V.)

A further experiment was thus made:—The gases were brought into the glass bulb containing ordinary concentrated sulphuric acid freed from air, well shaken, then left in the dark for about two days, and then exposed to the powerful acetylene light; no reaction could be observed after several hours during two days, but on exposure to sunlight the two gases combined, though only exceedingly slowly. Since the concentrated sulphuric acid was of sp. gr. 1·84, it contained water, and it must still have had (REGNAULT) a vapour pressure of water, though an extraordinarily small one, so that the pressure of water vapour was still not absolutely excluded, and this may be the cause why an exceedingly slow reaction could still take place in sunlight.

Thus, the less water vapour is present with the gases the slower is the reaction. Reaction takes place in the presence of an exceedingly small quantity of water vapour in the mixture; small, apparently immeasureable, differences in the amount of water vapour, at any rate when the vapour is present only in small quantities, produces great differences in the velocity of the reaction.

It should be observed that we could not use greater quantities of water vapour for the experiments, still less could we have the gases in presence of water, because water decomposes the carbonyl chloride formed, giving carbonic and hydrochloric acids.

BUNSEN and ROSCOE used their mixture of chlorine and hydrogen in the presence of water saturated with these gases. PRINGSHEIM found later on that, if chlorine and hydrogen are taken quite dry, they do not combine in light at all. This phenomenon PRINGSHEIM thought possible to explain in the following manner:—The chlorine and hydrogen, according to his conception, do not combine directly to hydrochloric acid, but chlorine and water first form an intermediate compound hypochlorous acid (and hydrogen), which with hydrogen forms the hydrochloric acid, setting free the same molecules of water which are again used in the reaction, *i.e.*, instead of having $H_2 + Cl_2 = 2HCL$, we have $Cl_2 + H_2O = Cl_2O + H_2$; $Cl_2O + H_4 = 2HCl + H_2O$. I doubt the correctness of this explanation for the following reason :—It is known that chlorine and water, when exposed to light, form not hypochlorous acid but hydrochloric acid (Wittwer, Bunsen, and Roscoe).* Still the difficulty remains that chlorine and hydrogen are not the only system having such properties. The system chlorine and carbon monoxide exhibits the same property. We also know that ammonia and hydrochloric acid do not combine when perfectly dry; carbon monoxide and hydrogen do not explode when perfectly dry (Dixon); perfectly dry hydrogen peroxide does not act upon a photographic plate (Russell). For this reason it seems that in gaseous systems a phenomenon is met which in other cases is called "catalytic action," in which a reaction is accelerated or caused by the presence of an extraneous substance, which apparently or in reality takes no part in the reaction, *e.g.*, the action of platinum-black upon the decomposition of hydrogen peroxide, &c.

The catalytic action of gases upon the velocity of reaction in the gaseous systems may be divided into "catalytic action with an accelerating influence" (to this belongs the action of water vapour upon the gaseous systems mentioned above) and into "catalytic action with a retarding influence" (to this belongs the action of oxygen or air upon the systems chlorine and hydrogen or chlorine and carbon monoxide). This division is, however, of a purely formal nature, and hardly anything is known of the ultimate nature of the phenomenon.

Velocity of Chemical Reaction and Chemical Equilibrium in Light.

Having thus established beyond any doubt that the velocity of reaction in light is governed in homogeneous systems by the same law of mass action as in the dark, the influence of temperature as well as of the intensity of light upon the value of the velocity constant, as well as the connexion between the velocity constant and the wave length on the monochromatic light, have still to be investigated; and finally the investigation of heterogeneous systems regulated by other fundamental principles remains necessary. This will form the subject of the author's future investigation.

On the other hand the solution of the problem for chemical kinetics in light evidently already shows with perfect certainty that the law of mass action, which governs chemical equilibrium in homogeneous systems in the dark must necessarily also govern chemical equilibrium in the light. It is most remarkable that we do not

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* Professor Dixon, in a private communication, makes a better suggestion—that the reaction between hydrogen and chlorine is to be conceived thus :—$Cl_2 + H_2O = 2HCl + \overset{\frown}{O}$ (nascent); $\overset{\frown}{O} + H_2 = H_2O$, the first equation being reversible.

know of any reversible system, in which the two opposite reactions do not go on in the dark but go on in the light. But we do know systems in which one reaction goes on in the dark and is modified in light, while the opposite reaction goes on in the light only, *e.g.*,

$$\begin{array}{lll} 2\mathrm{AgCl}\text{ in solution} & \rightleftharpoons & \mathrm{Ag_2}\text{ (or }\mathrm{Ag_2Cl}\text{) in sol.} + \mathrm{Cl_2}\text{ in sol.} \\ \quad\downarrow\uparrow & & \quad\downarrow\uparrow \\ \mathrm{AgCl}\text{ solid} & & \mathrm{Ag}\text{ (or }\mathrm{Ag_2Cl}\text{) solid.} \end{array}$$

Here is an homogeneous system, on the one hand silver chloride is decomposed by light into silver and chlorine or silver sub-chloride and chlorine (this question is at present unsettled), on the other hand silver (or silver sub-chloride) and chlorine combine in the dark forming silver chloride, and this combination evidently goes on in light also (though probably with a different speed). Let the volume of the solution be V. For the first reaction in light we have according to the law found above $\frac{dx}{d\tau} = c\,\frac{(\mathrm{A} - x)^2}{v^2}$, where $\frac{\mathrm{A} - x}{v}$ is the concentration of the molecules of silver chloride in solution (however small this may be) at the time τ, and x/v is the concentration of the chlorine as well as of the silver molecules formed in solution; c is the velocity constant which changes with the intensity and composition of the light passing through the system. For the second reaction we have according to the law of mass action in the dark $\left(\frac{dx}{d\tau}\right)' = c'\left(\frac{x}{v}\right)^2$, where c' is the velocity constant for the reaction in which silver chloride is formed from silver and chlorine. The velocity constant in light is different from that in the dark, say c'', however small this difference may be, for the reason that chlorine and silver are in a different state of energy in the dark and in the light. It follows from this that when equilibrium takes place in the light, or when no further variation in the masses takes place,

$$\frac{dx}{d\tau} - \left(\frac{dx}{d\tau}\right)' = 0\,; \qquad \frac{c\,(\mathrm{A} - x)^2}{v^2} - c''\left(\frac{x}{v}\right)^2 = 0\,; \qquad \frac{(\mathrm{A} - x)^2}{x^2} = \frac{c''}{c} = \mathrm{K}\,;$$

that is, we must at the point of equilibrium get a constant K, which will regulate the masses forming the reversible system with the variation of the volume or of the concentrations or of the partial pressures of the substances, because both opposite reactions have each a separate velocity constant before equilibrium. Though this proof of the necessity of the existence of a constant of equilibrium is absolute, it would have been very valuable and desirable to directly illustrate the equilibrium constant K in a reversible system from the varying masses at equilibrium, as we succeeded in doing for the velocity of reaction. Unfortunately there is not one homogeneous system known where such a proof could be successfully carried out. It is well to remember the enormous difficulties one meets with in this region, when even such apparently simple reactions as the combination of carbon monoxide and chlorine or of chlorine and hydrogen, are to be measured quantitatively. The author is at present engaged in such attempts to test directly the constants of equilibrium, not so much because the law needs further confirmation, as on account of the very interesting thermodynamic connection which must exist between the constant of equilibrium, the heat of reaction in light, and the absolute temperature on the one hand, and the constant of equilibrium and the intensity of light on the other.

APPENDIX: *Thermodynamical Considerations.*

The above experimental results find their rational basis and explanation in thermodynamics. The condition of equilibrium in a homogeneous system, when only chemical, thermal, and mechanical energy are taken into consideration, is according to GIBBS: $dE = td\eta - pdv + \mu_1 dm_1 + \mu_2 dm_2 \ldots + \mu_n dm_n \geqq 0$, where E is the energy, η the entropy, $m_1, m_2 \ldots m_n$ the quantities of the substances $S_1, S_2 \ldots$, μ_1, μ_2 the chemical potentials of $S_1, S_2 \ldots$ Let us now assume that the system is exposed to light of constant intensity and composition, and that the system is in such thin layer that the intensity of the light is the same in all parts of it. Since all substances absorb light and the light absorbed is not completely transformed into heat, a part of the light will appear as other forms of kinetic energy of the atoms and molecules. From a molecular mechanical point of view this will mean that under the influence of light the amount of work present in the molecules as energy of the atoms increases. Obviously the ratio of the amount of light transformed into heat to that transformed into kinetic energy of the atoms is not constant. At first the energy of the atoms and molecules gradually increases (induction period of energy), until a reaction, a shifting of the point of equilibrium to another one, becomes possible (chemical induction period), which is observed by an increase of the velocity constant. Under the action of light the storage of energy in the atoms and molecules ultimately reaches a maximum, after which light produces no more strain upon the atoms, preventing them only from losing the energy once acquired, and the whole of the light entering into the system is transformed into heat. This maximum kinetic energy of the atoms is a function of the intensity and composition of light, of the nature of the substance, of the surrounding medium, &c., and becomes apparent in the fact that a velocity constant, indicative of constant properties of the atoms and molecules, is obtained. When light is removed from the system the energy stored in the atoms and molecules, under the impulses of the light waves, gradually disappears, changing either into chemical energy and heat (as long as the reaction continues in the dark, chemical deduction period) or into heat alone (deduction period of energy). When the maximum kinetic energy of the atoms is reached under the action of light, it is evident that the energy stored up must be directly proportional to the mass of each substance. To the above equation for equilibrium the terms $\nu_1 dm_1 + \nu_2 dm_2 \ldots + \nu_n dm_n$ must therefore be added. By means of a cycle process at a constant temperature it can also be shown that the entropy of the system changes in light. When chemical transformation takes place in the system this is also accompanied by variation in its mechanical energy. The kinetic explanation of the phenomena of absorption, dispersion, fluorescence, by STOKES and HELMHOLTZ, led the author to the conclusion that the energy stored in the atoms and molecules under the action of light, partly transforms into chemical, partly into kinetic energy *sui generis*, which may be called light-kinetic energy,—a conclusion strengthened by the author's experiments on the effect of light upon two plates of the same element, when they are immersed in a liquid, connected with a galvanometer, and one plate is exposed to light while the other is kept in the dark. Thus, under the action of light, the chemical potential of each substance increases and each substance acquires a new light-kinetic potential. Instead of equation (i.) we now have for equilibrium in light

$$\begin{aligned} d\mathrm{E} + d\mathrm{E}_1 = d\mathrm{E}' = t'd\eta' - p'dv' + \mu_1'dm_1' + \mu_2'dm_2' \ldots + \mu_n dm_n' \\ + \lambda_1'dm_1' + \lambda_2'dm_2' \ldots + \lambda_n'dm_n' \geqq 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii.)}. \end{aligned}$$

Integrating this equation, then differentiating in the most general way and subtracting (ii.) we get

$$\eta'dt' - v'dp' + m'd\lambda_1' + m'd\mu_1' \ldots + m_n'd\lambda_n' + m_n'd\mu_n' = 0 \quad . \quad . \quad \text{(iii.)}.$$

General considerations show that for the system to be in equilibrium the sum of both potentials of each substance must be constant through the whole system, *i.e.*, $\mu_1' + \lambda_1' = c_1$, $\mu_2' + \lambda_2' = c_2 \ldots (\gamma)$. (iii.) and ($\gamma$) give the variation of temperature or pressure, or of the chemical potential, or of the light-kinetic potential, or of several of them, with the variation of one or more of the rest of the variables. The sum of both potentials $\mu_1' + \lambda_1'$ being $= \left(\frac{d\mathrm{E} + d\mathrm{E}_1}{dm_1}\right)_{\eta_1' v_1' m_2' \ldots m_n'}$, and the equation for chemical reaction being $n_1\mathrm{A}_1 + n_2\mathrm{A}_2 = n_3\mathrm{A}_3$ (α), we still find that, under due considerations,

$$n_1(\mu_1' + \lambda_1') + n_2(\mu_2' + \lambda_2') = n_3(\mu_3' + \lambda_3') \quad . \quad . \quad . \quad . \quad . \quad . \quad (\beta).$$

Taking in equation (iii.) the grammolecule as unit of mass (which is not the case in GIBBS' deductions), in order to get subsequently a result which in its form and content expresses our present molecular conceptions of a chemical reaction, &c., we get, if the system is a gaseous one, consisting of one substance only, and its total mass is m_1' grammolecules, that the total chemical energy is $\mu_1'm_1'$, the variation in the same $m_1'd\mu_1'$, the total light-kinetic energy is $\lambda_1'm_1'$, the variation in the same $m_1'd\lambda_1'$, the total mechanical energy $p'v' = m_1'\mathrm{RT}$, since $p'v'$ of 1 grammolecule $= \mathrm{RT}$, and $v'\,dp' = v'd\left(\frac{m_1'\mathrm{RT}}{v'}\right)$, the total entropy of the mass $\eta' = m_1'\left(\frac{\mathrm{H}'}{\mathrm{T}} + \mathrm{K}'\right)$, when the entropy of 1 grammolecule $= \frac{\mathrm{H}' \text{ (of 1 grammolecule)}}{\mathrm{T}} + \mathrm{K}'$. Thus putting in (iii.) these values and integrating we get $\mu_1 + \lambda_1 = \mathrm{RT} + \mathrm{RT} \log \frac{m_1'}{v'} - \mathrm{H}' \log \mathrm{T} + \mathrm{K}'\mathrm{T} + \mathrm{K}''$, where

K' and K'' are integration constants. Assuming now that the system consists of several substances, as given in (α), and that the law of Dalton holds good for the chemical and for the light-kinetic potentials, then we get from (β) that

$$\log\left\{\left(\frac{m_1'}{v'}\right)^{n_1}\cdot\left(\frac{m_2'}{v'}\right)^{n_2}\Big/\left(\frac{m_3'}{v'}\right)^{n_3}\right\} = \frac{1}{\mathrm{RT}}\left[(n_3\mathrm{K}_3' - n_1\mathrm{K}_1' - n_2\mathrm{K}_2')\,\mathrm{T} - (n_2 + n_1 - n_3)\,\mathrm{RT}\right.$$
$$\left. + (n_1\mathrm{H}_1' + n_2\mathrm{H}_2' - n_3\mathrm{H}_3')\log \mathrm{T} + (n_3\mathrm{K}_3'' - n_1\mathrm{K}_1'' - n_2\mathrm{K}_2'')\right] \quad . \quad . \quad \text{(iv.)},$$

where $\frac{m_1'}{v'}$, $\frac{m_2'}{v'}$, $\frac{m_3}{v'}$ are the concentrations of each substance expressed in grammolecules, n_1, n_2 . . . the numbers of grammolecules of each substance taking part in the reaction, $n_3\mathrm{K}_3'-n_1\mathrm{K}_1'-n_2\mathrm{K}_2'=$constant K^{iv}, $-(n_2+n_1-n_3)$ RT is the work done by the system (α) during the transformation in light, $(n_1\mathrm{H}_1' + n_2\mathrm{H}_2' - n_3\mathrm{H}_3')\log \mathrm{T} + (n_3\mathrm{K}_3'' - n_1\mathrm{K}_1'' - n_2\mathrm{K}_2'')$ is the heat of reaction *in light*. Thus the connection between the logarithm of the constant of chemical equilibrium in homogeneous systems in light, the heat of reaction or of transformation of n_1 grammolecules of S_1 *plus* n_2 grammolecules of S_2 into n_3 grammolecules of S_3 in light, the work done during the transformation, and the absolute temperature, follows the same law in light as it does in the dark. The effect of light upon a system therefore consists in shifting it to a new point of equilibrium. It is further easy to show that at a constant volume, since the work $-(n_2 + n_1 - n_3)\,\mathrm{RT} = 0$, and $\eta' t'$ can be put $= \mathrm{C}_s\mathrm{T}$, where C_s is the specific heat at a constant volume, T the absolute temperature, an equation is arrived at, which after differentiation gives $\frac{d}{d\mathrm{T}}\left[\log\left(\frac{m_1'}{v'}\right)^{n_1} + \log\left(\frac{m_2'}{v'}\right)^{n_2} - \log\left(\frac{m_3'}{v'}\right)^{n_3}\right]$ $= \frac{\mathrm{A} + \mathrm{BT}}{\mathrm{RT}^2}$,(v.), where A and B are constants (equation of Van't Hoff and Kooy), which at a constant temperature gives $\left(\frac{m_1'}{v'}\right)^{n_1}\cdot\left(\frac{m_2'}{v'}\right)^{n_2}\Big/\left(\frac{m_3'}{v'}\right)^{n_3} =$ constant (vi.), *i.e.*, the law of mass action holds good for chemical equilibrium in light, as found experimentally. Decomposing this equation for homogeneous systems in the usual manner into two, giving the two opposite velocities of reaction, which at equilibrium become equal, we get

$$\left(\frac{dx}{d\mathrm{T}}\right)' = c'\left(\frac{m_1'}{v'}\right)^{n_1}\cdot\left(\frac{m_2'}{v'}\right)^{n_2} \text{ and } \left(\frac{dx}{d\mathrm{T}}\right)'' = c''\left(\frac{m_3'}{v'}\right)^{n_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii.)},$$

i.e., the velocity of chemical reaction in light must also follow the laws of mass action, as found experimentally.

In conclusion, I should like to express my thanks to the Managers of the Davy-Faraday Laboratory of the Royal Institution for having allowed me to make use of the splendid arrangements of the Laboratory, and especially to Dr. Ludwig Mond, who by his kind assistance has enabled me to undertake and carry out the above research, and who by his valuable advice on many occasions has very essentially contributed to the success of the same.

INDEX SLIP.

DUNSTAN, W. R., and HENRY, Thos. A.—Cyanogenesis in Plants. Part II.—The Great Millet, *Sorghum vulgare*.
Phil. Trans., A, vol. 199, 1902, pp. 399–410.

HENRY, Thos. A., and DUNSTAN, W. R.—Cyanogenesis in Plants. Part II.—The Great Millet, *Sorghum vulgare*.
Phil. Trans., A, vol. 199, 1902, pp. 399–410.

Dhurrin, Constitution and Reactions of—Formation of Dhurrinic Acid from.
DUNSTAN, W. R., and HENRY, T. A.
Phil. Trans., A, vol. 199, 1902, pp. 399–410.

Hydrocyanic Acid, Formation of, from *Sorghum vulgare*.
DUNSTAN, W. R., and HENRY, T. A.
Phil. Trans., A, vol. 199, 1902, pp. 399–410.

Parahydroxymandelic Acid, Preparation of.
DUNSTAN, W. R., and HENRY, T. A.
Phil. Trans., A, vol. 199, 1902, pp. 399–410.

Sorghum vulgare, Glucoside and Enzyme of.
DUNSTAN, W. R., and HENRY, T. A.
Phil. Trans., A, vol. 199, 1902, pp. 399–410.

VII. *Cyanogenesis in Plants.*—Part II. *The Great Millet,* Sorghum vulgare.

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In a previous paper, our first communication on this subject ('Phil. Trans.,' B, vol. 194, 1901, p. 515), we have shown that the poisonous effects produced by the young plants of *Lotus arabicus* are due to prussic acid, which is not present in the plant as such, but originates in the hydrolytic action of an enzyme, lotase, on a glucoside, lotusin. Recently we have examined a large number of plants which, like this Egyptian vetch, appear, under certain conditions, to possess poisonous properties, and at other times to be innocuous and often valuable as fodder plants or food stuffs, with the view of ascertaining to what extent they contain glucosides furnishing prussic acid.

Among the first of these plants we examined was the Great Millet, *Sorghum vulgare*, a plant widely cultivated in tropical countries for the sake of its nutritious grain, which in many districts of India is the staple food, known as "Juar," of the natives. In the West Indies what is apparently the same plant yields the important "Guinea Corn" and in South Africa "Kaffir Corn."

We were informed by Mr. E. A. Floyer, of Cairo, that in Egypt it is well known to the Arabs that the green portions of the young plant—the vernacular name of which is "Dhurra Shirshabi"—are poisonous, and that during this period the plantations are protected in various ways in order to prevent cattle from feeding on the immature growth. It is to be noted that in Egypt the name "dhurra" is also applied to a variety of maize which is largely cultivated.

Mr. Floyer has given us the following account of the plant in Egypt. "Dhurra shirshabi" is not grown in Egypt as a crop, the yield of corn being too small. It is planted chiefly in order to shade the "Arachis" (ground nut), to which it also affords protection in forming a poisonous hedge. The "thinnings" of the young Millet are often strewn around a cultivated crop, and the neighbours are warned to keep their cattle off. The poison is most intense when young plants, 1 foot high or less, are kept without water for a long time, and such unwatered young plant is highly toxic to cows. The plant appears to have been brought to Egypt from Syria, and is now grown chiefly at Bir Abu Bala, near Ismailia. The "fellaheen" do not plant it.

Cases of poisoning by young *Sorghum* have been also recorded in America and in Australia, where the plant is grown for forage purposes.

In India the poisonous properties of the plant—which bears the vernacular name "juar" or "jowar"—do not appear to be so generally known, although several well authenticated cases of the poisoning of cattle by it, especially during drought, have been recorded, and much has been written on the subject by veterinary surgeons and others, who have, as a rule, assumed that the toxicity is due to the presence of a poisonous fungus or insect upon the plant, or that the Great Millet is not naturally poisonous, and that the deaths of cattle as the result of eating it are due to immoderate consumption, which causes a kind of suffocation from indigestion, technically known as "hoven." The symptoms of "hoven" are not unlike those of prussic acid poisoning, and it is possible that the various leguminous fodders which are known to be particularly liable to produce these effects may, at any rate in some cases, prove, like *Lotus arabicus*, and, as will be shown in the present paper, *Sorghum vulgare*, to furnish prussic acid.

For the material we have employed in the course of this investigation we are indebted to Mr. E. A. FLOYER, who was good enough to undertake its collection in Egypt at different stages of growth.

Considerable confusion exists as to the identity of the "Great Millets" grown in different tropical countries. Thus in India the plant is cultivated both as a spring and an autumn crop. The varieties ripening in the spring are probably originally derived from *Sorghum halapense*, a species indigenous to India, whilst the autumn crops are generally referred to *Sorghum vulgare*, yet both spring and autumn crops are called "juar" or "jowar," and are used by the natives indiscriminately. Again, in India a plant with an inflorescence more branched than that of *Sorghum vulgare* has been regarded as a distinct species, and named *Sorghum saccharatum;* this name is however given in the 'Index Kewensis' as a synonym for *Sorghum vulgare*, of which the plant is probably merely a variety.

The plant we have examined has been identified for us by Dr. SCHWEINFURTH as undoubtedly true *S. vulgare*.

Preliminary Experiments.

It was observed that the young plant when crushed and moistened with cold water soon acquired a strong odour of hydrocyanic acid. The production of this acid was confirmed by pressing out a little of the liquid from the moist plant, and distilling it, when a liquid was obtained which gave the characteristic reactions of hydrogen cyanide.

A few grammes of the plant were next exhausted by hot methylated alcohol in a Soxhlet extractor. The solvent was distilled from the solution and the residue boiled with water until nothing more dissolved. The aqueous liquid was then distilled at first alone, and afterwards with the addition of dilute hydrochloric acid; in the former case none, but in the second, where hydrolysis had occurred, considerable quantities of hydrocyanic acid were found in the distillate.

These observations led us to conclude that *Sorghum vulgare* contains a glucoside which under the influence of some hydrolytic agent simultaneously present undergoes hydrolysis, furnishing as one product hydrocyanic acid, to which the observed toxicity of the young plants must be ascribed.

A determination of the amount of acid which the air-dried plant is capable of producing at different stages of growth was made by leaving a weighed quantity in contact with water for 12 hours, and distilling off the acid formed in a slow current of steam, the liquid being titrated by LIEBIG's method.

The following results were obtained :—

(*a*) From bright green plants about 12 inches in height;

20 grammes gave a distillate requiring 7·45 cub. centims. $\frac{N}{10}$ silver nitrate, equivalent to ·201 per cent. HCN.

20 grammes gave a distillate requiring 7·8 cub. centims. $\frac{N}{10}$ silver nitrate, equivalent to ·216 per cent. HCN.

(*b*) From plants about 3 feet high, yellowish-green and ripe; 20 grammes of these mature plants gave no indication of prussic acid, and larger quantities on distillation with water gave amounts too small to be satisfactorily estimated. No prussic acid was obtained from the seeds of the Millet.

It has been asserted by GRESHOFF and TREUB that in many tropical plants hydrocyanic acid occurs as such, that is, in the free state. The existence of the free acid was demonstrated by these observers by immersing a thin section of the plant first in alkali, then in a mixture of ferrous and ferric chlorides, and finally in strong hydrochloric acid. If the plant tissue was stained blue, it was concluded that prussic acid in the free state was present. This test, however, appears to us to be quite inconclusive, as the mere moistening of plant tissue containing both a glucoside capable of furnishing prussic acid on hydrolysis and a hydrolytic enzyme, leads to the immediate production of free acid, which by GRESHOFF and TREUB's method would be regarded as occurring pre-formed in the plant. We have carefully examined various specimens of dhurra for free prussic acid by the following methods.

About 20 grammes of the finely-powdered plant were placed in a distilling flask attached by its branch tube to a long condenser. Into the closed flask a rapid current of steam was passed, which served the double purpose of immediately destroying any enzyme, and of carrying through the condenser any volatile product present in the plant. In the distillate of the plant thus obtained we never found prussic acid, either with young *Sorghum vulgare* or *Lotus arabicus*.

It therefore appears that, like *Lotus arabicus*, the poisonous effects of the young dhurra are due to the presence of a glucoside, which yields prussic acid under the influence of an enzyme also present in the plant.

Extraction of the Glucoside (Dhurrin).

The finely-powered plant was extracted with alcohol, the solvent distilled off and the residue warmed with water until nothing more dissolved.

To this liquid aqueous lead acetate was added so long as a precipitate formed. The precipitate (lead tannate, &c.) was removed. The filtrate, which was now bright yellow, was treated with sulphuretted hydrogen, care being taken to avoid a large excess, and the lead sulphide was removed by filtration. A stream of air was then drawn through the liquid to remove hydrogen sulphide, and the solution evaporated in a vacuum. After several weeks the syrup deposited a small quantity of a crystalline substance, and more was obtained by adding small quantities of alcohol and dissolving the mixture of precipitated sugar and glucoside in a little water, and setting aside to crystallise as before. This process was very tedious, and the two following methods have been since found to yield the glucoside much more rapidly.

A. The liquid, after the hydrogen sulphide treatment, is evaporated in a vacuum to a convenient volume, and the amount of free sugar determined with FEHLING'S solution. A little more than the calculated quantity of phenylhydrazine necessary to convert this amount of sugar into the osazone is then added, and the mixture heated for 30 minutes at 100° C., filtered, and the filtrate shaken with ether to remove any excess of phenylhydrazine. On evaporation in a vacuum the residue generally solidified to a mass of crystals, which were easily purified by recrystallisation from alcohol. The method always involves the loss of some of the glucoside, and cannot be employed in the isolation of small quantities.

B. The second method, which is the more effective, consists in evaporating in a vacuum the extract left after the lead acetate and hydrogen sulphide treatment with sufficient purified animal charcoal to convert the whole into a powder, which is then exposed in a vacuous desiccator until quite dry, when it is extracted in a Soxhlet apparatus with dry acetic ether. This solvent slowly removes the glucoside, leaving behind nearly all dextrose and brown extractive matter. On distilling off the solvent a syrupy residue is left, which if necessary is again treated in the same manner; usually, however, it crystallises after standing in a vacuum over sulphuric acid for a few days. The substance may be recrystallised from hot alcohol or boiling water.

The glucoside crystallises from water in brilliant leaflets, and from alcohol in small, transparent, rectangular prisms. It has no definite melting point, becoming brown when heated much beyond 100°, decomposing completely at 200°. It is easily soluble in hot alcohol, hot acetic ether and boiling water, separating in crystals on cooling. It is however retained in solution by aqueous solutions of dextrose, a peculiarity which accounts for the great difficulty we at first experienced in isolating it from the plant.

It appears to contain water of crystallisation, since it loses weight when heated for some time in a water oven, but the amount cannot be accurately determined owing to the decomposition which occurs when the substance is heated near 100°.

Some trouble was met with in obtaining the material in a satisfactory state for analysis owing to the difficulty of removing the water of crystallisation without causing decomposition.

The following combustions were made :—

A. Material recrystallised from alcohol and dried until of constant weight in a vacuous desiccator over sulphuric acid.

·0961 gramme gave	·1887	gramme	CO_2	C	53·6	per cent.
	·0572	,,	H_2O	H	6·5	,,
·1385 ,, ,,	·2698	,,	CO_2	C	53·1	,,
	·0885	,,	H_2O	H	7·07	,,

B. Material recrystallised from water and dried at the ordinary atmospheric temperature on filter paper.

·1260 gramme gave	·2323	gramme	CO_2	C	50·29	per cent.
	·0736	,,	H_2O	H	6·42	,,

C. Material recrystallised from alcohol and dried in a current of warm air at 80° to 90°C.

·1021 gramme gave	·2051	gramme	CO_2	C	54·7	per cent.
	·0452	,,	H_2O	H	4·9	,,

$C_{14}H_{17}O_7N.C_2H_5OH$	requires	C 53·7	H 6·44	per cent.
$C_{14}H_{17}O_7N.H_2O$	,,	C 51·1	H 5·8	,,
$C_{14}H_{17}O_7N$	,,	C 54·0	H 5·5	,,
$C_{20}H_{27}O_{12}N$	,,	C 50·74	H 5·7	,,

The glucoside therefore has the composition represented by the formula $C_{14}H_{17}O_7N$, but when crystallised from alcohol or water the crystals which separate contain one molecular proportion of these solvents.

For the glucoside thus isolated from Egyptian Dhurra we propose the name *dhurrin*.

Hydrolysis of Dhurrin by Acids. Formation of Prussic Acid, Parahydroxybenzaldehyde and Dextrose.

When an aqueous solution of dhurrin is warmed on the water-bath with dilute hydrochloric acid, hydrocyanic acid is almost immediately evolved. If the heating is continued for some time, the liquid becomes considerably discoloured owing to the further action of the acid upon the products of hydrolysis. In addition to prussic acid, a sugar and a substance soluble in ether are produced.

Parahydroxybenzaldehyde.

About 2 grammes of the dhurrin were dissolved in 50 cub. centims. of distilled water, and to the solution 10 cub. centims. of dilute hydrochloric acid were added, and the mixture heated on the water-bath for 5 minutes. The liquid was then extracted with ether and the ethereal solution dried and distilled. The residue was a brownish oil which, on standing, solidified to a mass of rosettes of needles. The crystals were dissolved in a small quantity of hot water, the solution filtered to remove resin, and cooled, when the substance separated in almost colourless needles, which could be picked out from a small quantity of the brown resin still adhering to them. After a second recrystallisation the melting-point remained unchanged at 118°. The substance is soluble in hot water, alcohol and ether. In aqueous solutions ferric chloride produces a purple coloration, and bromine water a white precipitate, which becomes crystalline on standing; phenylhydrazine produces an immediate crystalline precipitate. When heated in a dry test-tube the substance melts and sublimes in needles on the cooler parts of the tube; the vapour has a pleasant aromatic odour.

A combustion of the purified material, dried at 100°, gave the following results:—

·1267 gramme gave ·3196 gramme CO_2, 68·7 per cent. carbon.
·0529 ,, H_2O, 5·13 ,, hydrogen.
$C_7H_6O_2$ requires C 68·8, H 4·91.

The substance has therefore the composition of parahydroxybenzaldehyde.

Owing to the small amount of material available, the action of bromine on this compound could only be studied by the addition of excess of bromine water to dilute solutions of the substance, a method of investigation which, as the sequel shows, gave rise to rather unexpected results. Under these conditions an amorphous precipitate is formed which soon crystallises in colourless needles, forming after recrystallisation from alcohol felted masses of needles melting at 92°, and having all the properties of tribromphenol.

When a saturated aqueous solution of phenylhydrazine is added to a similar solution of the substance, a crystalline hydrazone is immediately formed, which is insoluble in ether and chloroform but soluble in hot alcohol. By operating in dilute solutions, a well-crystallised product is obtained, melting at 178°. It crystallises from hot alcohol in white needles which, on drying at 100°, become slightly green.

A combustion of the hydrazone gave the following result:—

·1117 gramme gave CO_2, ·3018 gramme 73·6 per cent. carbon.
H_2O, ·0613 ,, 6·07 ,, hydrogen.
$C_6H_4(OH)CH{:}N{\cdot}NHC_6H_5$ requires C 73·52 H 5·6.

The ether soluble hydrolytic product of dhurrin is therefore undoubtedly parahydroxybenzaldehyde, which melts at 118°, gives a purple colour with ferric chloride, and forms a colourless hydrazone melting at 178°.

The occurrence of tribromphenol amongst the products obtained by brominating parahydroxybenzaldehyde has been observed by WERNER ('Bull.,' 46, 278), but it does not appear to have been previously noticed that, by using bromine water and dilute aqueous solutions of the aldehyde, the latter is converted almost exclusively into tribromphenol. This result was confirmed with a specimen of the aldehyde prepared from phenol and carefully purified from all traces of the latter.

$$C_6H_2(OH)CHO + H_2O + 4Br_2 = C_6H_2Br_3OH + 5HBr + CO_2.$$

Dextrose.

The acid liquid, after removal of the parahydroxybenzaldehyde, was mixed with powdered animal charcoal, warmed for several hours, and filtered. It was slightly yellow, but was sufficiently transparent for observation in a polarimeter, when it showed a marked dextro-rotation. It was next heated with phenylhydrazine for an hour on the water-bath, and the separated osazone collected and recrystallised from hot alcohol, when the characteristic bright yellow needles of glucosazone melting at 204° were obtained. The sugar produced is therefore d-glucose, that is, ordinary dextrose.

The Hydrolysis of Dhurrin and its Chemical Constitution.

Hydrolysis of Dhurrin by Emulsin.—About 1 gramme of the glucoside was dissolved in cold water, and a filtered extract of sweet almonds added, the mixture being then set aside for 12 hours at the ordinary temperature. After a few minutes the odour of hydrocyanic acid was perceptible, and at the end of the experiment over 90 per cent. of the possible quantity of parahydroxybenzaldehyde was obtained. This method of hydrolysing the glucoside is to be preferred to that involving the use of acids, since the aldehyde produced is more easily purified.

The quantitative determination of the acid hydrolytic products of dhurrin appeared to afford a method of confirming the formula assigned to this glucoside from the results of combustion, which are perhaps not completely satisfactory owing to the difficulty of obtaining the substance anhydrous without decomposing it. Attempts were therefore made to determine the amounts of hydrocyanic acid and dextrose produced on hydrolysis. For this purpose a weighed quantity of dhurrin dissolved in water was placed in a small Jena flask, and sufficient dilute (10 per cent.) hydrochloric acid added.

The flask was then corked and secured by wire and heated in a water-bath for 5 minutes. In this way complete hydrolysis is secured without much secondary decomposition. The prussic acid formed was distilled off in a gentle current of steam, collected in alkali and titrated. The sugar in the residue was estimated gravimetrically by reduction of FEHLING'S solution.

·156 gramme gave a distillate requiring 2·58 cub. centims. $\frac{N}{10}$ silver nitrate = 8·9 per cent. HCN.

·1702 gramme cuprous oxide = ·085 gramme dextrose = 54·5 per cent.

$C_{14}H_{17}O_7N$ requires 8·6 per cent. HCN and 57·1 per cent. dextrose.

$C_{20}H_{27}O_{12}N$,, 6·01 ,, HCN and 80·1 ,, ,,

The formula $C_{14}H_{17}O_7N$ for dhurrin is therefore confirmed, and the hydrolysis of dhurrin by emulsin, or by dilute acid, may be expressed by the equation $C_{14}H_{17}O_7N + H_2O = C_7H_6O_2 + C_6H_{12}O_6 + HCN$.

Alkaline Hydrolysis of Dhurrin, Dhurrinic Acid.—When the glucoside is warmed with aqueous alkalis, it dissolves, with the evolution of ammonia, but no dextrose is formed. On evaporation the solution leaves a sticky hygroscopic residue which cannot be induced to crystallise.

When the hydrolysis is carried out in alcoholic solution by adding a solution of sodium in absolute alcohol to a similar solution of the glucoside, a precipitate forms after a few minutes, consisting of the sodium salt of the acid corresponding to dhurrin, which is its nitrile. This acid may therefore be called *dhurrinic acid.* The sodium salt is highly hygroscopic, it absorbs moisture and becomes gummy when removed from the dry alcohol, and is therefore difficult to free completely from the accompanying sodium carbonate. The free acid is almost more intractable than the sodium salt, and, so far, has only been obtained as a syrup containing sodium chloride. Recourse was therefore had to an examination of its decomposition products in order to establish its constitution.

Hydrolysis of Dhurrinic Acid.—A quantity of the crude sodium salt, prepared as above described, was dissolved in water and dilute hydrochloric acid added. The mixture was heated on the water-bath for an hour, and when cold extracted several times with ether. The ethereal solution was dried and the solvent removed by distillation, leaving a brown oil, which after several days deposited minute transparent needles. These were dried by absorption of the viscous mother liquid in a porous tile.

The substance thus obtained is at first colourless, but in a few days becomes slightly brown. It is soluble in boiling water, alcohol, and ether, and after recrystallisation melts at 180°. With ferric chloride in aqueous solution it gives a slight brown coloration, and with bromine water a precipitate, which after recrystallisation from alcohol melts at 185°.

The acid liquid after extraction with ether strongly reduces FEHLING'S solution, and therefore probably contains dextrose.

The yield of the crystalline hydrolytic product furnished by the hydrolysis of dhurrinic acid is so small that sufficient material for analysis and identification could not be obtained. A small quantity of the acid was converted into silver salt, and a weighed quantity of the latter ignited, with the following result :—

·1058 gramme gave ·0399 Ag = 38·65 per cent., $C_8H_7O_4Ag$ requires 39·05 per cent.

It seemed highly probable that the alkaline hydrolysis of dhurrin with the formation of dhurrinic acid, and the decomposition of the latter by dilute acids, might be strictly comparable with the similar reactions of amygdalin, which, when hydrolysed by alkalis, furnishes amygdalic acid, this acid by heating with dilute acids being hydrolysed into mandelic acid and dextrose.

Amygdalin.	Amygdalic acid and ammonia.	Mandelic acid + 2 mols. dextrose.
$C_{20}H_{27}NO_{11}$ . . .	$C_{20}H_{28}O_{13} + NH_3$ . . .	$C_8H_8O_3 + 2C_6H_{12}O_6$.
Dhurrin.	Dhurrinic acid and ammonia.	Parahydroxymandelic acid + 1 mol. dextrose.
$C_{14}H_{17}O_7N$ . . .	$C_{14}H_{18}O_9 + NH_3$ . . .	$C_8H_8O_4 + C_6H_{12}O_6$.

On this analogy the crystalline hydrolytic product of dhurrinic acid would be parahydroxymandelic acid. We have established the identity of the two substances by comparing the hydrolytic product with parahydroxymandelic acid prepared by the hydrolysis of the cyanhydrin of parahydroxybenzaldehyde.

As parahydroxymandelic acid is now prepared for the first time, the following outline of the process employed may be given.

Preparation of Parahydroxymandelic Acid.—Ten grammes of parahydroxybenzaldehyde were dissolved in 50 cub. centims. of boiling water, and 30 grammes of potassium cyanide added to the solution, which was then cooled in a freezing mixture and 50 cub. centims. of strong hydrochloric acid gradually added, the whole being set aside for about 12 hours. The mixture was extracted with ether, the latter being allowed to spontaneously evaporate, leaving an oily residue, which was mixed with 20 cub. centims. of strong hydrochloric acid and sufficient alcohol to keep it in solution. This mixture was boiled for 3 hours, neutralized with sodium carbonate, filtered from the large quantity of resin formed, and extracted with ether in order to remove unaltered aldehyde. The residual liquid was then made acid with dilute sulphuric acid and extracted with ether until exhausted. The solvent was then distilled off, the oily residue boiled with water, to which a little animal charcoal had been added, and the filtered solution evaporated in a vacuum. After several days rosettes of needles appeared in the oily residue, and these after recrystallisation from alcohol melted at 180°, and further resembled the acid obtained from dhurrin in giving a brown coloration with ferric chloride, and a crystalline bromine derivative melting at 185°.

The yield of parahydroxymandelic acid furnished by the process described above is only about 1 per cent., as this acid is readily converted by hydrochloric acid into a resin dissolving in alcohol with a fine purple colour. The cyanhydrin of parahydroxybenzaldehyde is also very unstable, being easily hydrolysed by water into prussic acid and the aldehyde, so that in each experiment about 50 per cent. of the latter is regenerated. Attempts were made to utilise anisaldehyde cyanhydrin for the preparation of the acid, but although this substance is somewhat more stable than its lower homologue, a considerable loss occurs in decomposing the methoxy-mandelic acid first formed.

A small quantity of the silver salt prepared from the acid obtained as described above gave the following results on analysis :—

·1286 gramme gave ·1642 gramme CO_2, C 34·83 per cent.
·0308 „ H_2O, H 2·67 „

·1286 gramme gave a residue of silver weighing ·0506 gramme = 39·35 per cent.
$C_8H_7O_4Ag$ requires C 34·9, H 2·48, Ag 39·09 per cent.

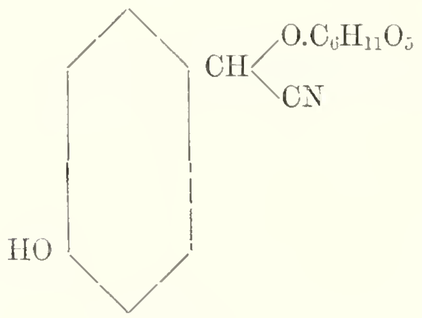
The properties and reactions of dhurrin, as described in the foregoing paragraphs, may for convenience be summarised as follows :—

(1) The glucoside is hydrolysed by emulsin and dilute acids into parahydroxybenzaldehyde, hydrocyanic acid, and dextrose.

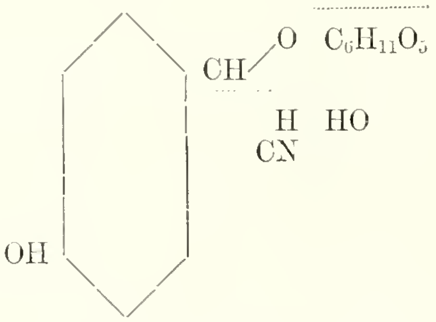
(2) It is decomposed hydrolytically by alkalis into dhurrinic acid and ammonia.

(3) Dhurrinic acid is hydrolysed by dilute acids into parahydroxymandelic acid and dextrose.

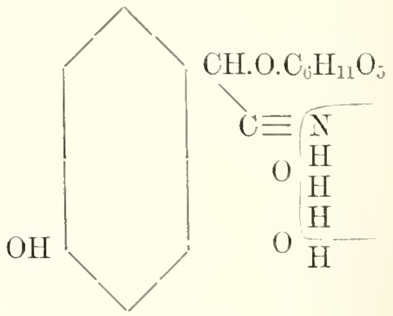
These reactions we believe are fully accounted for by assigning to dhurrin the constitution of a dextrose ether of the cyanhydrin of parahydroxybenzaldehyde, which may be represented by the formula given below



Dhurrin



Hydrolysis by acids and emulsin (prussic acid, dextrose, parahydroxybenzaldehyde).



Hydrolysis by alkalis (dhurrinic acid and ammonia).

Dhurrin is therefore the parahydroxy-derivative of the glucoside of mandelic nitrile which was prepared by FISCHER by the partial hydrolysis of amygdalin with invertase, and resembles this glucoside in the ease with which it undergoes hydrolysis by emulsin. It is the first member of the class of dextrose ethers (glucosides) of cyanhydrins which has so far been found in nature, amygdalin and lotusin being maltose derivatives.

The Enzyme of Sorghum vulgare.

In the introduction to this paper attention has been drawn to the fact that the plant when moistened with cold water evolves hydrocyanic acid, whilst it no longer does so after exposure to a temperature of 100°, nor is the acid formed when the plant is placed in boiling water. These results point to the presence in the plant of an enzyme, destroyed by heat, which has the power of hydrolysing dhurrin. This enzyme was isolated by extracting the finely-ground plant with cold water, and evaporating the extract so obtained in a vacuous desiccator over quicklime to remove as much hydrocyanic acid as possible. The activity of this extract was then tested by the addition of small quantities to solutions of amygdalin, salicin and dhurrin, these experiments being controlled by the addition of boiled and filtered dhurra extract to similar solutions of these glucosides.

In all three cases the glucoside was quickly hydrolysed, the formation of benzaldehyde, saligenin, and parahydroxybenzaldehyde respectively being recognized by the usual tests for these substances. Comparative experiments in which the action of an extract of sweet almonds was tried side by side with the dhurra enzyme on the same glucosides, showed that the two extracts behaved in precisely the same way. Similar preparations made by precipitating aqueous extracts of sweet almonds and dhurra with alcohol and by precipitating calcium phosphate in such extracts, showed no difference of activity in effecting the hydrolysis of salicin. The glucosidolytic enzyme of *Sorghum vulgare* therefore performs the same functions as the enzyme emulsin which occurs in sweet almonds, and in the present state of our knowledge of the chemistry of enzymes, the two substances may provisionally be regarded as identical.

The Cyanogenetic Constituents of Plants.

Besides lotusin and dhurrin, the glucosides we have isolated from young plants of *Lotus arabicus* and *Sorghum vulgare* respectively, only one other cyanogenetic glucoside is definitely known, that is, the amygdalin derived from bitter almonds, which, however, is found in the seeds of the plant.

The results of our investigations have rendered it probable that the production of prussic acid in a number of other plants may be associated with the presence of cyanogenetic glucosides. Moreover, the question of the occurrence of prussic acid, and the part played by it in vegetable metabolism, involves problems of the first importance in vegetable physiology, with which we intend to deal when we have obtained a further insight into the nature of other cyanogenetic glucosides now under investigation. So far as *Lotus arabicus* and *Sorghum vulgare* are concerned, it would appear that the existence of a cyanogenetic glucoside in the young plant up to the period when the seeds ripen at any rate may serve as an important protection to the plant from the attacks of animals. It appears that animals, indigenous to the countries in which these plants are native, refuse to eat them in the earlier and poisonous stages of growth. The part played by the glucoside in the general metabolism of these plants and the origin and fate of the cyanogenetic group still remain to be ascertained. The temporary presence in a plant of a considerable quantity of a cyanogenetic glucoside, together with an enzyme capable of decomposing it, appears to us to be a fact which must have an important biological meaning.

As so much interest attaches to the subject from several points of view, we are engaged in investigating the constituents of other plants which furnish prussic acid. Among them we may mention *Phaseolus lunatus* (seeds), *Lotus australis*, *Manihot utilissima*, and *Linum usitatissmum*, as well as a number of little known plants derived from the Colonies which have proved to be poisonous to cattle, some of which may contain cyanogenetic glucosides. From the chemical point of view it is important, in the first instance, to isolate these glucosides and to ascertain their properties, composition, and molecular structure. This work we have now accomplished with the glucosides of *Lotus arabicus* and *Sorghum vulgare*, which are shown to be radically different in chemical constitution, whilst each belongs to a type chemically distinct from that of amygdalin, the only naturally occurring cyanogenetic glucoside hitherto definitely known.

INDEX SLIP.

Barnes, E. W.—A Memoir on Integral Functions.
Phil. Trans., A, vol. 199, 1902, pp. 411–500.

Asymptotic Expansions—General Theory, Application to Integral Functions—Exponential Function.
Barnes, E. W. Phil. Trans., A, vol. 199, 1902, pp. 411–500.

Divergent Series—Theory of Summation.
Barnes, E. W. Phil. Trans., A, vol. 199, 1902, pp. 411–500.

Functions (Integral)—Types, Genres, Orders, &c.—Functions of $P_\rho(z)$, &c.—Repeated Integral Functions.
Barnes, E. W. Phil. Trans., A, vol. 199, 1902, pp. 411–500.

Lambert's Function—Properties and Asymptotic Expansion.
Barnes, E. W. Phil. Trans., A, vol. 199, 1902, pp. 411–500.

Maclaurin Sum Formula—Proof of.
Barnes, E. W. Phil. Trans., A, vol. 199, 1902, pp. 411–500

VIII. *A Memoir on Integral Functions.*

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Index.

Part I.—Introduction.

History of the Subject.

Classification of Integral Functions.

PART II.—THE THEORY OF DIVERGENT SERIES.

PART III.—THE ASYMPTOTIC EXPANSION OF SIMPLE INTEGRAL FUNCTIONS.

PART IV.—THE ASYMPTOTIC EXPANSION OF REPEATED INTEGRAL FUNCTIONS.

PART V.—APPLICATIONS OF THE PREVIOUS ASYMPTOTIC EXPANSIONS.

Part I.

Introduction.

§ 1. Since the fundamental discoveries of Weierstrass, much progress has been made with regard to uniform transcendental functions; but the advances of modern mathematics appear to have included no attempt formally to classify and investigate the properties of natural groups of such functions.

Consider, for instance, the case of transcendental integral functions which admit one possible essential singularity at infinity. They form the most simple class of uniform functions of a single variable, and yet of them we know, broadly speaking, the nature of but four types :—

(1) The exponential function, with which are associated circular and (rectangular) hyperbolic functions;
(2) The gamma functions;
(3) The elliptic functions and functions derived therefrom, such as the theta functions and Appell's generalisation of the Eulerian functions;
(4) Certain functions which arise in physical problems (such as $x^{-n} J_n(x)$) whose properties have been extensively investigated for physical purposes.

There are, of course, isolated examples of other types of functions; yet, broadly speaking, except for algebraic polynomials, the four types just mentioned comprise the extent of our knowledge.

§ 2. Take now an example of the first type of function.

We may write $\dfrac{\sinh \pi\sqrt{z}}{\pi\sqrt{z}} = \prod_{n=1}^{\infty}\left[1 + \dfrac{z}{n^2}\right]$, and hence we have

$$\prod_{1}^{\infty}\left[1 + \frac{z}{n^2}\right] = \frac{e^{\pi z^{\frac{1}{2}}} - e^{-\pi z^{\frac{1}{2}}}}{2\pi z^{\frac{1}{2}}};$$

so that when $|z|$ is very large, the approximate value of $\prod_{1}^{\infty}\left[1 + \dfrac{z}{n^2}\right]$ is $(2\pi)^{-1} z^{-\frac{1}{2}} e^{\pi z^{\frac{1}{2}}}$, so long as $-\pi < \arg z < \pi$.

That is to say, for all points in the region of $z = \infty$ which are not at a finite distance from the zeros of $\pi^{-1} z^{-\frac{1}{2}} \sinh \pi \sqrt{z}$, this function admits what we may call the asymptotic expansion $(2\pi)^{-1} z^{-\frac{1}{2}} e^{\pi z^{\frac{1}{2}}}$, and a similar property is true of all functions of the first class.

§ 3. Consider next the second class of functions.

We have as the simplest example

$$\frac{1}{\Gamma(z)} = e^{\gamma z} z \prod_1^\infty \left[\left(1 + \frac{z}{n}\right) e^{-\frac{z}{n}} \right].$$

Since the time of STIRLING it has been known that, when z is a large positive integer,

$$\Gamma(z) = (2\pi)^{\frac{1}{2}} z^{z-\frac{1}{2}} e^{-z + \sum\limits_{s=0}^{\infty} \frac{(-)^s \quad B_{s+1}}{2s+1 \,.\, 2s+2} \frac{1}{z^{2s+1}}}$$

approximately—the terms neglected involving exponentials of a lower order than those retained.

In 1889 STIELTJES* proved that this asymptotic expansion is valid for all values of z in the region of $z = \infty$, except those which are at a finite distance from the zeros of $\Gamma^{-1}(z)$.

By a different method it is possible to establish both STIELTJES' result and the analogous theorem that the double gamma function†

$$\Gamma_2^{-1}(z) = e^{\gamma_{21} \frac{z^2}{2} + z\gamma_{22}} \,.\, z \,.\, \prod_{m_1=0}^{\infty} \prod_{m_2=0}^{\infty}{}' \left[\left(1 + \frac{z}{\Omega}\right) e^{-\frac{z}{\Omega} + \frac{1}{2} \frac{z^2}{\Omega^2}} \right]$$

in which $\Omega = m_1\omega_1 + m_2\omega_2$, admits the asymptotic expansion

$$\log \frac{\Gamma_2(z)\, e^{2\pi\iota(m+m')\,{}_2S'_1(0)}}{\rho_2(\omega_1, \omega_2)} = - {}_2S'_1(z) \left\{ \log_{\omega_1+\omega_2} z - 2(m + m')\pi\iota \right\}$$
$$+ z\,{}_2S_1^{(2)}(0) + \frac{z^2}{2}\,{}_2S_1^{(3)}(0) \left\{\tfrac{1}{1} + \tfrac{1}{2}\right\} + \sum_{m=1}^{\infty} \frac{(-)^m\,{}_2S'_{m+1}(0)}{m(m+1)z^m}.$$

This expansion was shown to be valid for all points in the plane of the complex variable z near infinity, which are not at a finite distance from the zeros of the integral function $\Gamma_2^{-1}(z)$.

A similar theorem is true for multiple gamma functions.

§ 4. As regards the elliptic functions and the integral functions associated with them which constitute the third type, there are no points in the neighbourhood of infinity which are not at a finite distance from the zeros of the function and no asymptotic approximations are known to exist.

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[*] 'Liouville' (4), vol. 5, pp. 425–444.

[†] See a paper by the Author, 'Phil. Trans.,' A, vol. 196, pp. 265–387.

§ 5. The best known example of the fourth type is BESSEL's function

$$\mathrm{J}_n(z) = \sum_{\mu=0}^{\infty} \frac{(-)^{\mu} \left(\frac{z}{2}\right)^{2\mu+n}}{\Gamma(\mu+1)\,\Gamma(\mu+n+1)}.$$

It is evident that $z^{-n}\mathrm{J}_n(z)$ is a uniform integral function.

The investigations of POISSON,* STOKES.† LIPSCHITZ,‡ and JORDAN,§ have finally led to a rigorous demonstration by the latter that asymptotically, when n is real.

$$z^{-n}\mathrm{J}_n(z) = \sqrt{\frac{2}{\pi}}\, z^{-n-\frac{1}{2}} \cos\left\{z - (n+\tfrac{1}{2})\frac{\pi}{2}\right\}, \text{ when } \mathfrak{R}(z) \text{ is positive,}$$

$$\text{and } z^{-n}\mathrm{J}_n(z) = \sqrt{\frac{2}{\pi}}\, e^{\overline{2n+1}\cdot\frac{\pi\iota}{2}}\, z^{-n-\frac{1}{2}} \cos\left\{z + (n+\tfrac{1}{2})\frac{\pi}{2}\right\}, \text{ when } \mathfrak{R}(z) \text{ is negative.}$$

The complexity of this result is reduced by the transformation $-z^2 = t$ or $z = \iota\sqrt{t}$, which gives $z^{-n}\mathrm{J}_n(z) = \sum\limits_{\mu=0}^{\infty} \frac{t^{\mu}}{2^{2\mu+n}\,\Gamma(\mu+1)\,\Gamma(\mu+n+1)}$, an integral function of t.

And now we have for the asymptotic value of $z^{-n}\mathrm{J}_n(z)$ the unique expression

$$(2\pi)^{-\frac{1}{2}}\, t^{-\frac{2n+1}{4}}\, e^{t^{\frac{1}{2}} + \frac{(\ldots)}{t} + \cdots},$$

which is valid for all values of arg t between $-\pi$ and π.

This shows at once that $z^{-n}\mathrm{J}_n(z)$, quâ function of t, has no imaginary roots which are not at a finite distance from the negative part of the real axis. In point of fact, these roots are known to be real and negative when $n > -1$ ‖. Hence the asymptotic expansion for

$$t^{-\frac{n}{2}}\, e^{\frac{-\pi\iota n}{2}}\, \mathrm{J}_n(e^{\frac{\pi\iota}{2}}\sqrt{t}) = \sum_{\mu=0}^{\infty} \frac{t^{\mu}}{2^{2\mu+n}\,\Gamma(\mu+1)\,\Gamma(\mu+n+1)}$$

is valid for all points in the neighbourhood of $t = \infty$ except those which are at a finite distance from the zeros of the function.

§ 6. The question now forces itself upon us:—"*Do all integral functions of a single variable z admit asymptotic approximations in the domain of $z = \infty$, which are valid for all points but those which are in the immediate vicinity of the zeros of the functions?*

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* POISSON, 'Journal de l'École Polyt.,' vol 19, 1823, pp. 349 *et seq.*

† STOKES, 'Camb. Phil. Trans.,' vol. 9, 1856, pp. 166 *et seq.*

‡ LIPSCHITZ, 'Crelle,' vol. 56, pp. 189 *et seq.*

§ JORDAN, 'Cours d'Analyse,' 1896, vol. 3, pp. 254–274.

‖ When n is negative and between m and $m + 1$ in absolute value, there may be a finite number $(2m)$ of imaginary roots of $z^{-n}\mathrm{J}_n(z)$, but these are not associated with the essential singularity. *Cf.* MACDONALD, 'Proc Lond. Math. Soc.,' vol. 29, pp. 575–584.

The present memoir is devoted to the answer of this question; and the question is closely connected with other subjects of enquiry.

§ 7. Soon after WEIERSTRASS, in 1876, published his great theorem relating to the formation of uniform functions with assigned zeros, LAGUERRE remarked the fundamental nature of the number of terms in the exponential function which is necessary to form the "prime factor." The number was by him termed the "genre" of the function; and the questions at once arose:—

> "Is the genre of a function equal to the genre of its derivative?"
>
> "Is the sum of two functions of the same or different genre a function of genre equal to the common genre or equal to the larger genre respectively?"

§ 8. Again, by ROLLE's Theorem it is known that the real roots of any algebraic equation, $\phi(x) = 0$, separate, and are separated by those of $\phi'(x) = 0$.

Is this true when $\phi(x)$ is an integral function?

Closely connected with this enquiry is the further one:—"If the roots of $\phi(x) = 0$ are all real, are those of $\phi'(x) = 0$ real, in the case when $\phi(x)$ is any integral function?"

Again, it is evident that the more quickly the zeros of an integral function increase, the more quickly will the TAYLOR's series for the function converge. Can any connection be discovered between the magnitude of the coefficients of the TAYLOR's series and the expression for the zeros of the function it represents? In other words, if we are given the general term of the TAYLOR's series for an integral function, can we approximately determine the nature of its zeros?*

All these questions fundamentally depend on the asymptotic approximation for the function. The nature of the latter *serves to classify the nature of the integral function.*

History of the subject.

§ 9. As already remarked, WEIERSTRASS† founded the theory of transcendental integral functions by constructing functions with any assigned zeros. LAGUERRE‡ invented the term "*genre*" to denote the number of terms in the exponential associated in the prime-factor—and for functions of genre 0 and 1 proved that the real roots of the transcendental integral function $\phi(x) = 0$ are separated by those of $\phi'(x) = 0$.

He also proved, as HERMITE§ had previously proved for $\frac{1}{\Gamma(x)}$, that if the roots of $\phi(x) = 0$ are real, those of $\phi'(x) = 0$ are real, provided $\phi(x)$ is of "genre" 0 or 1.

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* This question is not formally considered in the present memoir, as the expansions which are obtained, although they will give closer inequalities than any hitherto published, must be still further developed before inequality can be replaced by that asymptotic equality which alone would be a complete solution of the problem.

† WEIERSTRASS, "Zur Theorie der eindeutigen analyt. Funct.," 'Gesamm. Werke,' vol. 2.

‡ LAGUERRE, 'Compt. Rend.,' vol. 94, pp. 160–163, 635–638; vol. 95, pp. 828–831; vol. 98, pp. 79–81.

§ HERMITE, 'Crelle,' vol. 90, p. 336.

His principal proposition is, 'If, as z tends to ∞, a very great value of $|z|$ can be found for which the limit of

$$z^{-n}\frac{\phi'(z)}{\phi(z)}$$

tends uniformly to the value zero, then $\phi(z)$ is of genre n.'

Shortly afterwards, POINCARÉ[*] gave further criteria for the genre of a function, and made the important step of pointing out that the near connection between the genre of the function and its behaviour near infinity lead to an approximate determination of the magnitude of the general term of the TAYLOR'S series for the function.

After a succession of notes by CESARO,[†] VIVANTI[‡] (who proved that the derivative of a function is of the same genre as the function itself), and HERMITE,[§] the subject remained in abeyance until HADAMARD,[‖] in a memoir crowned by the French Academy, gave a valuable extension of POINCARÉ'S results.

The latter had proved that in the TAYLOR'S series for an integral function of genre E, the coefficient of x^m multiplied by the $(E+1)^{\text{th}}$ root of $m\,!$ tends to zero, as m indefinitely increases.

HADAMARD proved that, if the coefficient of x^m is less than $\left(\frac{1}{m\,!}\right)^{\frac{1}{\lambda}}$, the function is, in general, of genre less than λ. He also showed that when the coefficient of x^m is of order $\left(\frac{1}{m\,!}\right)^{\frac{1}{\lambda}}$, where λ is not an integer, the function represented by the series is of genre E, designating by $(E+1)$ the integer immediately superior to λ.

Finally, BOREL,[¶] continuing HADAMARD'S researches, introduced a more precise notion than that of genre († § 12), and attacked the difficult problem of functions of infinite order whose convergence is very slow.

[*Note added March 20th*, 1902.] In his recent text-book, "Leçons sur les Fonctions Entières,"[**] BOREL has given a valuable précis of our present knowledge of integral functions. And a paper by MELLIN[††] has recently come to my notice, which should be carefully read by all interested in the subjects with which the present memoir deals.

§ 10. The present contribution to this interesting theory differs from previous investigations in that it is shown to be possible to substitute actual asymptotic equalities for the inequalities which have been previously obtained.[‡‡]

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[*] POINCARÉ, 'Bull. des Sciences Math.,' vol. 15, pp. 136–144.

[†] CESARO, 'Compt. Rend.,' vol. 99, pp. 26, 27.

[‡] VIVANTI, 'Battaglini,' vol. 22, pp. 243–261, and 378–380; vol. 23, pp. 96–122; vol. 26, pp. 303–314.

[§] HERMITE, 'Battaglini,' vol. 22, pp. 191–200.

[‖] HADAMARD, 'Liouville' (4), vol. 9, pp. 171–215.

[¶] BOREL, 'Acta Mathematica,' vol. 20, pp. 357–396.

[**] Paris, Gauthier-Villars, 1900.

[††] MELLIN, 'Acta Societatis Fennicae,' 1900, vol. 29, No. 4

[‡‡] [MELLIN has obtained results of this nature.]

The memoir deals almost exclusively with simple integral functions of finite or zero order (*vide* the definitions of the succeeding paragraphs.)

I reserve the consideration of functions of infinite order, and also the results which I have obtained in connection with functions of double or multiple sequence. The latter form a self-contained theory, which is a natural extension of the investigations of the present memoir. The consideration of the asymptotic expansion of integral functions defined by a TAYLOR'S series is also postponed, although certain noteworthy extensions of HADAMARD'S results can be at once deduced from the present theory.*

My thanks are due to Professor FORSYTH for the kind way in which he has supplied me with references and criticism.

The Classification of Integral Functions.

§ 11. An *integral* function we define to be a uniform transcendental function with no poles, and a single essential singularity at infinity. [Sometimes it is convenient to include algebraic polynomials.] An integral function is thus the same as a holomorphic function, to use the translation of CAUCHY'S name; it is the equivalent of the French "*fonction entière*," and the German "*ganze Funktion.*" Every meromorphic function can be expressed as the quotient of two integral functions.

The most simple integral function can be written in the form

$$e^{H(z)} \prod_{n=1}^{\infty} \left[\left(1 - \frac{z}{a_n}\right) e^{\sum_{m=1}^{\rho_n - 1} \frac{1}{m} \left(\frac{z}{a_n}\right)^m} \right],$$

where $H(z)$ is an integral function of z, where the zero a_n depends solely upon n and certain definite constants, and where the law of dependence of a_n upon n is the same for all zeros. Such a function we call a simple integral function with a single sequence of non-repeated zeros. The law of dependence may be broken for a finite number of arbitrary zeros in the finite part of the plane. The existence of such zeros is equivalent to the multiplication of the transcendental function by an arbitrary polynomial coupled possibly with an exponential function of the type $e^{\rho(z)}$, where $\rho(z)$ is another algebraic polynomial. Such terms do not substantially alter the character of the function.

Functions of the type $e^{H(z)}$, where $H(z)$ is an integral function, belong to a class apart. The integral function which we consider we shall suppose to be deprived of such extraneous factor.

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* The present memoir was largely written during the summer of the year 1898. In consequence, and in spite of rigorous revision, results may sometimes appear to be tacitly claimed as new which have since been published in papers to which reference is made in connection with other investigations of the memoir.

The standard reduced simple integral function with a single simple sequence of non-repeated zeros is thus

$$\prod_{n=1}^{\infty}\left[\left(1-\frac{z}{a_n}\right)e^{\sum\limits_{m=1}^{\rho_n-1}\frac{1}{m}\left(\frac{z}{a_n}\right)^m}\right].$$

We shall call this briefly a *simple integral function.*

§ 12. The quantity ρ_n is the smallest integer such that the series $\sum\limits_{n=1}^{\infty} a_n^{-\rho_n}$ is absolutely convergent. When the convergency of the series can be assured by taking for ρ_n some number p independent of n, the function is said to be of finite *genre** p. In this case, if ρ is a real positive quantity such that $\sum\limits_{n=1}^{\infty}\frac{1}{|a_n|^{\rho+\epsilon}}$ converges and $\sum\limits_{n=1}^{\infty}\frac{1}{|a_n|^{\rho-\epsilon}}$ diverges, however small the real positive quantity ϵ be, the function is said to be of *order*† ρ, and ρ is called the *convergence-exponent*‡ of the series $\frac{1}{a_1}, \frac{1}{a_2}, \ldots, \frac{1}{a_n}, \ldots$ It is sufficient that the function a_n depends uniquely upon n; if we put $a_n = \phi(n)$, the quantity $\phi(n)$ is not necessarily a uniform function: it may be a definite value of some multiform function of n.

§ 13. When there is no finite quantity ρ which will make the series $\sum\limits_{n=1}^{\infty}\frac{1}{|a_n|^{\rho}}$ converge, the function is said to be of infinite genre and infinite order. The convergency of the series can, as WEIERSTRASS first showed, always be obtained by taking $\rho = n$. A theorem due to CAUCHY proves this at once, since

$$\underset{n=\infty}{\mathrm{L}^t}\sqrt[n]{\frac{1}{|a_n|^n}} = 0.$$

It is equally sufficient to take $\rho = \log n$, for then $\sum\limits_{n=1}^{\infty}\frac{1}{|a_n|^{\log n}} = \sum\limits_{n=1}^{\infty}\frac{1}{n^{\log|a_n|}}$; and the latter series is convergent, since $|a_n|$ increases indefinitely with n.

But a smaller number still is a sufficient value for ρ, namely, the greatest integer contained in $\frac{(1+\epsilon)\log n}{\log|a_n|}$, where ϵ is any positive quantity as small as we please.§

The great difficulty in the theory of asymptotic approximations for functions of infinite order consists in finding the minimum value of ρ. I do not intend to consider such functions in the present memoir. Functions of the type $e^{\mathrm{H}(z)}$, where $\mathrm{H}(z)$ is holomorphic, are of course integral functions of infinite order.

§ 14. It is evident that if a_n does not increase more quickly than some (possibly fractional) power of n, however small, the associated integral function will be of

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* LAGUERRE, 'Comptes Rendus,' vol. 94; 'Œuvres,' vol. 1, pp. 167 *et seq.*

† BOREL, 'Acta Mathematica,' vol. 20, p. 360.

‡ VON SCHAPER, 'Hadamard'schen Functionen,' p. 35; BOREL, 'Fonctions Entières,' p. 18.

§ BOREL, 'Acta Mathematica,' vol. 20, p. 360.

infinite order. On the other hand, if a_n increases faster than any algebraic power of n, however large, provided it be not actually infinite, the function is of zero order. In other words, functions whose order is "finite both ways," to use De Morgan's phrase, have zeros which are to a first approximation algebraic.

The zeros of the function are said to be actually *algebraic* when they are given by

$$a_n = c_0 n^\rho \left[1 + \frac{c_1}{n^{\rho_1}} + \frac{c_2}{n^{\rho_2}} + \ldots\right],$$

when ρ is of course positive and rational, the c's are constants, and $\rho_1, \rho_2, \ldots$ are in ascending order of magnitude.

It is now evident that we can form a scale of integral functions; thus, in between functions with the algebraic zeros

$$a_n = n^{\rho_1} \quad \text{and} \quad a_n = n^{\rho_2}, \quad \text{where } \rho_2 > \rho_1,$$

will come functions with zeros like

$$n^{\rho_1} \log n, \quad n^{\rho_1} \log n \,.\, \log \log n \text{ and so on.*}$$

Such functions we call simple integral functions of finite order with a single simple transcendental sequence of zeros; or, in brief, functions of transcendental sequence.

Thus
$$\prod_{n=1}^{\infty} \left[1 + \frac{z}{(n \log n)^2}\right]$$

is a function of transcendental sequence of order $\frac{1}{2}$ and genre zero.

§ 15. Functions of zero order, which must always be of transcendental sequence, can be classified in the same way. The most simple is $\prod\limits_{n=1}^{\infty} \left[1 + \frac{z}{c^n}\right]$.

Then we consider functions whose zeros are obtained by multiplying c^n by an algebraic function of n. The next step is obviously to introduce intermediate functions by means of logarithmic terms, and so on. Then we introduce functions formed from sets of zeros of still more emphatic convergence, such as

$$\prod_{n=1}^{\infty} \left[1 + \frac{z}{e^{e^n}}\right].$$

The range is obviously limitless.

§ 16. It is worth noticing that the *density* of the zeros along the (possibly curved) line on which they lie, decreases with the increase of the convergence of the function. The zeros of the higher functions of zero order have therefore a density which becomes less as we go higher. The conception of the density of a function is perhaps the most easy way of intuitively classifying it.

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[*] The analogy of the De Morgan and Bertrand scales of convergence is almost too obvious to need mention.

The investigation of the character at infinity of the zero-lines of simple integral functions belongs to the theory of functions of real variables. I do not propose to undertake it here. It is, however, evident that such lines cannot curl round infinity when they belong to functions of finite non-zero order with algebraic zeros:* they approach this point in a line which becomes ultimately straight.

§ 17. A function with a finite number of simple sequences of zeros can evidently be built up of a number of functions, each with a single sequence of zeros.

The function will thus have a finite number of lines of zeros tending to infinity.

When the zeros of a function of order ρ are all of the same character and form m lines symmetrically ranged round the origin, the function will be equal to a function of $\zeta\ (= z^m)$ of order $\dfrac{\rho}{m}$.

Thus a function of order $\frac{1}{2}$ with the sequences

$$\left.\begin{aligned} a_n' &= n^2 \\ a_n'' &= \omega n^2 \\ a_n''' &= \omega^2 n^2 \end{aligned}\right\} \text{where } \omega^3 = 1,$$

is given by the product $\prod\limits_{n=1}^{\infty}\left[1 - \dfrac{z^3}{n^6}\right]$ which, considered as a function of z^3, is of order $\frac{1}{6}$.

§ 18. A function, each of whose zeros is repeated a definite number of times, k (say), is substantially the k^{th} power of a function with the same sequences of non-repeated zeros.

When the n^{th} zero of a function of simple sequence is repeated a number of times dependent upon n, we call the function in brief a *simple repeated function.* We can obviously have repeated functions with any number of sequences of zeros. We may, as before, limit our consideration to a function with a single sequence of zeros; such a one may be written

$$\mathrm{F}(z) = \prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{a_n}\right)^{\mu_n} e^{\mu_n \sum\limits_{m=1}^{\rho_n - 1} \frac{1}{m}\left(-\frac{z}{a_n}\right)^m}\right].$$

The quantity μ_n must, in order that the repetition of the zero may not be meaningless, be an integral number depending upon n; but, if we take the principal values of the ensuing expressions, it is evident that we may get a generalised repeated function by regarding μ_n as a general function of n.

The quantity ρ_n must be so chosen that $\sum\limits_{n=1}^{\infty} \dfrac{\mu_n}{a_n^{\rho_n}}$ is convergent.

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[*] This statement does not deny that they can curl a finite number of times in the finite part of the plane.

We must then, in general, have $\underset{n=\infty}{\mathrm{L}t}\left[\dfrac{\mu_n^{\frac{1}{n}}}{a_n^{\frac{\rho_n}{n}}}\right] = 0$; that is to say, $a_n^{\frac{\rho_n}{n}}\mu_n^{-\frac{1}{n}}$ must increase indefinitely with n. We can no longer assign $\log n$ as a value for ρ_n, which is always sufficient to ensure convergence, as was the case with simple non-repeated functions.

§ 19. It is evident that we may regard the value of ρ for which, ϵ being a small real positive quantity,

$$\sum_{n=1}^{\infty} \frac{\mu_n}{a_n^{\rho+\epsilon}} \text{ is convergent and } \sum_{n=1}^{\infty} \frac{\mu_n}{a_n^{\rho-\epsilon}} \text{ is divergent}$$

as the *order* of the repeated function. When ρ is an integer, the order is equal to the genre: in other cases the genre is the integer next greater than ρ.

If the order is not infinite, and the sequence of zeros to a first approximation algebraic, μ_n must be algebraic also.

Suppose that

$$\underset{n=\infty}{\mathrm{L}t}\ \frac{a_n}{n^{\rho}} = 1 \quad\text{and}\quad \underset{n=\infty}{\mathrm{L}t}\ \frac{\mu_n}{n^{\sigma}} = 1,$$

then, we shall have for the determination of ρ_n, $\rho\rho_n - \sigma > 1$, or $\rho_n > (\sigma + 1)/\rho$.

Repeated functions of infinite order will not be considered in the present memoir.

§ 20. Hitherto we have limited ourselves to integral functions which possess a finite number of simple sequences of zeros. But we have not thus exhausted the category of integral functions. Instead of the typical zero being a definite function of the single number necessary to define its position in the series to which it belongs, it may be a function of two or more numbers and belong to a doubly or multiply infinite sequence. In such case we say that the function is a double or multiple integral function.

Thus the Weierstrassian σ function is a double integral function, and another function of the same category is the double-gamma function to which reference has been made in § 3.

The multiple integral functions always have ultimately a lacunary space* in the region near infinity. In the case of WEIERSTRASS' σ function, this lacunary space covers the whole region near infinity; for the double-gamma function this space lies between the negative directions of the axes of ω_1 and ω_2.

By a well-known theorem due to JACOBI,† functions of treble or higher sequence with periodic zeros cannot exist. This theorem may be extended, and we may prove that there must, in functions whose sequence is greater than double, be such relations

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* The zeros will, of course, only crowd together indefinitely on the equivalent NEUMANN sphere. The possibility, or otherwise, of summable divergent expansions is the reason for the nomenclature.

† 'Ges. Werke,' vol. 2, pp. 27–32.

among the parameters that the region near infinity is not ultimately a lacunary space. The parameters are, of course, the constants which enter into the expression of the general zero in the form

$$a_{n_1, n_2} \ldots = \phi(n_1, n_2, \ldots).$$

Such functions have been scarcely considered in analysis. The n^{ple} gamma function is the most simple example which it is possible to give. The theory requires development, since from quotients of multiple integral functions can be built up the general solution of a linear difference equation.

It is to be noticed that, by the coalescence of the parameters, multiple integral functions give rise to functions of lower sequence with repeated zeros. Thus the function*

$$\mathrm{G}(z) = \frac{1}{\Gamma(z)} (2\pi)^{\frac{z}{2}} e^{-\frac{z}{2} - \frac{1+\gamma}{2} z^2} \prod_{k=1}^{\infty} \left[\left(1 + \frac{z}{k}\right)^k e^{-z + \frac{z^2}{2k}}\right]$$

arises from the double gamma function when the parameters ω_1 and ω_2 each become equal to unity.

The separation of multiple functions into functions with repeated and non-repeated zeros and their classification would be carried out on parallel lines to the process adopted for simple functions. As, however, detailed developments of the asymptotic expansions of such functions are not investigated in the present memoir, I do not intend to consider such functions further.

It has been already observed that by the substitution of z^m (m integral) for z, we derive from any simple integral function a function with m times as many sequences of zeros. The substitution of e^z for z will transform a simple function into one of double sequence. [An example of this is given subsequently (§ 62), where LAMBERT's function is derived from one of simple sequence.] By transformations of greater complexity we may evidently construct functions of limitless range.

§ 21. We are still far from exhausting the category of integral functions. For instance, we may have *ring* functions, that is to say, functions whose zeros are situated on concentric circles : the number of zeros on the n^{th} circle depending upon n.

We can readily see that such a function is given by the product $\prod_{n=1}^{\infty} \left[1 - \left\{\frac{z}{\phi(n)}\right\}^{\chi(n)}\right]$, where $\chi(n)$ is a function of n which is equal to an integer for all values of n, and where, if $\chi(n) = r$, inversely $n = \psi(r)$, and

$$\underset{r=\infty}{\mathrm{Lt}} \left|\sqrt[r]{\phi[\psi(r)]}\right| = \infty.$$

For, the product will converge with

$$\prod_{n=k}^{\infty} \left[1 - \left\{\frac{z}{\phi(n)}\right\}^{\chi(n)}\right]$$

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[*] See a paper by the author, 'Quart. Journ. Math.,' vol. 31, pp. 264 *et seq.*

the first $k - 1$ terms for which $|z| \geqq \phi(n)$ being omitted. Thus it converges with

$$\text{Exp.}\left[-\sum_{m=1}^{\infty}\sum_{n=k}^{\infty}\frac{1}{m}\left\{\frac{z}{\phi(n)}\right\}^{m\chi(n)}\right].$$

The modulus of the term inside the bracket is less than

$$\sum_{m=1}^{\infty}\sum_{n=k}^{\infty}\left[\frac{|z|}{|\phi(n)|}\right]^{m\chi(n)} < \sum_{n=k}^{\infty}\frac{\left|\dfrac{z}{\phi(n)}\right|^{\chi(n)}}{1-\left|\dfrac{z}{\phi(n)}\right|^{\chi(n)}}.$$

Now $1 - \left|\dfrac{z}{\phi(n)}\right|^{\chi(n)}$ $(n = k, k + 1 \ldots \infty)$ has for its greatest value a finite positive quantity A (say). The product then converges if $\sum\limits_{n=k}^{\infty}\left|\dfrac{z}{\phi(n)}\right|^{\chi(n)}$ converges, which is ensured by the condition assigned at the outset.

The function whose existence has thus been established has $\chi(n)$ zeros on a circle of radius $|\phi(n)|$. If, since the assigned condition makes the order of $\phi(n)$ greater than that of $\chi(n)$, the zeros will ultimately be separated by arcs of infinite length.

§ 22. A little ingenuity will enable us to construct other functions of types innumerable, among them what BOREL has called functions "*à croissance irrégulière*."[*] The survey gradually forces upon us the conclusion that we cannot expect to find any general law as to the behaviour of all integral functions near their essential singularity which is not a disguised truism.[†] MM. HADAMARD[‡] and BOREL have given laws relating to the increase of all integral functions. It seems to me that such laws must be limited to particular classes of functions, and that such delimitation cannot be stated too explicitly. Consequently in this memoir I have taken the most simple functions and have endeavoured to study in detail their behaviour near the essential singularity, for I believe that by such means the progress made will be sure, if slow.

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[*] BOREL, ['Fonctions Entières,' Note III.], gives an example of such a function in the form of a TAYLOR'S series.

[†] Such a term I should apply to M. BOREL'S law "the maximum value of a function is equal to the inverse of its minimum value on an infinite number of circles at infinity." For this law is an immediate consequence of the possibility of asymptotic expansions (*see* Part II. of this memoir).

[‡] OSGOOD ('Bulletin of the American Math. Soc.,' Nov., 1898, note, p. 80) states that the analysis used to prove HADAMARD'S most general law requires revision. And it is to be noted that HADAMARD ('Liouville,' 4 ser., t. 9, p. 173) assumes that $\phi(m)$ is continuous, increasing, and such that $\mathrm{L}\phi(m) + \dfrac{k}{m}$ constantly increases ultimately.

PART II.

The Theory of Divergent Series.

§ 23. The development of the theory of divergent series is an interesting instance of the progress of mathematical thought. The beginning was purely arithmetic: to find some approximation to the value of $n\,!$, where n is a very large integer.* In the result it appeared that the value of $\log n\,!$ could be more and more nearly calculated by adding on successive terms of a series proceeding by powers of $\frac{1}{n}$. The error is of the order of magnitude of the term of the series next after the one at which we stop. And, most important fact of all, the series is divergent.

If $n\,!$ be replaced by $\Gamma(n+1)$, a similar result can be obtained, which holds for all real positive values of n.

Finally, there comes the enquiry as to what meaning, if any, can be attached to the equality in the case in which n is any complex quantity.

Other approximations undergo the same process of development, so that it becomes necessary to try and construct a formal theory.

What we may call the arithmetic theory has been given by POINCARÉ,† for the case in which all the quantities involved are real:—a restriction which the author subsequently assumes to be unnecessary.

For the more extended case, when z is any complex quantity, we may say that the divergent series $a_0 + \frac{a_1}{z} + \ldots + \frac{a_n}{z^n} + \ldots$ of which the sum of the first $(n+1)$ terms in S_n, will, when $|z|$ is very large, be an asymptotic expansion for a function $J(z)$ if the expression $|z^n(J - S_n)|$ tends to zero, as z tends to infinity.

Thus, if z be sufficiently large, $|z^n(J - S_n)| < \epsilon$ where ϵ is very small.

The error $J - S_n = e/z^n$ committed in taking for the function J the first $\overline{n+1}$ terms of the series has a modulus which is infinitely smaller than the modulus of the error $J - S_{n-1} = a_n + e/z^n$ obtained by taking only the first n terms, for $|a_n|$ is in general finite, and $|e|$ is very small.

In view of subsequent results, it proves necessary to define the equality of the function and divergent series for values of z which lie along some definite line tending to infinity. We do not then assume that the expansion is possible all round the point $z = \infty$.

It will be sufficient to recapitulate the results which POINCARÉ obtains.

We may multiply two asymptotic series together by the same rules as we should apply to absolutely convergent series.

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* Stirling, 'Methodus Differentialis' (1730).

† 'Acta Mathematica,' 8, pp. 295–344; 'Mécanique Céleste,' vol. 2, pp. 12–14.

In particular, we may raise an asymptotic series to any finite power, and it will then represent the corresponding power of the function represented by the original series.

The term-by-term integral of an asymptotic series is equal to the integral of the function which it represents: in brief, we may integrate an asymptotic series.

In general, we may not differentiate an asymptotic equality.

[Nevertheless, we may differentiate most of the expansions which arise naturally in analysis, and are not constructed artificially.]

Similarly, if an asymptotic equality involves an arbitrary parameter, we may not in general (but we may fairly safely in practice) differentiate with respect to that parameter.

Such are the main propositions of the arithmetic theory of asymptotic expansions.

The difficulties inherent in the theory are obvious when we attempt its application. We have, in all cases, to investigate a superior limit to the remainder of the series after the first $(n + 1)$ terms have been taken; and, to do this, we must have command, even for the most simple cases, of analytical processes of great complexity and power.

§ 24. We proceed then to consider these series from the function-theoretic point of view.

That is to say, on the one hand, we attempt to give a definition to a divergent series which shall harmonise with the development of WEIERSTRASS' theory, and on the other, we enter more deeply into the nature of the essential singularity of the function of which the divergent series is the expansion.

Suppose first that we have a series $a_0 + a_1 z + \ldots + a_n z^n + \ldots$ of finite radius of convergency ρ, so that by CAUCHY'S rule, $\underset{n=\infty}{Lt} \sqrt[n]{a_n} = \rho^{-1}$.

When $|z|$ is greater than ρ, the series is divergent and our fundamental conception of a series as a command to add in order successive terms leads to no result.

And yet, if the function which the series represents be not one which has the circle of radius ρ as a line of essential singularity, the function exists outside this circle, and admits an analytic continuation. Thus the function exists even when the series is divergent.

Can we not then regard the series when divergent as a command to perform certain operations which shall yield the analytic continuation of the function? We can do so, and in an infinite number of ways.

The most simple is, perhaps, given by an extension of a process developed by BOREL.*

Let the plane of the variable x be dissected by some line going from 0 to ∞ to the right of the axis of y.

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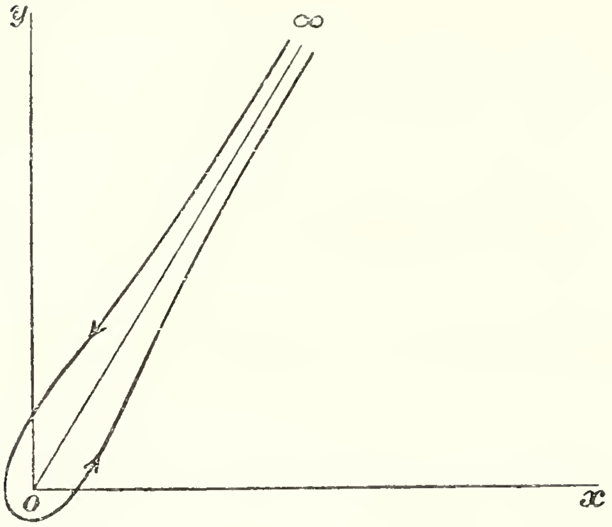
* "Théorie des séries divergentes sommables," 'Liouville,' 5 sér., t. 2, pp. 103 *et seq.* "Mémoire sur les séries divergentes," Ann. de l'École Normale Supérieure, 3 sér., t. 16, pp. 1 *et seq.*

This line of section will render $(-x)^{z-1} = e^{(z-1)\log(-x)}$ uniform, and we shall take that value which is real when x is real and negative.

Then it is known that*



$$\Gamma(\theta) = \frac{\iota}{2\sin\pi\theta}\int(-x)^{\theta-1}e^{-x}\,dx$$

where the contour of the integral embraces the line of section as in the figure.

From the original series

$$a_0 + a_1z + \ldots + a_nz^n + \ldots$$

and an auxiliary function

$$\chi(z) = c_0 + c_1z + \ldots + c_nz^n + \ldots$$

in which $c_n = \dfrac{1}{\Gamma(n+\theta)}$—$\theta$ being any arbitrary quantity—construct the function

$$G(x) = a_0c_0 + a_1c_1x + \ldots + a_nc_nx^n + \ldots$$

This function will be an integral function, for

$$\underset{n=\infty}{\mathrm{L}t}\sqrt[n]{a_nc_n} = \underset{n=\infty}{\mathrm{L}t}\frac{\sqrt[n]{a_n}}{\sqrt[n]{\Gamma(n+\theta)}} = \underset{n=\infty}{\mathrm{L}t}\frac{c}{\rho n} = 0.$$

Consider now the integral

$$\frac{\iota}{2\sin\pi\theta}\int G(xz)\,e^{-x}(-x)^{\theta-1}\,dx.$$

This integral is equal to

$$\frac{\iota}{2\sin\pi\theta}\int\sum_{n=0}^{\infty}\left[a_nc_nx^nz^n\right]e^{-x}(-x)^{\theta-1}\,dx, \quad \text{or} \quad \sum_{n=0}^{\infty}a_nz^n.$$

That is to say, when $|z| < \rho$, the integral represents the same function as the original series. For *all* values of $|z|$, the integral, provided it has a meaning, represents the analytic continuation of the series. And if, when the series is divergent, we regard it as a command to perform the processes which lead to the integral

$$\frac{\iota}{2\sin\pi\theta}\int G(xz)\,e^{-x}(-x)^{\theta-1}\,dx,$$

we shall obtain a conception of such a divergent series which is in harmony with WEIERSTRASS' theory of functions.

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* See a paper by the author, 'Messenger of Mathematics,' vol. 29, p. 105.

§ 25. We now enquire whether the domain of existence of the integral is coextensive with the domain of existence of the analytic function defined by the original series. Just as the series ceases to define the function by becoming divergent, so the integral may cease to be an adequate expression by becoming infinite.

Consider the series $1 + z + z^2 + \ldots + z^n + \ldots$

The "sum" of this series, when divergent, is represented by the integral

$$\frac{\iota}{2 \sin \pi\theta} \int \mathrm{G}(xz)\, e^{-x} (-x)^{\theta-1}\, dx, \text{ in which } \mathrm{G}(xz) = \sum_{n=0}^{\infty} \frac{(xz)^n}{\Gamma(n+\theta)},$$

and the integral is taken round some contour embracing an axis in the positive half of the z-plane.

Make now θ tend to unity. Then $\mathrm{G}(xz)$ becomes e^{xz}, and the integral becomes $\int_0^{\infty} e^{-x(1-z)}\, dx$, taken along some line in the positive half of the z-plane.

Suppose now that $x = \rho e^{\iota\theta}$, $z = 1 + re^{\iota\phi}$ where θ and ϕ are both in absolute value not greater than π. Since the axis of the integral lies in the positive half of the z-plane, $\frac{\pi}{2} - \epsilon \geqq \theta \geqq -\frac{\pi}{2} + \epsilon$, where ϵ is a positive quantity as small as we please. The amplitude of $x(z-1)$ is $\theta + \phi$, and that the integral may be finite this quantity must be such that $\mathfrak{R}(z-1)$ is negative. Therefore $\frac{3\pi}{2} > \theta + \phi > \frac{\pi}{2}$ or $-\frac{\pi}{2} > \theta + \phi > -\frac{3\pi}{2}$. These conditions can always be satisfied by values of θ within the assigned range, if ϕ does not lie between or at the limits of the range bounded by ϵ and $-\epsilon$.

We thus see that the function $1/(1-z)$ is represented by the series

$$1 + z + z^2 + \ldots + z^n + \ldots$$

within a circle of radius unity; and by the integral

$$\frac{\iota}{2 \sin \pi\theta} \int \left[\sum_{n=0}^{\infty} \frac{(xz)^n}{\Gamma(n+\theta)} \right] e^{-x} (-x)^{\theta-1}\, dx$$

for all values of z except those which lie on that part of the real axis between the points 1 and ∞.

§ 26. Similarly the series $\sum_{n=0}^{\infty} \frac{z^n}{n+1}$, or its integral equivalent when it is divergent, will represent $-z^{-1} \log(1-z)$, provided z does not lie on that part of the real axis between 1 and ∞. And the same is true of $(1-z)^{-m}$ and its equivalent series, when m is not necessarily an integer. These statements form easy examples which the reader can at once work out for himself.

It is interesting to notice that the lines from the singularities to infinity intervene to give uniformity to the non-uniform functions to which divergent series may "sum." Thus the divergent series $\sum\limits_{n=0}^{\infty} \frac{z^n}{n+1}$ represents the non-uniform function $z^{-1}\log(1 - z)$, which becomes uniform when a cross-cut is made along the real axis from 1 to $+ \infty$.

§ 27. Suppose now that we have any function with singularities lying outside a circle of radius ρ, within which the function is represented by the convergent series

$$a_0 + a_1 z + \ldots + a_n z^n + \ldots$$

We may join the singularities by straight lines to infinity, each line being the continuation of the direction from the origin to its initial point. Then within the simply connected area thus formed we may replace the function by a set of integrals of the type

$$\frac{\iota}{2\sin\iota\theta}\int G(xz)\, e^{-x}(-x)^{\theta-1}\, dx.$$

Which we can therefore regard as the "sum" of the divergent series within the region in question, whenever this set of integrals has a meaning.

Although in general this will not be the case, we can nevertheless, if the function represented by the series has only a finite number of poles outside its circle of convergence and within a circle of finite radius σ, greater than the radius of convergence ρ, split up the given series into a sum of others each of which, except the last, will be divergent, but capable of being represented by an integral of the foregoing type, while the last series is convergent within this circle of radius σ. The circumstances under which the whole series can be represented by a definite integral over the region of its existence I hope to discuss elsewhere. The problem is bound up with the determination of the number and nature of the singularities of a TAYLOR's series and is, therefore, connected naturally with the researches of DARBOUX,[*] HADAMARD,[†] BOREL,[‡] FABRY,[§] LE ROY,[||] LINDELOF,[¶] and LEAU.[**]

§ 28. So far we have been concerned with the summation of divergent series of ascending powers of z which are convergent for sufficiently small values of $|z|$. We will now *define* asymptotic series as those which are divergent, however small $|z|$ may be, and we proceed to consider their summation.

At the outset we can see that the problem is essentially different from the one

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[*] DARBOUX, 'Liouville' (1878), 3 sér., t. 4, pp. 5–56, 377–416.

[†] HADAMARD, 'Liouville' (1892), 4 sér., t. 8, pp. 101–186.

[‡] BOREL, 'Comptes Rendus,' October 5 and December 14, 1896; December 12, 1898; 'Acta Mathematica,' 21; 'Liouville' (1896), 5 sér., t. 2.

[§] FABRY, 'Ann. de l'Éc. Nor. Sup.' (1896), 3 sér., t. 13, pp. 367–399; 'Acta Mathematica' (1899), t. 22, pp. 65–87; 'Liouville' (1898), 5 sér., t. 4, pp. 317–358.

[||] LE ROY, 'Comptes Rendus,' October 21, 1898, and February 20, 1899.

[¶] LINDELOF, 'Acta Societatis Fennicæ,' 1898.

[**] LEAU 'Liouville' (1899), 5 sér., t. 5, pp. 365–425.

just considered. Instead of the process of summation leading to the same result, whatever the nature of the integral process chosen, we can obtain an infinite number of results, each associated function leading to a different function, of which the given series may be regarded as the asymptotic expansion. For when the divergent series is convergent for sufficiently small values of $|z|$, it defines a function over that area of convergence, and any summation process can only lead to the analytic continuation of a definite branch of that function. But a true asymptotic series has no area of convergence, and any meaning which we care to attach to it will harmonise with WEIERSTRASS' theory of functions.

The essential nature of the difference between the two kinds of series may be brought out in another way. A series convergent for sufficiently small values of $|z|$ represents a function regular in the neighbourhood of the origin. But any function which a true asymptotic series can represent will have the origin as an essential singularity. And, therefore, not only can many functions with an essential singularity at the origin have the same asymptotic expansion, but also the same function may have different asymptotic expansions in different areas having the origin as apex. It is almost impossible to imagine a vagary which an essential singularity will not possess, and this fact we cannot, throughout the whole of the investigation, too carefully bear in mind.

Inasmuch as any means of regarding an asymptotic series leads to a result peculiar to that means, we must choose our process with care so as to obtain the most simple result, and, if possible, so as to ensure that our conception of such series agrees with the arithmetic point of view by which historically they were generated.

§ 29. Suppose, in the first place, that we have given the asymptotic series

$$a_0 + a_1 z + a_2 z^2 + \ldots + a_n z^n + \ldots ,$$

in which, by CAUCHY's rule, $\mathop{\mathrm{L}t}\limits_{n=\infty} \sqrt[n]{a_n} = \infty$. And suppose further that $\mathop{\mathrm{L}t}\limits_{n=\infty} \dfrac{\sqrt[n]{a_n}}{n} = 0$.

Then the associated function

$$\mathrm{G}(z) = a_0 c_0 + a_1 c_1 z + \ldots + a_n c_n z^n + \ldots ,$$

in which $c_n = \dfrac{1}{\Gamma(n+\theta)}$, will be an integral function.

It is a natural extension, then, of our previous ideas to regard the asymptotic series as the expansion of the integral

$$\frac{\iota}{2 \sin \pi\theta} \int \mathrm{G}(xz)\, e^{-x} (-x)^{\theta-1}\, dx,$$

and, conversely, to regard the integral as the "sum" of the asymptotic series.

The point $z = 0$ will be an essential singularity of the function of which the integral is the formal expression. For certain values of z near $z = 0$ the integral can probably take values which differ infinitely for the smallest change in the value of z. This will happen when z lies on a line of zeros or poles crowding to $z = 0$. Along such lines, or quite possibly within areas of the same nature, the asymptotic series will cease to represent the function.

Further, there must always be such lines or areas of non-representation, for the only functions to the essential singularities of which poles or zeros or other singularities do not crowd are of the types $e^{\frac{1}{x}}$, $e^{e^{\frac{1}{x}}}$ . . . . , which cannot admit of asymptotic expansion.

We have then the fundamental result that the integral cannot represent the "sum" of the series right round $z = 0$. There will be certain lines or areas with $z=0$ as extremities or vertices along which the asymptotic series cannot be "summed" by any process which we may employ: these lines or areas will differ with the different processes, but will never be absent altogether.

There are, of course, asymptotic series of the prescribed type which can never be "summed" by any process which we may employ. Such a one is $\sum\limits_{n=0}^{\infty} a_{c_n} z^{c_n}$, in which $\mathop{\text{Lt}}\limits_{n=\infty} (c_{n+1} - c_n) = \infty$ and $\mathop{\text{Lt}}\limits_{n=\infty} \sqrt[n]{a_n} = \infty$. But such series will never arise naturally in analysis, and we do not, therefore, need to trouble about them.

§ 30. We have now to consider whether, when a series of the prescribed type is "summed" by means of the process indicated, the function which results admits the series as an arithmetically asymptotic expansion according to POINCARÉ's definition.

Denote by $f(z)$ the integral which is the result of summing the series

$$a_0 + a_1 z + \ldots + a_n z^n + \ldots ,$$

in which $\mathop{\text{Lt}}\limits_{n=\infty} \sqrt[n]{a_n} = \infty$ and $\mathop{\text{Lt}}\limits_{n=\infty} \dfrac{\sqrt[n]{a_n}}{n} = 0$.

The associated function for the series is

$$G(z) = a_0 c_0 + a_1 c_1 z + \ldots + a_n c_n z^n + \ldots ,$$

and for s_n, the sum of the first n terms of the series, is

$$a_0 c_0 + a_1 c_1 z + \ldots + a_n c_n z^n.$$

Hence

$$\frac{f(z) - s_n}{z^n} = \frac{\iota}{2 \sin \pi\theta} \int \frac{G_{n+1}(z, x)}{z^n} e^{-x} (-x)^{\theta-n-1}\, dx,$$

where

$$z^{-n} G_{n+1}(z, x) = zx \left[a_n c_n + a_{n+1} c_{n+1} (xz) + \ldots\right].$$

Now $z^{-n} G_{n+1}(z, x)$ is an absolutely convergent series, and $|z^{-n} G_{n+1}(zx)|$ tends to zero as n tends to infinity.

Moreover $z^{-n} G_{n+1}(zx)$ and $G(xz)$ are functions which, while n has any finite value, have the same character near $|xz| = \infty$, for they only differ by the polynomial $a_0c_0 + a_1c_1zx + \ldots + a_nc_n(zx)^n$.

Therefore the integral $\frac{\iota}{2 \sin \pi\theta} \int \frac{G_{n+1}(zx)}{z^n} e^{-x}(-x)^{\theta-n-1}\, dx$ will represent an analytic function of z whenever $\frac{\iota}{2 \sin \pi\theta} \int G(xz)\, e^{-x}(-x)^{\theta-1}\, dx$ does so; and the two functions will have the same character near $z = 0$.

Therefore, within those areas for which the second integral represents the "sum" of the given asymptotic series, the first integral is finite, and $|z^{-n}\{f(z) - s_n\}|$ tends to zero as $|z|$ tends to zero.

Thus the asymptotic equality satisfies POINCARÉ'S arithmetic definition. The reader must note very carefully that this theorem does *not* apply to divergent series which have a finite radius of convergence. It is necessary that $|z|$ should tend to zero. No computer, for instance, could make $1 - 2 + 2^2 - 2^3 + \ldots$ tend to $\frac{1}{1+2}$.

§ 31. Suppose now that we differentiate the series

$$a_0 + a_1z + \ldots \qquad + a_nz^n + \ldots$$

in which

$$\underset{n=\infty}{\mathrm{L}t} \sqrt[n]{a_n} = \infty, \text{ and } \underset{n=\infty}{\mathrm{L}t} \frac{\sqrt[n]{a_n}}{n} = 0.$$

We shall obtain the series

$$a_1 + 2a_2z + \ldots + na_nz^{n-1} \ldots$$

If we "sum" this series by the exponential process (the name which it is convenient to give to the process employed in the preceding paragraphs) we obtain the integral

$$\frac{\iota}{2 \sin \pi\theta} \int G_1(xz)\, e^{-x}(-x)^{\theta-1}\, dx, \text{ in which}$$

$$G_1(xz) = a_1c_1 + 2a_2c_2xz + \ldots + na_nc_n(xz)^{n-1} + \ldots$$

We thus see that, since this series is an integral function,

$$G_1(xz) = \frac{\partial}{\partial z} G(xz).$$

Therefore the "sum" of the series $a_1 + 2a_2z + \ldots + na_nz^{n-1} + \ldots$ is

$$\frac{\iota}{2 \sin \pi\theta} \int \frac{\partial}{\partial z} G(xz)\, e^{-x}(-x)^{\theta-1}\, dx$$

Now so long as the integral

$$\frac{\iota}{2 \sin \pi\theta} \int \mathrm{G}(xz)\, e^{-x} (-x)^{\theta-1}\, dx$$

is within the regions surrounding $z = 0$, for which the original series can be summed, the differential coefficient of the function which it represents is the function represented by the integral

$$\frac{\iota}{2 \sin \pi\theta} \int \frac{\partial}{\partial z} \mathrm{G}(xz)\, e^{-x} (-x)^{\theta-1}\, dx,$$

for we do not transgress the rules which govern differentiation under the sign of integration.*

Therefore, within the region for which an asymptotic equality is valid, such equality may be differentiated.

Similarly such equality may be integrated. And the process of differentiation or integration may be repeated any number of times.

§ 32. We have hitherto limited ourselves to the consideration of asymptotic series of the type

$$a_0 + a_1 z + \ldots \qquad + a_n z^n + \ldots$$

in which $\underset{n=\infty}{\mathrm{Lt}} \sqrt[n]{a_n} = \infty$ and $\underset{n=\infty}{\mathrm{Lt}} \dfrac{\sqrt[n]{a_n}}{n} = 0.$

The first condition is necessary that the series may have zero radius of convergency, that is to say, that it may be asymptotic.

The second condition was requisite in order to ensure the applicability of the exponential process.

It is convenient to call an asymptotic series for which $\underset{n=\infty}{\mathrm{Lt}} \dfrac{\sqrt[n]{a_n}}{n} = 0$ an asymptotic series of the first order; one for which this limit is greater than zero, but $\underset{n=\infty}{\mathrm{Lt}} \dfrac{\sqrt[n]{a_n}}{n^2} = 0$, a series of the second order, and so on.

We have given in the preceding paragraphs the theory of summation of series of the first order. But suppose that we wish to sum one of the most simple asymptotic series, that for $\log \dfrac{\Gamma(z+a)}{\Gamma(z)\, z^a}$, namely $\sum\limits_{n=1}^{\infty} \dfrac{(-)^{n-1} \mathrm{S}_n(a)}{n z^n}$, where $\mathrm{S}_n(a)$ is HERMITE's Bernoullian function.

By CAUCHY's theorem, re-discovered by HADAMARD, we know that

$$\underset{n=\infty}{\mathrm{Lt}} \sqrt[n]{\frac{\mathrm{S}n(a)}{n\,!}} = 2\pi\,;$$

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* JORDAN, 'Cours d'Analyse,' 2nd edition, vol. 2, pp. 154–157.

for the expansion

$$\frac{e^{ax}-1}{e^x-1}-a=\sum_{n=1}^{\infty}\frac{S_n(a)}{n\,!}x^n$$

is only valid within a circle of radius 2π.

We see then that the asymptotic series is such that, if we denote the coefficient of $\frac{1}{z^n}$ by a_n,

$$\underset{n=\infty}{\mathrm{L}t}\frac{\sqrt[n]{a_n}}{n}>0,\quad\text{and}\quad\underset{n=\infty}{\mathrm{L}t}\frac{\sqrt[n]{a_n}}{n^2}=0.$$

The series is thus of the second order. And the associated function formed as in the preceding paragraphs will be

$$G(n)=\sum_{n=1}^{\infty}\frac{(-)^{n-1}S_n(a)}{n\,.\,n\,!}n^n$$

which is not an integral function.

Our analytical machinery therefore breaks down, and we must attempt to extend it.

Just as the original problem admitted of an infinite number of solutions, so we may now proceed in an infinite number of ways to give an analytical meaning to asymptotic series of the second or higher orders.

Of these two would appear to be most natural. We may either use some more powerful associated function than we used in the exponential process, or we may repeat the exponential process until we arrive at a finite analytical function.

§ 33. Let us consider in the first place the second of these alternatives.

If we have the asymptotic series

$$a_0+a_1z+\ldots,+a_nz^n+\ldots,$$

we have agreed to say that this series is the expression of the analytic function $\frac{\iota}{2\sin\pi\theta}\int G_1(xz)\,e^{-x}(-x)^{\theta-1}\,dx$, whenever this integral has a meaning, that is, whenever $G_1(xz)$ is an integral function, and the integral is not infinite.

Now

$$G_1(z)=\frac{a_0}{\Gamma(\theta)}+\frac{a_1}{\Gamma(1+\theta)}z+\ldots+\frac{a_n}{\Gamma(n+\theta)}z^n+\ldots$$

$$=a_0'+a_1'z+\ldots+a_n'z^n+\ldots\text{ (say)},$$

and, if the series is not absolutely convergent over the whole plane, we shall be consistent with our former generalised point of view, if we regard it as determining an analytic function

$$\frac{\iota}{2\sin\pi\theta}\int G_2(xz)\,e^{-x}(-x)^{\theta-1}\,dx,$$

whenever this integral has a meaning.

Now

$$G_2(z) = \frac{a_0'}{\Gamma(\theta)} + \ldots + \frac{a_n'}{\Gamma(n+\theta)} z^n + \ldots$$

$$= a_0'' + \ldots + a_n'' z^n + \ldots \text{ (say).}$$

If the series $G_1(z)$ had a finite radius of convergence, or zero radius of the first order, the function $G_2(z)$ will be an integral function, and by the process just sketched, a definite meaning has been assigned to $G_1(z)$ and the original series.

When, however, $G_1(z)$ has zero radius of convergency of the second or higher order, $G_2(z)$ will not be an integral function, but we must regard the series which it denotes as determining an analytic function

$$\frac{\iota}{2 \sin \pi\theta} \int G_3(xz)\, e^{-x} (-x)^{\theta-1}\, dx,$$

whenever this integral has a meaning, that is, as a preliminary condition, whenever

$$G_3(z) = \frac{a_0''}{\Gamma(\theta)} + \ldots + \frac{a_n''}{\Gamma(n+\theta)} z^n + \ldots$$

is convergent over the whole plane.

The procedure may be repeated indefinitely. If we have started with an asymptotic series which does not ultimately give rise to a function $G_n(z)$ whose finite radius of convergency is a line of essential singularity, we shall ultimately get an analytic function of which the original series is the asymptotic expansion in the vicinity of its essential singularity $z = 0$.

§ 34. The extension which we have just indicated is in harmony with the general theory, but we have still to determine the important point as to whether the asymptotic equality of series and functions satisfies POINCARÉ's arithmetic definition.

Take for simplicity the series of the second order $a_0 + a_1 z + \ldots + a_n z^n + \ldots$, for which the associated series

$$\frac{a_0}{\Gamma(\theta)} + \frac{a_1}{\Gamma(1+\theta)} z + \ldots + \frac{a_n}{\Gamma(n+\theta)} z^n + \ldots$$

has finite radius of convergency and represents the function

$${}_1G(z).$$

The given series gives rise to the function

$$G(z) = \frac{\iota}{2 \sin \pi\theta} \int {}_1G(xz)\, e^{-x} (-x)^{\theta-1}\, dx.$$

Let

$$G_n(z) = a_0 + \ldots + a_n z^n,$$

then

$$G(z) - G_n(z) = \frac{\iota}{2\sin\pi\theta}\int\{{}_1G(xz) - {}_1G_n(xz)\}\,e^{-x}(-x)^{\theta-1}\,dx,$$

where

$${}_1G_n(z) = \sum_{r=0}^{n}\frac{a_r}{\Gamma(r+\theta)}z^n.$$

Now $z^{-n-1}\{{}_1G(xz) - {}_1G_n(xz)\}$ is an analytic function of x of the same character as ${}_1G(xz)$: hence the natures of the two functions $G(z)$ and $z^{-n-1}\{G(z) - G_n(z)\}$ near $z = 0$ are substantially the same. And therefore, in general, if $G(z)$ tends uniformly to a finite limit as z tends to zero in any direction, $z^{-n-1}\{G(z) - {}_nG(z)\}$ also tends uniformly to a finite limit as z tends to zero in the same direction. That is to say, $|z^{-n}\{G(z) - {}_nG(z)\}|$ tends to zero as z tends to zero, so that the divergent series is arithmetically asymptotic for the function $G(z)$.

It is evident that a repetition of the same argument will prove the arithmetic nature of the asymptotic dependence of a series of any order and the function to which it gives rise by successive applications of the exponential process. But one case of exception must be noticed. At each step the equivalence of the asymptotic series and the derived function fails along certain lines or within certain areas radiating from $z = 0$. And, since the effect of such failure is cumulative, it may happen that before the process is finished the equivalence has failed over the whole area around $z = 0$. Either the series is hopeless—an artificial monstrosity that cannot arise in practice—or we need some other process by means of which it can be interpreted.

§ 35. As an example of the process just sketched, consider the asymptotic expansion

$$-\frac{1}{1-s}z^{s-1} + \sum_{n=1}^{\infty}\binom{-s}{n}\frac{S_n'(a)\,z^{n+s-1}}{s+n-1},$$

which, *quâ* function of z, is an asymptotic series of the second order and wherein s and a are any complex or real parameters.

Applying the integral process associated with the exponential function to the series, we obtain the integral

$$\frac{\iota}{2\pi}\int G_1(zx)\,e^{-x}z\,dx,$$

where

$$G_1(u) = -\Gamma(1-s)(-u)^{s-2}\left\{1 + \sum_{n=1}^{\infty}\frac{(-)^n S_n'(a)}{n!}u^n\right\},$$

and we have, for convenience, taken the auxiliary function to be

$$\sum_{n=0}^{\infty}(-)^n\Gamma(2-n-s)\,x^n,$$

so that θ is absorbed in s.

Now $G_1(u)$ is a series of finite radius of convergency, and the analytic function which we take the series to represent is the function of which the series is the expansion within the circle of convergency. The series will therefore denote, with our present conceptions, the function

$$-\Gamma(1-s)\,\frac{e^{-au}}{1-e^{-u}}(-u)^{s-1}.$$

The series with which we commenced may therefore be regarded as giving rise to the analytic function

$$-\frac{\iota}{2\pi}\Gamma(1-s)\int\frac{e^{-axz}}{1-e^{-xz}}(-xz)^{s-1}e^{-x}z\,dx=-\frac{\iota}{2\pi}\Gamma(1-s)\int\frac{e^{-\left(a+\frac{1}{z}\right)t}}{1-e^{-t}}(-t)^{s-1}\,dt$$

on making the substitution $t = xz$.

This function admits when $|z|$ is small, the arithmetically asymptotic expansion from which we started.

When z^{-1} is a large real positive integer, the series and integral become fundamental in the asymptotic definition of the extended Riemann ζ function.

But there can be obtained by other processes an indefinite number of analytic functions, each of which has an essential singularity at $z = 0$, near which point it admits the given series as an arithmetically asymptotic expansion. We proceed to indicate one alternative process by which such an analytic function can be obtained at a single step.

§ 36. For this purpose we use certain results of the theory of the connection between linear difference and differential equations.

Consider the function

$$F(\alpha,\rho_1,\ldots,\rho_m,-x)=1-\frac{\alpha}{1.\rho_1\ldots\rho_m}x+\ldots+\frac{\alpha\,\overline{\alpha+1}\ldots\overline{a+r-1}}{r!\,\rho_1\ldots\rho_m\ldots\overline{\rho_1+r-1}\ldots\overline{\rho_m+r-1}}(-x)^r+\ldots$$

It is evidently a transcendental integral function which is a solution of the differential equation

$$\left[(\vartheta+\alpha)+\frac{1}{x}\vartheta(\vartheta+\rho_1-1)\ldots(\vartheta+\rho_m-1)\right]y=0,$$

wherein the operator $\vartheta = x\dfrac{d}{dx}$.

If y be any solution of this equation, form the function

$$\frac{\iota}{2\sin\pi z}\int y(-x)^{z-1}\,dx,$$

where the contour of the integral and the prescription for $(-x)^{z-1}$ are exactly those employed in the definition of the integral for $\Gamma(z)$ previously employed (§ 24).

On integrating by parts, we have

$$zf(z) = -\frac{\iota}{2\sin\pi z}\int[\vartheta y](-x)^{z-1}\,dx,$$

a relation which may also be written

$$(z+1)f(z+1) = -\frac{\iota}{2\sin\pi z}\int[x\vartheta(y)](-x)^{z-1}\,dx.$$

We thus see that

$$z(z+1-\rho_1)\ldots(z+1-\rho_m)f(z)$$
$$= (-)^{m+1}\frac{\iota}{2\sin\pi z}\int[\vartheta(\vartheta+\rho_1-1)\ldots(\vartheta+\rho_m-1)y](-x)^{z-1}\,dx,$$

and also

$$(z+1-\alpha)f(z+1) = \frac{-\iota}{2\sin\pi z}\int[x(\vartheta+\alpha)y](-x)^{z-1}\,dx.$$

Therefore, since y is a solution of the equation

$$\vartheta(\vartheta+\rho_1-1)\ldots(\vartheta+\rho_m-1)y = -x(\vartheta+\alpha)y,$$

we have

$$f(z+1) = (-)^{m-1}\frac{z.(z+1-\rho_1)\ldots(z+1-\rho_m)}{(z+1-\alpha)}f(z).$$

The general solution of this difference-equation is

$$\Gamma(z)\frac{\Gamma(\alpha-z)}{\Gamma(\alpha)}\cdot\frac{\Gamma(\rho_1)\ldots\Gamma(\rho_m)}{\Gamma(\rho_1-z)\ldots\Gamma(\rho_m-z)}\varpi(z,\alpha,\rho_1,\ldots\rho_m),$$

where $\varpi(z,\alpha,\rho_1,\ldots\rho_m)$ is a simply periodic function of z of period unity.

We have then established the identity

$$\frac{\iota}{2\sin\pi z}\int F_m(\alpha,\rho_1,\ldots\rho_m,-x)(-x)^{z-1}\,dx$$
$$= \frac{\Gamma(z)\Gamma(\alpha-z)}{\Gamma(\alpha)}\cdot\frac{\Gamma(\rho_1)\ldots\Gamma(\rho_m)}{\Gamma(\rho_1-z)\ldots\Gamma(\rho_m-z)}\varpi(z,\alpha,\rho_1,\ldots\rho_m).$$

When $\alpha=\rho_1$, the expression on the left-hand side, and therefore that on the right-hand side must involve $\rho_2\ldots\rho_m$ only. Thus, when $\alpha=\rho_1$, $\varpi(z,\alpha,\rho_1,\ldots\rho_m)$ involves $\rho_2\ldots\rho_m$ only. It must therefore be a function of $\alpha-\rho_1,\ldots\alpha-\rho_m$. Not only so, but it cannot involve these quantities at all; for when $\alpha=\rho_1$, ϖ will be a function of $\rho_1-\rho_2,\ldots\rho_1-\rho_m$, and yet it is independent of ρ_1; and so on when $\alpha=\rho_2,\ldots\alpha=\rho_m$. Thus ϖ is a function of z, simply periodic of period unity, independent of $\alpha,\rho_1,\ldots\rho_m$ and m.

Let $m=1$, $\alpha=\rho_1=1$; then $F_m(\alpha,\rho_1,\rho_2,\ldots\rho_m,-x)$ becomes e^{-x}, and the integral becomes

$$\frac{\iota}{2\sin\pi z}\int e^{-x}(-x)^{z-1}\,dx = \Gamma(z).$$

Thus $\varpi(z) = 1$, and we have finally for all values of $\alpha, \rho_1, \ldots \rho_m$ and z the identity

$$\frac{\iota}{2 \sin \pi z} \int \mathrm{F}_m(\alpha, \rho_1, \ldots \rho_m, -x)(-x)^{z-1}\, dx = \Gamma(z) \cdot \frac{\Gamma(\alpha - z)}{\Gamma(\alpha)} \cdot \frac{\Gamma(\rho_1) \ldots \Gamma(\rho_m)}{\Gamma(\rho_1 - z) \ldots \Gamma(\rho_m - z)}.^{*}$$

This identity is the direct generalisation of the identity

$$\frac{\iota}{2 \sin \pi z} \int e^{-x}(-x)^{z-1}\, dx = \Gamma(z),$$

and we may therefore expect to be able to use it to extend our former process of "summing" asymptotic series.

§ 37. We may, in fact, show at once that we can sum any series of convergency zero $f(z) = a_0 + a_1 z + \ldots + a_n z^n + \ldots$, in which $\underset{n=\infty}{\mathrm{Lt}}\, a_n = (n\,!)^k$, where k is any finite quantity.

For this purpose we put $\alpha = \rho_1 = \ldots = \rho_m = 1$;

$\mathrm{F}_m(x) = 1 + \frac{x}{(1\,!)^m} + \ldots + \frac{x^r}{(r\,!)^m} + \ldots$, and we have $\frac{\iota}{2\pi} \int \frac{\pi^m \mathrm{F}_m(-x)}{[\sin \pi z]^m} (-x)^{z-1}\, dx = [\Gamma(z)]^m$.

Then, with our former notation, we take the auxiliary function

$$\chi(z) = \sum_{n=0}^{\infty} c_n z^n, \text{ where } 1/c_n = [\Gamma(n + \theta)]^m = \frac{\iota}{2\pi} \int \frac{\pi^m \mathrm{F}_m(-x)}{[\sin \pi\theta]^m} (-)^{nm} (-x)^{\theta-1} (-x)^n\, dx.$$

And now $f(z)$ is defined by the integral

$$\frac{\iota}{2\pi} \int \mathrm{G}(-xz)\, \frac{\pi^m \mathrm{F}_m(-x)(-x)^{\theta-1}}{[\sin \pi\theta]^m}\, dx,$$

in which

$$\mathrm{G}(u) = \sum_{n=0}^{\infty} (-)^{nm} a_n c_n u^n.$$

We take $m > k$, and then $\mathrm{G}(u)$ will be an integral function.

For $\underset{n=\infty}{\mathrm{Lt}}\, a_n c_n = n^{n(k-m)} e^{-n(k-m)+\cdots}$; and therefore $\underset{n=\infty}{\mathrm{Lt}} \sqrt[n]{a_n c_n} = 0$.

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[*] In connection with the proof of this formula, the reader may with advantage refer to:—

MELLIN, 'Acta Mathematica,' 8, pp. 37–80; 9, pp. 137–166; 15, pp. 317–384.

" 'Acta Societatis Fennicæ,' t. 20, pp. 1–115.

POINCARÉ, "American Journal," vol. 7, pp. 203–258.

PINCHERLE, 'Accad. dei Lincei,' ser. iv., t. 4, pp. 694–700.

POCHAMMER, 'Mathematische Annalen,' Bd. 38, pp. 586–597; Bd. 41, pp. 197–218.

" 'Crelle,' Bd. 71, pp. 316–352.

ORR, 'Cambridge Phil. Trans.,' vol. 17, pp. 182–199.

We can thus sum any natural series of convergency zero whose n^{th} coefficient is of the same order as a finite power of $n\,!$*

§ 38. But we can go further than this: we can construct inverse functions which will enable us to sum any series of convergency zero.

For we have seen that

$$\frac{\iota}{2\pi}\int \frac{\pi^{2m}\mathrm{F}_{2m}(-x)}{(\sin\pi\theta)^{2m}}(-x)^{n+\theta-1}\,dx = [\Gamma(n+\theta)]^{2m}.$$

Suppose, now, that we construct the function $f(x) = \sum\limits_{m=1}^{\infty} \dfrac{\pi^{2m}\mathrm{F}_{2m}(-x)}{(\sin\pi\theta)^{2m}}$.

This function will be an integral function of x, for we have

$$\begin{aligned} f(x) &= \sum_{r=0}^{\infty}(-x)^r \sum_{m=1}^{\infty}\left[\frac{\pi}{r!\sin\pi\theta}\right]^{2m} \\ &= \sum_{r=0}^{\infty}(-x)^r \frac{\left(\dfrac{\pi}{r!\sin\pi\theta}\right)^2}{1-\left(\dfrac{\pi}{r!\sin\pi\theta}\right)^2}, \end{aligned}$$

which is absolutely convergent for all values of $|x|$.

But, if we operate by our integral on this function, we have $\dfrac{\iota}{2\pi}\displaystyle\int f(x)(-x)^{n+\theta-1}\,dx = \sum\limits_{m=1}^{\infty}[\Gamma(n+\theta)]^{2m}$; and the function $\sum\limits_{m=1}^{\infty}[\Gamma(n+\theta)]^{2m}$ is infinite if $\mathfrak{R}(n+\theta)$ be positive.

If, now, we take $f(x) = \sum\limits_{m=1}^{\infty}\dfrac{b_m\pi^{2m}\mathrm{F}_{2m}(-x)}{(\sin\pi\theta)^{2m}}$, where b_m is so chosen as to make the series $\sum\limits_{m=1}^{\infty} b_m[\Gamma(n+\theta)]^{2m}$ converge for all finite values of n, it is obvious that $f(x)$ will itself converge for all values of x, and so be an integral function.

We may now take for the associated function

$$\chi(z) = c_0 + c_1 z + \ldots + c_n z^n + \ldots, \text{ where } c_n^{-1} = \sum_{m=1}^{\infty} b_m[\Gamma(n+\theta)]^{2m};$$

and by suitable choice of the coefficients b we may make c_n vanish to an order as great as we please.

We can then sum the series $a_0 + a_1 z + \ldots + a_n z^n + \ldots$, where a_n is infinite with n to an order as high as we please. In other words, we have invented the analytical machinery necessary to sum any (natural) asymptotic series.

§ 39. As an example, suppose that we wish to sum a series $a_0 + a_1 z + \ldots + a_n z^n + \ldots$, where a_n is infinite like $e^{\alpha\{\Gamma(n)\}^2}$, where $0 < \alpha < 1$.

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[*] This theorem corrects a mistake in my paper, 'Theory of the Gamma Function,' p. 112.

With our previous notation we take $b_m = \frac{1}{m\,!}$ and

$$f(x) = \sum_{m=1}^{\infty} \frac{\pi^{2m} \mathrm{F}_{2m}(-x)}{m\,!\,(\sin \pi\theta)^{2m}} = \sum_{r=0}^{\infty} (-x)^r \sum_{m=1}^{\infty} \frac{1}{m\,!} \left[\frac{\pi}{r\,!\sin \pi\theta}\right]^{2m} = \sum_{r=0}^{\infty} (-x)^r \left[e^{\left(\frac{\pi}{r\,!\sin \pi\theta}\right)^2} - 1\right]$$

so that $f(x)$ is a transcendental integral function.

Then we have $\frac{\iota}{2\pi} \int f(x)\,(-x)^{n+\theta-1}\,dx = \sum_{m=1}^{\infty} \frac{[\Gamma(n+\theta)]^{2m}}{m\,!} = e^{[\Gamma(n+\theta)]^2} - 1.$

We take the associated function

$$\chi(z) = c_0 + c_1 z + \ldots + c_n z^n + \ldots \text{ where } c_n^{-1} = e^{[\Gamma(n+\theta)]^2} - 1\,;$$

and the integral function

$$\mathrm{G}(z) = a_0 c_0 + \ldots + a_n c_n z^n + \ldots \text{ in which } \mathop{\mathrm{Lt}}_{n=\infty} a_n c_n = \mathop{\mathrm{Lt}}_{n=\infty} \frac{e^{\alpha[\Gamma(n)]^2}}{e^{[\Gamma(n+\theta)]^2}} = 0.$$

Then the sum of the series will be represented by*

$$\frac{\iota}{2\pi} \int \mathrm{G}(-xz)\, f(x)\, (-x)^{\theta-1}\, dx.$$

§ 40. We have now, by means of the generalised exponential functions, given the machinery by which we may expect to be able to "sum" a natural asymptotic series of any order.

It may be proved just as for the fundamental exponential process that the series and the function derived from it have asymptotic equality of the arithmetic type.

Moreover, if we regard the series as having a finite radius of convergency, on which one or more singularities lie, which has shrunk indefinitely, we, as it were, magnify it again by means of the function $\mathrm{F}_m(x)$ so as to obtain the associated function

$$\mathrm{G}(u) = \sum_{n=0}^{\infty} (-)^{nm}\, a_n c_n u^n$$

whose radius of convergency is infinite.

The alternative process consists in successive magnifications by means of the function e^x.

These two processes will in general lead to different results: in each case we shall obtain functions with $z = 0$ as an essential singularity; both functions will have the

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* When we take $b_m^{-1} = (m\,!)^{\frac{1}{s}}$, we have

$$\frac{\iota}{2\pi} \int f(x)\,(-x)^{n+\theta-1}\,dx = \sum_{m=1}^{\infty} \frac{[\Gamma(n+\theta)]^{2m}}{(m\,!)^{1/s}}\,;$$

and, when n is large, the series is, by a theorem due to STOKES, infinite like exp. $\left\{\frac{1}{s}[\Gamma(n+\theta)]^{2s}\right\}$ to the first approximation. We thus sum any series for which a_n is of order exp. $\{[\Gamma(n)]^r\}$, by taking s greater than r.

same arithmetically asymptotic expansion. But the expansion in all probability will not be valid in the two cases along the same lines or within the same areas tending to $z = 0$. Moreover, such a result is not surprising. The original series, except from the point of view of the computer, had no meaning; it did not define an analytic function over any area of the plane of the complex variable and therefore could not uniquely represent such a function. We have, however, now given two processes (out of an infinite number) by which we may conceive the series to define an analytic function, and the functions thus defined each satisfy all that the computer can demand.

§ 41. It will, perhaps, elucidate the theory which has been developed if we give two actual examples of its application.

We will first investigate the Maclaurin sum formula, which gives an asymptotic value for $\sum_{n=1}^{m-1} \phi(n)$ when m is large, under certain restrictions as to the nature of the function $\phi(n)$.

In the first place it is evident that such restrictions must exist: the function must either be uniform or be limited to a definite branch of a multiform function; and, as z takes increasing integral values, $\phi(z)$ must increase uniformly.

We will assume, therefore, that $\phi(z)$ is an integral function, which may be represented by a TAYLOR'S series, $a_0 + a_1 z + \ldots + a_r z^r + \ldots$

Then, if the integral be taken along a contour embracing an axis in the positive half of the z plane, we shall have, by the usual expression for the gamma function,

$$\sum_{n=1}^{m} \phi(n) = \sum_{n=1}^{m} \frac{\iota}{2\pi} \int \sum_{r=0}^{\infty} a_r \Gamma(1+r)\, e^{-nz} (-z)^{-r-1}\, dz = \frac{\iota}{2\pi} \int e^{-z} \frac{1-e^{-mz}}{1-e^{-z}} \sum_{r=0}^{\infty} \frac{a_r \Gamma(1+r)}{(-z)^{r+1}}\, dz.$$

Suppose now that the series $\sum_{r=0}^{\infty} a_r \Gamma(1+r) z^r$ has a finite radius of convergence ρ.

Then $\sum_{r=0}^{\infty} a_r \Gamma(1+r)(-z)^{-r-1}$ will be the expansion of a function convergent outside a circle of radius ρ^{-1}.

We can always make the bulb of the contour along which the fundamental integral is taken expand so as to entirely include this circle of radius ρ^{-1}, and the subsequent integral will then be finite.

Let now $Z = \frac{\iota}{2\pi} \int \frac{e^{-z}}{1-e^{-z}} \sum_{r=0}^{\infty} \frac{a_r r!}{(-z)^{r+1}}\, dz$, so that Z is a definite finite quantity depending on the coefficients in the expansion of $\phi(z)$.

Then $\sum_{n=1}^{m-1} \phi(n) = Z - \frac{\iota}{2\pi} \int \frac{e^{-(m+1)z}}{1-e^{-z}} \sum_{r=0}^{\infty} \frac{a_r \Gamma(1+r)}{(-z)^{r+1}}\, dz.$

The second integral may be written in the form

$$\frac{\iota}{2\pi}\int\left\{1+\ldots+(-z)^n\frac{S'_n(1)}{n!}+\ldots\right\}e^{-mz}\sum_{r=0}^{\infty}\frac{a_r\Gamma(1+r)}{(-z)^{r+2}}\,dz,$$

if we postulate that we are reversing the process by which we "sum" an asymptotic series.

The integral is equal to the asymptotic expansion

$$\sum_{n=0}^{\infty}\frac{S_n'(1)}{n!}\,\frac{\iota}{2\pi}\int e^{-mz}\sum_{r=0}^{\infty}\frac{a_r\Gamma(1+r)}{(-z)^{r+2-n}}\,dz=\sum_{n=0}^{\infty}\frac{S'_n(1)}{n!}\left[\sum_{r=0}^{\infty}\frac{a_r\Gamma(1+r)}{\Gamma(2+r-n)\,m^{n-r-1}}\right]$$

$$=\sum_{r=0}^{\infty}\frac{a_r m^{r+1}}{1+r}+\tfrac{1}{2}\sum_{r=0}^{\infty}a_r m^r+\sum_{n=2}^{\infty}\frac{S_n'(1)}{n!}\left\{\sum_{r=0}^{\infty}a_r m^{r+1-n}\,r\,.\,\overline{r-1}\ldots\overline{r+2-n}\right\}$$

$$=\int^{m}\phi(m)\,dm+\tfrac{1}{2}\phi(m)+\sum_{n=1}^{\infty}\frac{S'_{n+1}(0)}{\overline{n+1}!}\,\frac{d^n}{dm^n}\,\phi(m).$$

When n is odd $S'_{n+2}(0)=0$: the integral is therefore equal to the asymptotic expansion

$$\int^{m}\phi(m)\,dm+\tfrac{1}{2}\phi(m)+\sum_{n=0}^{\infty}\frac{S'_{2n+2}(0)}{\overline{2n+2}!}\,\frac{d^{2n+1}}{dm^{2n+1}}\,\phi(m)$$

$$=\int^{m}\phi(m)\,dm+\tfrac{1}{2}\phi(m)+\sum_{n=0}^{\infty}\frac{(-)^n B_{n+1}}{(2n+2)!}\,\frac{d^{2n+1}}{dm^{2n+1}}\,\phi(m).$$

We have finally the asymptotic equality*

$$\sum_{n=1}^{m-1}\phi(n)=Z+\int^{m}\phi(m)\,dm-\tfrac{1}{2}\phi(m)+\sum_{n=0}^{\infty}\frac{(-)^n B_{n+1}}{(2n+2)!}\,\frac{d^{2n+1}}{dm^{2n+1}}\,\phi(m).$$

This equality is valid when $\phi(z)$ is a uniform integral function of z such that if it be expanded in the form $a_0+a_1z+\ldots+a_rz^r+\ldots$, the series $\sum_{r=0}^{\infty}a_r\Gamma(1+r)z^r$ has a finite or infinite radius of convergency.

We must therefore have $\sqrt[n]{a_n n!}$ equal to a finite or zero quantity, so that $a_n^{-\frac{1}{n}}$ must increase as fast as or faster than n. The function $\phi(z)$ must therefore be a function whose "order" is greater than or equal to unity.

In the particular case when the series $\sum_{r=0}^{\infty}a_r\Gamma(1+r)z^r$ represents an integral function, we may conveniently express Z in terms of the Riemann ζ functions of negative integral argument.

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* In a subsequent paper I shall show that it is better to write this formula in the form

$$\sum_{n=0}^{m-1}\phi(a+n\omega)=Z+\sum_{n=0}^{\infty}\frac{S'_n(a\mid\omega)}{n!}\,\frac{d^n}{dx^n}\left[\int^{x}\phi(x)\,dx\right]_{x=m\omega}$$

in order to exhibit its analogy to more general extensions.

For in this case the bulb of the contour integral which expresses Z may be taken so small as not to include the poles of $\frac{1}{e^z - 1}$, and we shall therefore have

$$Z = \frac{\iota}{2\pi} \sum_{r=0}^{\infty} a_r r! \int \frac{dz}{e^z - 1} (-z)^{-r-1} = \sum_{r=0}^{\infty} a_r \zeta(-r) = \sum_{t=0}^{\infty} a_{2t+1} \frac{(-)^{t-1} B_{t+1}}{2t+2}.$$

This series is evidently convergent if $\phi(z)$ is an integral function whose order is greater than or equal to 2, a condition which is equivalent to the convergency for all values of $|z|$ of the series

$$\sum_{r=0}^{\infty} a_r \Gamma(1+r) z^r.$$

It is evident that the Maclaurin sum formula will hold good in many cases in which $\phi(z)$ is not a uniform function. If it be a function like $z^{\frac{1}{\rho}}$ or $z^{\frac{1}{\rho} \log z}$, or either of these functions multiplied by an integral function of order greater than unity, the Maclaurin formula will be valid if we suitably specify the branch of the function considered. Instead of attempting to tabulate such cases, it is perhaps better that we should go back to the genesis of the formulae when they actually arise. Applications of the formulae which will be made subsequently in this memoir will usually be to cases in which $\phi(z)$ has very simple values; and all general formulæ will be tacitly supposed subordinate to what we may call the Maclaurin restrictions.

§ 42. As a second example of the theory of asymptotic series we propose to try and find the function of which the series

$$e^x \left[\frac{1}{x} + \frac{1!}{x^2} + \frac{2!}{x^3} + \ldots + \frac{n!}{x^{n+1}} + \ldots \right]$$

is the asymptotic expansion near the essential singularity $x = \infty$.

We know that, if n be a positive integer,

$$\Gamma(n) = \int_0^{\infty} e^{-t} t^{n-1} \, dt$$

where the line integral is taken along any straight line L from the origin to infinity which lies in the half of the z plane to the right hand side of the imaginary axis.

Therefore the given expansion asymptotically represents the function

$$\int_0^{\infty} (\mathrm{L}) \frac{e^x}{x} \, \mathrm{G}\left(\frac{t}{x}\right) e^{-t} \, dt$$

where $\mathrm{G}(u)$ is the function which is represented by the series $\sum_{n=0}^{\infty} u^n$, and the integral is taken along the straight line L.

The given series is therefore the asymptotic expansion of the function

$$f(x) = \int_0^\infty (\mathrm{L}) \frac{e^{x-t}}{x} \cdot \frac{1}{1 - \dfrac{t}{x}}\, dt.$$

Suppose first that the real part of x is positive; then, putting $t = xz$ we have

$$f(x) = \int_0^\infty \frac{e^{x(1-z)}}{1-z}\, dz,$$

the integral being taken along a line along which $\mathfrak{R}(z)$ is positive, that is, along which $\mathfrak{R}(1-z)$ is negative. [These two conditions only differ when we consider a line practically parallel to the imaginary axis and therefore initially excluded.]

Putting $1 - z = -y$, we have $f(x) = -\int_{-1}^\infty \frac{e^{-xy}}{y}\, dy$, the integral being taken along a line along which $\mathrm{R}(y)$ is positive; and therefore

$$f(x) = -\int_{-x}^\infty \frac{e^{-z}\, dz}{z} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

the integral being taken along a line still in the positive half of the z plane. Thus $f(x) = -\int_\epsilon^\infty \frac{e^{-z}\, dz}{z} - \int_{-x}^{+\epsilon} \frac{e^{-z} - 1}{z}\, dz - \int_{-x}^{\epsilon} \frac{dz}{z}$, where we take $|\epsilon|$ to be very small.

Hence, if γ be EULER'S constant,*

$$f(x) = \log \epsilon + \gamma - \int_{-x}^{\epsilon} \frac{e^{-z} - 1}{z}\, dz - \log \epsilon + \log(-x) + \text{terms which vanish with } |\epsilon|.$$

Finally, on making $|\epsilon| = 0$,

$$f(x) = \gamma + \log(-x) + \int_0^x \frac{e^z - 1}{z}\, dz.$$

It will be noticed that the integral (1) obtained for $f(x)$ has a pole along the line of integration so that it has an infinite number of values, all differing by $2\pi\iota$, which are implicitly involved in the logarithmic term.

We see then that, when the real part of x is positive, the given series is the asymptotic expansion of the function $\gamma + \log(-x) + \sum_{r=1}^{\infty} \frac{x^r}{r \cdot r!}$.

Take next the case when the real part of x is negative. As in the first case, the series in the asymptotic expansion of $\int_0^\infty \frac{e^{x(1-z)}}{1-z}\, dz$, the integral being taken along a line for which $\mathfrak{R}(z)$ is negative.

Thus it is the expansion of

$$-\int_{-1}^\infty \frac{e^{-xy}}{y}\, dy \text{ along a line for which } \mathfrak{R}(y) \text{ is negative}$$

$$= -\int_{-x}^\infty \frac{e^{-z}\, dz}{z} \text{ along a line for which } \mathfrak{R}(z) \text{ is positive.}$$

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* See the author's paper, 'Messenger of Mathematics,' vol. 29, pp. 98 and 99.

On pursuing the same course as before we find that the given series is the asymptotic expansion of the function

$$\gamma + \log(-x) + \int_0^x \frac{e^z - 1}{z}\, dz.$$

But there is the important difference that now the integral which has led to this result has no pole along the line of integration. And $\log(-x)$, instead of being allowed to take any one of an infinite number of values, has such a value that $\log(-x)$ is real when x is real and negative, and has for complex values of x whose real part is negative an amplitude which lies between $\pm \frac{\pi}{2}$.

We see then that the process employed has led, when $\mathfrak{R}(x)$ is positive to an infinite number of functions, all of which have the same asymptotic expansion; and, when $\mathfrak{R}(x)$ is negative, to but one such function.

Evidently when we seek an asymptotic expansion for the function*

$$f(x) = e^{-x} \sum_{r=1}^{\infty} \frac{x^{r+1}}{r \cdot r!}$$

we may say that we get, when $\mathfrak{R}(x)$ is positive,

$$f(x) = \left[1 + \frac{1!}{x} + \ldots + \frac{n!}{x^n} + \ldots\right]$$

for terms like $x\{\gamma + \log(-x) + 2m\pi\iota\} e^{-x}$ are negligible compared with the least term of the asymptotic series; but when $\mathfrak{R}(x)$ is negative, we get

$$f(x) = e^{-x}x\{-\log(-x) - \gamma\} + 1 + \frac{1!}{x} + \ldots + \frac{n!}{x^n} + \ldots$$

in which successive terms are of decreasing order of magnitude.

The zeros of the function $f(x)$ near the essential singularity $x = \infty$, are ultimately along the imaginary axis.

We thus have an illustration of two important propositions:—

(1.) A uniform integral function may admit of asymptotic expansions of different form in different areas with their vertices at its essential singularity.

(2.) These portions of the plane are separated by lines of zeros of the function.

§ 43. Inasmuch as in Parts III. and IV. of this paper we proceed to actually obtain asymptotic expansions satisfying these laws for all the most simple types of

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* I was asked to investigate this function by Mr. G. W. WALKER, Fellow of Trinity College, who desired to compute it in certain physical researches. Originally I obtained the expansion by considering the differential equation $x^2 \frac{dy}{dx} + y = x$, in a way bearing great resemblance to that employed by HORN, 'Crelle,' vol. 120, pp. 17 and 18.

integral functions, we now proceed to sketch the process which will be adopted, and, in the course of our outline, to prove at once the validity of that process and the laws which govern its results.

Suppose, in the first place, that we have the absolutely convergent expansion $F(z) = a_0 + a_1 z + \ldots + a_s z^s + \ldots$ in which the coefficients are functions of a variable t, asymptotically given for large values of $|t|$ by expansions of the type $a_n = \frac{b_{n_0}}{t^{n_0}} + \frac{b_{n_1}}{t^{n_1}} + \frac{b_{n_2}}{t^{n_2}} + \ldots$ where the quantities $b_{n_0}, b_{n_1}, \ldots$ are constants and $n_0, n_1, \ldots$ are numbers arranged in ascending orders of magnitude and tending to $+\infty$ as a limit, the first numbers of the series being possibly negative.

Suppose that we substitute these asymptotic values of the coefficients and rearrange the expression for $F(z)$ in powers of $\frac{1}{t}$.

We shall obtain, when $|t|$ is large, an asymptotic equality

$$F(z) = \frac{1}{t^{n_0}}\left[b_{00} + b_{10} z + \ldots + b_{m0} z^m + \ldots\right] + \frac{1}{t^{n_1}}\left[b_{01} + b_{11} z + \ldots + b_{m1} z^m + \ldots\right]$$
$$+ \ldots + \frac{1}{t^{n_s}}\left[b_{0s} + b_{1s} z + \ldots + b_{ms} z^m + \ldots\right] + \ldots$$

This expansion will be arithmetically asymptotic: the computer would use it to calculate $F(z)$ for given values of z and t when $|t|$ is large.

The series which enter as coefficients will be, in all probability, divergent; but, as we are looking at the whole matter from the point of view of the computer, we are at liberty to "sum" them by the methods which have been developed in the present part of this memoir.

If, as will be the case in the applications which we subsequently make of this theory, these series have a finite radius of convergence, we can "sum" them each to a definite, possibly non-uniform, analytic function; and we shall have an expansion $F(z) = \sum_{s=0}^{\infty} \frac{f_s(z)}{t^{n_s}}$, which will satisfy POINCARÉ's definition of arithmetically asymptotic dependence. We shall thus have obtained a unique asymptotic expansion for the function $F(z)$. The case in which the series of the type

$$b_{0s} + b_{1s} z + \ldots + b_{ms} z^m + \ldots$$

have zero radius of convergence does not arise. In such a case we should be able to obtain an infinite number of functions, of which these series are the asymptotic expansions, and we should have the absurdity that the asymptotic expansion of $F(z)$ in ascending powers of $\frac{1}{t}$ is not unique.

§ 44. A function cannot, as has already been stated, be represented by the same asymptotic expansion for all values of z in the neighbourhood of $z = \infty$, unless the function is an integral function of z^{-1}, and the series absolutely convergent.

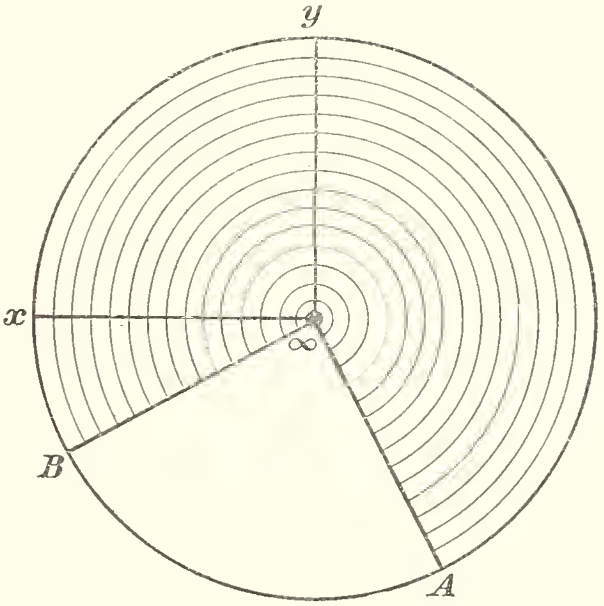
For unless J (z) and the series $a_0 + \frac{a_1}{z} + \ldots + \frac{a_n}{z^n} + \ldots$ have such a character, it is impossible that Lt $z^n \left[\text{J}(z) - a_0 - \frac{a_1}{z} - \ldots - \frac{a_n}{z^n} \right]$ should, as z approaches infinity, always tend uniformly to zero, whatever be the argument of z.

But, as we proceed to show, a uniform function of finite "genre," with an essential singularity at infinity can, in general, be represented by one or more asymptotic expansions valid for all points near infinity except those in the immediate vicinity of the zeros and poles of the function.

Two different asymptotic expansions cannot exist within the same region, and the regions are separated by the lines or areas of zeros or poles of the function. The theorem is true whether the function be a quotient of repeated or non-repeated integral functions, with zeros of simple or multiple sequence.

We need only consider the case of integral functions—the general theorem will follow, since every function of the type just mentioned can be represented as a quotient of two integral functions of finite genre.

The zeros of the function must proceed according to fixed laws, and therefore, in our diagram of the region near infinity, they will mass themselves infinitely close together as we approach infinity itself. They will therefore form certain lines (not necessarily straight) or areas of ultimate singularity. If the areas entirely surround $z = \infty$ there will be no asymptotic expansion possible. We thus assume that there exists an area such as ∞ AB, non-shaded in the figure, within which, if the radius ∞ A is sufficiently small, there are no zeros of $f(z)$.



Suppose first, that the zeros of the function form a single simple sequence, and are non-repeated; then it may be written

$$\text{F}(z) = e^{\text{H}(z)} \prod_{n=1}^{\infty} \left[\left(1 - \frac{z}{a_n}\right) e^{\sum_{n=1}^{\rho-1} \frac{1}{m} \left(\frac{z}{a_n}\right)^m} \right] = e^{\text{H}(z)} \phi(z), \text{ (say)},$$

where ρ is the "genre" (independent of n), and H (z) is a holomorphic function.

Suppose that z lies between circles of radii $|a_n|$ and $|a_{n+1}|$ where n is very large, then those terms of the product $\phi(z)$ for which $|z| < a_{n+1}$ may be written, as in the proof of WEIERSTRASS' fundamental theorem,

$$e^{\text{P}_1(z)}$$

where $\text{P}_1(z)$ is a function represented by a series of positive powers of z. For those terms which correspond to the first n zeros, we can expand $\log\left(1-\frac{z}{a_s}\right)$ in the form

$$\log z - \log(-a_s) - \frac{a_s}{z} - \tfrac{1}{2}\left(\frac{a_s}{z}\right)^2 - \ldots$$

We thus obtain $F(z) = e^{H(z)}\phi(z) = e^{P(z)}$, where, when $|a_n| < |z| < |a_{n+1}|$, $P(z)$ is an absolutely convergent double series of positive and negative powers of z, together with logarithmic terms.

Now, unless z be in the immediate vicinity of the zeros of the function, this expression, considered from the point of view of divergent summable series, will be valid for *all* values of $|z|$. For, when $|z| > a_n$, the expression of $\log\left(1-\frac{z}{a_n}\right)$ in the form

$$-\left[\frac{z}{a_n} + \ldots + \frac{z^s}{sa_n{}^s} + \ldots\right]$$

still exists as a divergent summable series outside the circle of radius $|a_n|$ for all points except those near a_n. Therefore the form of $P(z)$ exists continuously as $|z|$ increases, provided we do not cross the line of, or come within the immediate vicinity of, the zeros of the function. And thus, if we treat the series entering into the expression of $P(z)$ as series which are summable though divergent, *the expansion will be independent of* n.

Now the expansion may be written

$$\sum_{r=-\infty}^{\infty}\left[\sum_{m=1}^{n}\phi_r(m)\right]z^r,$$

where $\phi_r(m)$ is a function of m which depends also on r. Expand $\sum_{m=1}^{n}\phi_r(m)$ asymptotically in a series of successive differentials of $\phi_r(n)$ by the Maclaurin sum formula, and rearrange the series.

We shall get

(A) a certain series of positive and negative powers of z, each multiplying terms like $\int^n \phi_r(m)\,dm$; and

(B) an expansion consisting of a finite number of positive and an infinite number of negative powers of z, each associated with a constant arising from a corresponding Maclaurin expansion.

The other terms depend upon n and vanish identically; the coefficient of each Bernouillian number is zero.

When we apply the processes of divergent summation which have been previously developed, the series which forms the group (A) of terms will reduce to a definite (possibly non-uniform) function $\psi(z)$ (say). The remaining (B) terms form the summable divergent series

$$\sum_{s=-p}^{\infty} \frac{A_p}{z^s}.$$

[There will only be a finite number of positive powers of z since the *genre* of the function is finite.]

We have then

$$F(z) = e^{\psi(z) + \sum_{s=-p}^{\infty} \frac{A_s}{z^s}}.$$

In other words

$$\log F(z) - \psi(z)$$

admits the asymptotic expansion $\sum_{s=-p}^{\infty} \frac{A_s}{z^s}$ valid for all points but those in the vicinity of the zeros of $F(z)$.

§ 45. The process just sketched will become much more clear when it is applied to various particular cases as in the following pages. The proof may, by mere verbal alterations, be extended so as to include functions of simple sequence with repeated zeros.

A function with a finite number of simple sequences of zeros can be expressed as a product of functions, each with a single simple sequence. The logarithm of each of these functions will admit an asymptotic expansion, and the sum of such expansions will be the asymptotic expansion for the logarithm of the function. But terms of the category $\psi(z)$ may be of different weight in different regions, separated by bands of zeros, and thus the asymptotic expansions may differ in such regions, as has previously been seen in the case of the integral function

$$e^{-x} \sum_{r=1}^{\infty} \frac{x^{r+1}}{r \,.\, r!}.$$

§ 46. The general theorem which has just been given may be proved *pari passu* for integral or meromorphic functions with multiple sequence. We refrain from formal proof, as the consideration of such functions is omitted from the subsequent development of this paper.

Neither do I make any attempt to consider functions of infinite order, or expansions near isolated essential singularities of uniform functions. The difficulties which arise are all subordinate to the main necessity of limiting the type of function under consideration; it seems doubtful whether it is possible to give any general theorem concerning integral functions and their behaviour near infinity, which will apply to every function which can be constructed. For exceptional classes must always be infinite in number compared with those which can be formally defined.

PART III.

The Asymptotic Expansion of Simple Integral Functions.

§ 47. We now proceed to consider in detail simple integral functions. After the discussion given in Part I., we may confine ourselves to functions with a single sequence of zeros.

We shall find that such functions divide themselves naturally into three groups:—

(1) Functions whose order is less than unity,

(2) Functions of non-integral order greater than unity,

(3) Functions of integral order greater than unity.

In connection with each group of functions with algebraic sequence of zeros we first consider a standard type with which all functions of the group may be compared.

These standard functions are

$$\mathrm{P}_\rho(z) = \prod_{n=1}^{\infty}\left[1 + \frac{z}{n^\rho}\right], \text{ where } \rho > 1.$$

$$\mathrm{Q}_\rho(z) = \prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{n^{1/\rho}}\right)e^{-\frac{z}{n^{1/\rho}} + \dots + \frac{(-)^p z^p}{p n^{p/\rho}}}\right],$$ where ρ is > 1 and not integral, and p is an integer such that $p + 1 > \rho > p$.

$$\mathrm{R}_\rho(z) = \prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{n^{1/\rho}}\right)e^{-\frac{z}{n^{1/\rho}} + \dots + \frac{(-z)^\rho}{\rho n}}\right], \text{ where } \rho \text{ is an integer} \geqq 1.$$

For the logarithms of each of these functions we obtain in turn the complete asymptotic expansion near $z = \infty$. We then show how all functions of the same order with algebraic sequence of zeros yield by the same method similar asymptotic expansions. And we indicate how it is possible to apply the same methods to wide classes of simple functions with a transcendental sequence of zeros.

§ 48. The constants which enter into the analysis arise from the Maclaurin sum formula (§ 41), which may for our present purpose be written

$$\sum_{n=1}^{m-1} \phi^s(n) = \int_{\gamma_s}^{m} \phi^s(n)\,dn - \tfrac{1}{2}\phi^s(m) + \frac{\mathrm{B}_1}{2!}\frac{d}{dm}\phi^s(m) + \dots$$
$$+ (-)^l \frac{\mathrm{B}_{l+1}}{(2l+2)!}\frac{d^{2l+1}}{dm^{2l+1}}\phi^s(m) + \dots,$$

s being any integer, positive or negative.

What we have called the Maclaurin restrictions for the function $\phi(z)$ are always supposed to apply. We shall call γ_s the Maclaurin integral-limit for $\phi^s(n)$. We shall also put $F_s = -\int^{\gamma_s} \phi^s(n)\,dn$, and call F_s the s^{th} Maclaurin constant for $\phi(n)$.

When $s = 0$, we have the formula

$$\sum_{n=1}^{m-1} \log\phi(n) = \int_{\gamma_0}^{m} \log\phi(n)\,dn - \tfrac{1}{2}\log\phi(m)\ldots + (-)^t \frac{B_{t+1}}{(2t+2)!}\frac{d^{2t+1}}{dm^{2t+1}}\log\phi(m)\ldots,$$

where γ_0 is the Maclaurin integral-limit for $\log\phi(n)$.

We put $\log F_0 = \int^{\gamma_0}\log\phi(n)\,dn$, and call F_0 the absolute Maclaurin constant for $\phi(n)$.

When s is a positive integer and $\underset{n=\infty}{\mathrm{L}t}\,[\phi^{-s}(n)] = 0$, it is evident that $\gamma_{-s} = -\infty$ and $F_{-s} = 0$.

§ 49. In the particular case when $\phi(n) = n^\rho$, ρ being real or complex, the Maclaurin constants are particular cases of RIEMANN'S ζ function.

For, for all values of s,

$$\sum_{n=1}^{m-1}\frac{1}{n^s} = \zeta(s) + \frac{1}{(1-s)\,m^{s-1}} - \frac{1}{2m^s} - \sum_{t=1}^{\infty}\binom{-s}{2t}\frac{(-)^{t-1}B_t}{(s+2t-1)\,m^{s+2t-1}}.$$

When $s = 1$, we have $\underset{\substack{s=1\\ m=\infty}}{\mathrm{L}t}\left[\zeta(s) + \frac{m^{1-s}}{1-s} - \log m\right] = \gamma$.

We have also the special values

$$\zeta(0) = -\tfrac{1}{2},$$

$$\zeta(s) = \frac{2^{s-1}\pi^s}{s!}B_{s+1}, \text{ when } s \text{ is an even positive integer,}$$

$$\zeta(s) = 0, \text{ when } s \text{ is an even negative integer,}$$

$$\zeta(s) = \frac{(-)^{t-1}B_{t+1}}{2t+2}, \text{ when } s \text{ is a negative odd integer equal to } -(2t+1).$$

We write, when s is any quantity real or complex, $\zeta(-s) = F(s)$, unless $s = 1$, in which case we put $\gamma = F(s)$.

Simple Integral Functions of Finite Order Less than Unity.

§ 50. Before we proceed to consider the general theory of the asymptotic expansion of functions typified by $P_\rho(z) = \prod_{n=1}^{\infty}\left[1 + \frac{z}{n^\rho}\right]$, where $\rho > 1$, we will consider the function $F(z) = \prod_{n=1}^{\infty} \left[1 + \frac{z}{n^2}\right]$, which is known to be equal to $(2\pi)^{-1} z^{-\frac{1}{2}} \{e^{\pi z^{\frac{1}{2}}} - e^{-\pi z^{\frac{1}{2}}}\}$.

We have $\log F(z) = \sum_{n=1}^{m-1} \log\left(1 + \frac{z}{n^2}\right) + \sum_{n=m}^{\infty} \log\left(1 + \frac{z}{n^2}\right)$, and, if $m > |z| \geqq m - 1$, we obtain on expanding the logarithms

$$\log F(z) = (m-1)\log z - 2\sum_{n=1}^{m-1} \log n + \sum_{n=1}^{m-1}\left[\frac{n^2}{z} - \ldots + \frac{(-)^{s-1} n^{2s}}{s z^s} + \ldots\right]$$
$$+ \sum_{n=m}^{\infty}\left[\frac{z}{n^2} - \ldots + \frac{(-)^{s-1} z^s}{s n^{2s}} + \ldots\right].$$

If now we employ the arithmetic asymptotic approximations given by the Maclaurin sum formula for $\log\{(m-1)!\}$, $\sum_{n=m}^{\infty} \frac{1}{n^{2s}}$; and $\sum_{n=1}^{m-1} n^{2s}$, we obtain, in the limit when k is infinite,

$$\log F(z) = (m-1)\log z - 2\left[(m - \tfrac{1}{2})\log m - m + \log\sqrt{2\pi} + \sum_{r=1}^{\infty} \frac{(-)^{r-1} B_r}{2r\,.\,\overline{2r-1}\,m^{2r-1}}\right]$$
$$+ \sum_{s=1}^{k} \frac{(-)^{s-1}}{s z^s}\left\{\frac{m^{2s+1}}{2s+1} - \frac{m^{2s}}{2} + \sum_{r=1}^{\infty} \frac{(-)^{r-1} B_r}{2r\,!} \frac{d^{2r}}{dm^{2r}} m^{2s}\right\}$$
$$+ \sum_{s=1}^{k} \frac{(-)^{s-1} z^s}{s}\left\{\frac{1}{(2s-1)\,m^{2s-1}} - \frac{1}{2m^{2s}} - \sum_{r=1}^{\infty} \frac{(-)^{r-1} B_r}{2r\,!} \frac{d^{2r}}{dm^{2r}} m^{-2s}\right\},$$

or
$$\log F(z) = (m-1)\log z - (2m-1)\log m + 2m - \log 2\pi$$
$$+ \sum_{s=1}^{k} (-)^{s-1}\left\{\frac{m^{2s+1}}{s(2s+1)\,z^s} + \frac{z^s}{s(2s-1)\,m^{2s-1}}\right\} + \sum_{s=1}^{k} \frac{(-)^s}{2s}\left\{\frac{m^{2s}}{z^s} - \frac{z^s}{m^{2s}}\right\}$$
$$+ \sum_{r=1}^{\infty} \frac{(-)^{r-1} B_r}{(2r)\,!}\left\{-2\frac{\overline{2r-2}\,!}{m^{2r-1}} + \sum_{s=1}^{k} \frac{(-)^{s-1}}{s z^s} \frac{d^{2r}}{dm^{2r}} m^{2s} - \sum_{s=1}^{k} \frac{(-)^{s-1} z^s}{s} \frac{d^{2r}}{dm^{2r}} m^{-2s}\right\}$$

where we have re-arranged the terms of our double series in accordance with § 43.

Now by the theory of summable divergent series

$$\sum_{s=1}^{k} \frac{(-)^s}{s}\left\{\frac{m^{2s}}{z^s} - \frac{z^s}{m^{2s}}\right\} = -\log\frac{m^2}{z},$$

and
$$-2\frac{\overline{2r-2}\,!}{m^{2r-1}} + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s z^s} \frac{d^{2r}}{dm^{2r}} m^{2s} = 0.$$

Hence we have, when m is large, the approximation, asymptotic with regard to m,

$$\log F(z) = m\log\frac{z}{m^2} + 2m - \log(2\pi z^{\frac{1}{2}})$$
$$+ 2\sum_{s=1}^{k} (-)^{s-1}\left\{\left(\frac{1}{2s} - \frac{1}{2s+1}\right)\frac{m^{2s+1}}{z^s} + \left(\frac{1}{2s-1} - \frac{1}{2s}\right)\frac{z^s}{m^{2s-1}}\right\},$$

or
$$\log \mathrm{F}(z) = -\log 2\pi z^{\frac{1}{2}} + 2m \left\{1 + \sum_{s=-k}^{k} \frac{(-)^s m^{2s}}{(2s+1) z^s}\right\}.$$

Suppose now that $|z|$ is large, and that

$$m^2 = ze^{-i\theta} \text{ where } \theta = \arg z.$$

[This assumes that $|z|$ is a large integer, a restriction which, as will be seen later, can easily be removed.]

Then, when $|z|$ is large, we have asymptotically

$$\log \mathrm{F}(z) = -\log 2\pi z^{\frac{1}{2}} + z^{\frac{1}{2}} e^{-\frac{\iota\theta}{2}} \left[2 + \sum_{s=-k}^{k}{}' \frac{(-)^s e^{-si\theta}}{s + \frac{1}{2}}\right].$$

The sum of the Fourier's series inside the square bracket is, when $-\pi < \theta < \pi$, equal to $\pi e^{\frac{\iota\theta}{2}}$.

Therefore, when $|z|$ is large, we have asymptotically

$$\log \mathrm{F}(z) = -\log 2\pi z^{\frac{1}{2}} + \pi z^{\frac{1}{2}}.$$

§ 51. In the preceding investigation we have assumed that the Maclaurin sum formula expresses asymptotically the values, when m is large, of the functions $\log(m!)$ and $\sum_{n=1}^{m-1} n^{2s}$ (s positive or negative).

Accurately we have of course

$$\log \overline{m-1}\,! = (m - \tfrac{1}{2}) \log m - m + \log \sqrt{2\pi} + \frac{1}{\iota} \int_0^\infty \frac{dy}{e^{2\pi y} - 1} \Big[\log(m + \iota y) - \log(m - \iota y)\Big];$$

$$\sum_{n=1}^{m-1} n^{2s} = \frac{m^{2s+1}}{2s+1} - \frac{m^{2s}}{2} + \frac{1}{\iota} \int_0^\infty \frac{dy}{e^{2\pi y} - 1} \Big[(m + \iota y)^{2s} - (m - \iota y)^{2s}\Big], \text{ when } s \text{ is positive;}$$

and

$$\sum_{n=m}^{\infty} \frac{1}{n^{2s}} = \frac{1}{(2s-1) m^{2s-1}} + \frac{1}{2m^{2s}} - \frac{1}{\iota} \int_0^\infty \frac{dy}{e^{2\pi y} - 1} \Big[(m + \iota y)^{-2s} - (m - \iota y)^{-2s}\Big] \text{ when } s \text{ is}$$
positive:

Hence, in the limit when k is infinite,

$$\log \mathrm{F}(z) = -\log(2\pi z^{\frac{1}{2}}) + 2m \left\{1 + \sum_{s=-k}^{k}{}' \frac{(-)^s m^{2s}}{z^s (2s+1)}\right\}$$
$$+ \frac{1}{\iota} \int_0^\infty \frac{dy}{e^{2\pi y} - 1} \left\{-2\log(m + \iota y) + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1} (m + \iota y)^{2s}}{s z^s}\right\}$$
$$- \frac{1}{\iota} \int_0^\infty \frac{dy}{e^{2\pi y} - 1} \left\{-2\log(m - \iota y) + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1} (m - \iota y)^{2s}}{s z^s}\right\}.$$

This formula is accurate and holds whatever positive integral value m may have.

Unfortunately we may not say that the sum of an infinite series of integrals is equal to the integral whose subject of integration is the function to which the series of subjects of integration can be "summed." The two integrals last written down can then only be evaluated by reducing them to an exceeding complicated extension of the type known as DIRICHLET'S integrals. The analysis is utterly intractable.

If we make $m^2 = ze^{-i\theta}$, and expand the subjects of integration in powers of z, then we can say that the last two terms will not contribute terms whose order of magnitude when z is large is comparable with that of any positive or negative power of z. And, as we know, the sum of these two terms is equal to $\log (1 - e^{-2\pi z^{\frac{1}{2}}})$.

The formula $\log \mathrm{F}(z) = \pi z^{\frac{1}{2}} - \log (2\pi z^{\frac{1}{2}})$ is thus asymptotic exactly as the Maclaurin series for $m\,!$ and $\sum\limits_{n=1}^{m-1} n^{2s}$, from which it is derived, are asymptotic. That is, for large values of $|z|$, the expression $z^{-n}\{\log \mathrm{F}(z) - \pi z^{\frac{1}{2}} + \log 2\pi z^{\frac{1}{2}}\}$ for all values of n tends to zero as $|z|$ tends to infinity. There is, in fact, POINCARÉ'S arithmetic asymptotic dependence.

The preceding example will serve to show the nature of the asymptotic expansions which we can now proceed to obtain.

§ 52. We consider first the function $\mathrm{P}_\rho(z) = \prod\limits_{n=1}^{\infty} \left[1 + \dfrac{z}{n^\rho}\right]$, where $\rho > 1$.

We have

$$\log \mathrm{P}_\rho(z) = (m-1)\log z - \rho \sum_{n=1}^{m-1} \log n$$

$$+ \sum_{n=1}^{m-1} \left[\frac{n^\rho}{z} - \ldots + \frac{(-)^{s-1} n^{\rho s}}{s z^s} + \ldots\right]$$

$$+ \sum_{n=m}^{\infty} \left[\frac{z}{n^\rho} - \ldots + \frac{(-)^{s-1} z^s}{s n^{\rho s}} + \ldots\right].$$

Therefore, if we substitute the approximations for $\log \overline{m-1}\,!$, $\sum\limits_{n=m}^{\infty} \dfrac{1}{n^{\rho s}}$, and $\sum\limits_{n=1}^{m-1} n^{\rho s}$ given by the Maclaurin sum formula, we shall obtain the expansion, arithmetically asymptotic with regard to m,

$$\log \mathrm{P}_\rho(z) = (m-1)\log z - \rho\left[(m - \tfrac{1}{2})\log m - m + \log\sqrt{2\pi} + \sum_{r=1}^{\infty} \frac{(-)^{r-1}\mathrm{B}_r}{2r\,.\,\overline{2r-1}\, m^{2r-1}}\right]$$

$$+ \sum_{s=1}^{k} \frac{(-)^{s-1}}{s z^s} \left\{\frac{m^{\rho s+1}}{\rho s + 1} - \frac{m^{\rho s}}{2} + \sum_{r=1}^{\infty} \frac{(-)^{r-1}\mathrm{B}_r}{\rho s - 2r + 1} \binom{\rho s}{2r} m^{\rho s - 2r + 1} + \mathrm{F}(\rho s)\right\}$$

$$+ \sum_{s=1}^{k} \frac{(-)^{s-1} z^s}{s} \left\{\frac{m^{-\rho s+1}}{\rho s - 1} + \frac{m^{-\rho s}}{2} + \sum_{r=1}^{\infty} \frac{(-)^{r-1}\mathrm{B}_r}{\rho s + 2r - 1} \binom{-\rho s}{2r} m^{-\rho s - 2r + 1}\right\},$$

or,
$$\log P_\rho(z) = (m-1)\log z - \rho\left(m - \tfrac{1}{2}\right)\log m + \rho m - \rho\log\sqrt{2\pi}$$
$$+ m\sum_{s=-k}^{k}{}' \left\{\frac{(-)^{s-1}}{sz^s}\cdot\frac{m^{\rho s}}{\rho s+1}\right\} + \sum_{s=-k}^{k}{}' \frac{(-)^s m^{\rho s}}{2sz^s} + \sum_{s=1}^{k}\frac{(-)^{s-1}F(\rho s)}{sz^s}$$
$$+ \sum_{r=1}^{\infty}\frac{(-)^{r-1}B_r}{m^{2r-1}}\left\{\frac{-\rho}{2r\,.\,2r-1} + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{\rho s - 2r + 1}\binom{\rho s}{2r}\frac{m^{\rho s}}{sz^s}\right\}.$$

This expansion is arithmetically asymptotic with regard to m, and the coefficients of various powers of $\frac{1}{m}$ are ultimately to be summable divergent series.

Let now $r = |z|$ be large, and such that $r^{\frac{1}{\rho}}$ lies between m and $m-1$. Then the modulus of $\frac{m^\rho}{r}$ is a quantity which is very nearly equal to unity. We proceed to "sum" the series $\sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s\,.\,(\rho s+1)}\cdot\frac{m^{\rho s}}{z^s}$, $\sum_{s=-k}^{k}{}' \frac{(-)^s}{2s}\frac{m^{\rho s}}{z^s}$, and

$$\frac{1}{2r!}\frac{d^{2r-1}}{dm^{2r-1}}\left\{-\rho\log m + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}m^{\rho s}}{sz^s}\right\}.$$

Write $t = \log\frac{m^\rho}{r}$, then the first series becomes

$$f(t) = \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s\,.\,(\rho s+1)}e^{s(t-i\theta)}.$$

Thus

$$f(t) = \sum_{s=-k}^{k}{}' (-)^{s-1}\left\{\frac{1}{s} - \frac{\rho}{\rho s+1}\right\}e^{s(t-i\theta)},$$

and

$$\rho\frac{\partial f(t)}{\partial t} = \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}\rho}{\rho s+1}e^{s(t-i\theta)}.$$

So that

$$f(t) = -\rho\frac{\partial f(t)}{\partial t} + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}e^{s(t-i\theta)}}{s}.$$

If now we "sum" the last series we obtain

$$f(t) = -\rho\frac{\partial f(t)}{\partial t} + t - i\theta;\ \text{and therefore}$$

$$f(t) = Ae^{-\frac{t}{\rho}} + t - i\theta - \rho,\ \text{where A is independent of } t.$$

When $t = 0$,

$$f(t) = \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s\,.\,(\rho s+1)}e^{-si\theta}.$$

Hence

$$f(0) = \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s}e^{-si\theta} + \rho\sum_{s=-k}^{k}{}' \frac{(-)^s}{\rho s+1}e^{-si\theta}.$$

Now, by the usual theory of FOURIER'S series, $\rho + \sum_{s=-k}^{k}{}' \frac{(-)^s}{s + \frac{1}{\rho}} e^{-si\theta} = \frac{\pi}{\sin \frac{\pi}{\rho}} e^{\frac{\iota\theta}{\rho}}$, provided $-\pi < \theta < \pi$.

Therefore
$$f(0) = -i\theta - \rho + \frac{\pi}{\sin \frac{\pi}{\rho}} e^{\frac{\iota\theta}{\rho}},$$

so that
$$f(t) = \frac{\pi}{\sin \frac{\pi}{\rho}} e^{\frac{\iota\theta}{\rho} - \frac{t}{\rho}} + t - i\theta - \rho.$$

Hence
$$\sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s(\rho s + 1)} \frac{m^{\rho s}}{z^s} = \frac{\pi}{\sin \frac{\pi}{\rho}} \frac{z^{\frac{1}{\rho}}}{m} + \log \frac{m^\rho}{z} - \rho.$$

The second series $\sum_{s=-k}^{k}{}' \frac{(-)^s}{2s} \cdot \frac{m^{\rho s}}{z^s}$ is at once seen to be equal to $-\frac{1}{2} \log \frac{m^\rho}{z}$.

And, since the term by term differential of a summable divergent series is equal to the differential of its sum, the third series vanishes identically for all positive integral values of r.

Thus, when $|z|^{\frac{1}{\rho}}$ lies between m and $m - 1$, or possibly is equal to the latter quantity, we have the asymptotic expansion, while $-\pi < \arg z < \pi$,

$$\log \mathrm{P}_\rho(z) = (m - 1) \log z - \rho (m - \tfrac{1}{2}) \log m + \rho m - \rho \log \sqrt{2\pi}$$

$$+ \frac{\pi}{\sin \frac{\pi}{\rho}} z^{\frac{1}{\rho}} + m \log \frac{m^\rho}{z} - \rho m - \tfrac{1}{2} \log \frac{m^\rho}{z} + \sum_{s=1}^{k} \frac{(-)^{s-1} \mathrm{F}(\rho s)}{s z^s};$$

or,
$$\log \mathrm{P}_\rho(z) = \frac{\pi}{\sin \frac{\pi}{\rho}} z^{\frac{1}{\rho}} - \rho \log \sqrt{2\pi} - \tfrac{1}{2} \log z + \sum_{s=1}^{k} \frac{(-)^{s-1} \mathrm{F}(\rho s)}{s z^s}.$$

Thus, when $|z|$ has any large value, and $-\pi < \arg z < \pi$, we have the arithmetically asymptotic expansion

$$\prod_{n=1}^{\infty} \left\{1 + \frac{z}{n^\rho}\right\} = (2\pi)^{-\frac{\rho}{2}} z^{-\frac{1}{2}} e^{\frac{\pi}{\sin \pi/\rho} z^{1/\rho} + \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{s z^s} \mathrm{F}(\rho s)}.$$

§ 53. The approximation represents an arithmetic not a functional equality. It does not vary with the argument of z, and it exists everywhere in the neighbourhood of infinity except at points on or near the line of zeros of the function. Not only so, but at points on the line of zeros of $\mathrm{P}_\rho(z)$ which are not in the immediate vicinity of one of its zeros, both the function and the asymptotic series have arithmetic continuity, and therefore the equality will hold at such points. These results accord with the general theory developed in Part II.

The series for $\log \dfrac{P_\rho(z)\, z^{\frac{1}{2}} (2\pi)^{\frac{\rho}{2}}}{\exp\left\{\dfrac{\pi}{\sin \pi/\rho}\, z^{\frac{1}{\rho}}\right\}}$ can be "summed" by the methods of Part II.

The function just written tends to zero near its essential singularity $z = \infty$, and the same will be true of the function which we get by any process of summation. But, in general, the function derived from

$$\sum_{s=1}^{\infty} \frac{(-)^{s-1}}{s z^s} \mathrm{F}(\rho s)$$

will not be equal to the function from which the series has been obtained.

Since $\mathrm{F}(\rho s) = \zeta(-\rho s)$, the series is equal to $\sum_{s=1}^{\infty} \frac{(-)^{s-1}}{s} z^{s} \frac{\iota}{2\pi} \Gamma(1 + s\rho) \int \frac{(-x)^{\rho s - 1}}{e^x - 1}\, dx$, the integral being taken round the fundamental contour of § 24.

The series is thus equal to $\frac{\iota\rho}{2\pi} \int \mathrm{G}(x^\rho z) \frac{dx}{x(e^x - 1)}$, where $\mathrm{G}(z) = \sum_{s=1}^{\infty} \Gamma(\rho s)\, z^s$.

The series for $\mathrm{G}(z)$ is divergent and of order ρ. The integral is interesting in that, in place of e^{-x}, we have used $(e^x - 1)^{-1}$ as our auxiliary of summation.

§ 54. We now pass on to consider the most general simple integral function with a single sequence of non-repeated zeros, whose order is any number (zero included) less than unity.

The function may be written $\mathrm{F}(z) = \prod_{n=1}^{\infty} \left[1 + \frac{z}{\phi(n)}\right]$, where $\sum_{n=1}^{\infty} \frac{1}{|\phi(n)|}$ is absolutely convergent. The n^{th} zero, $-\phi(n)$, is a definite function of n and any finite number of given constant quantities.

Suppose that if $r = \phi(n)$, then inversely $n = \psi(r)$.

Let $|z| = \mathrm{R}$ and suppose that m is a large integer such that $m - 1 < \psi(\mathrm{R}) \leqq m$.

Then $\log \mathrm{F}(z) = \sum_{n=1}^{\infty} \log\left(1 + \frac{z}{\phi(n)}\right) = \sum_{n=1}^{m-1} \log\left(1 + \frac{z}{\phi(n)}\right) + \sum_{n=m}^{\infty} \log\left(1 + \frac{z}{\phi(n)}\right)$,

so that if we expand the logarithms in convergent series we shall get

$$\begin{aligned} \log \mathrm{F}(z) = {} & (m - 1) \log z - \sum_{n=1}^{m-1} \log \phi(n) \\ & + \sum_{n=1}^{m-1} \left[\frac{\phi(n)}{z} - \frac{\phi^2(n)}{2z^2} + \ldots + \frac{(-)^{s-1}\phi^s(n)}{s z^s} + \ldots\right] \\ & + \sum_{n=m}^{\infty} \left[\frac{z}{\phi(n)} - \frac{z^2}{2\phi^2(n)} + \ldots + \frac{(-)^{s-1} z^s}{s\phi^s(n)} + \ldots\right]. \end{aligned}$$

Now, by the Maclaurin sum formula, if s be positive,

$$\sum_{n=1}^{m-1} \phi^s(n) = \int_{\gamma_s}^{m} \phi^s(n)\, dn - \tfrac{1}{2}\phi^s(m) + \frac{\mathrm{B}_1}{2\,!} \frac{d}{dm} \phi^s(m) \ldots + (-)^t \frac{\mathrm{B}_{t+1}}{2t + 2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \phi^s(m) + \ldots$$

where γ_s is a constant quantity, depending on s and the form of $\phi(n)$, which we have proposed to call the Maclaurin integral limit for $\phi^s(n)$.

If s be negative, we have

$$-\sum_{n=m}^{\infty}\phi^s(n)=\int_{\gamma_s}^{m}\phi^s(n)\,dn-\tfrac{1}{2}\phi^s(n)+\ldots+(-)^t\frac{B_{t+1}}{2t+2\,!}\frac{d^{2t+1}}{dm^{2t+1}}\phi^s(m)+\ldots,$$

where $\gamma_s=\infty$, there being no term independent of m on the right-hand side.

And

$$\sum_{n=1}^{m-1}\log\phi(n)=\int_{\gamma_0}^{m}\log\phi(n)\,dn-\tfrac{1}{2}\log\phi(m)-\ldots+(-)^t\frac{B_{t+1}}{2t+2\,!}\frac{d^{2t+1}}{dm^{2t+1}}\log\phi(m)+\ldots$$

Hence, in the limit when $k=\infty$,

$$\begin{aligned}\log F(z)=(m-1)\log z&-\int_{\gamma_0}^{m}\log\phi(n)\,dn\\&+\sum_{s=1}^{k}\left[\frac{(-)^{s-1}}{sz^s}\int_{\gamma_s}^{m}\phi^s(n)\,dn+\frac{(-)^s z^s}{s}\int_{\gamma_{-s}}^{m}\frac{dn}{\phi^s(n)}\right]\\&-\tfrac{1}{2}\left\{-\log\phi(m)+\sum_{s=1}^{k}\left[\frac{(-)^{s-1}}{sz^s}\phi^s(m)+\frac{(-)^s z^s}{s\phi^s(m)}\right]\right\}\\&+\sum_{t=0}^{\infty}\frac{(-)^t B_{t+1}}{2t+2\,!}\frac{d^{2t+1}}{dm^{2t+1}}\left\{-\log\phi(m)+\sum_{s=1}^{k}\frac{(-)^{s-1}\phi^s(m)}{sz^s}-\sum_{s=1}^{k}\frac{(-)^{s-1}z^s}{s\phi^s(m)}\right\}.\end{aligned}$$

Now, when the limiting values for $k=\infty$ of the summable divergent series are taken,

$$\begin{aligned}&\sum_{s=1}^{k}\left[\frac{(-)^{s-1}}{sz^s}\phi^s(m)+\frac{(-)^s z^s}{s\phi^s(m)}\right]-\log\phi(m)\\&\qquad=\log\left(1+\frac{\phi(m)}{z}\right)-\log\left(1+\frac{z}{\phi(m)}\right)-\log\phi(m)=-\log z.\end{aligned}$$

Hence, asymptotically,

$$\begin{aligned}\log F(z)&=(m-\tfrac{1}{2})\log z-\int_{\gamma_0}^{m}\log\phi(n)\,dn+\sum_{s=1}^{k}(-)^{s-1}\left[\int_{\gamma_s}^{m}\frac{\phi^s(n)\,dn}{s\,z^s}-\int_{\gamma_{-s}}^{m}\frac{z^s dn}{s\phi^s(n)}\right]\\&=(m-\tfrac{1}{2})\log z-\big[n\log\phi(n)\big]_{\gamma_0}^{m}+\int_{\gamma_0}^{m}n\frac{d\phi(n)}{\phi(n)}\\&\qquad+\sum_{s=1}^{k}(-)^{s-1}\left[\left\{\frac{\phi^s(n)\,n}{s\,z^s}\right\}_{\gamma_s}^{m}-\left\{\frac{z^s n}{s\phi^s(n)}\right\}_{\gamma_{-s}}^{m}\right]\\&\qquad\qquad\sum_{s=1}^{k}(-)^s\left[\int_{\gamma_s}^{m}\frac{n\phi^{s-1}(n)}{z^s}\,d\phi(n)+\int_{\gamma_{-s}}^{m}\frac{z^s n}{\phi^{s+1}(n)}\,d\phi(n)\right]\\&=-\tfrac{1}{2}\log z+\big[n\log\phi(n)\big]_{\gamma_0}+\sum_{s=1}^{k}\frac{(-)^s}{s\,z^s}\big[\phi^s(n)\,n\big]_{\gamma_s}\\&\qquad+\int_{\phi(\gamma_0)}^{\phi(m)}\psi(t)\frac{dt}{t}+\sum_{s=1}^{k}(-)^s\left[\int_{\phi(\gamma_s)}^{\phi(m)}\psi(t)\frac{t^{s-1}}{z^s}\,dt+\int_{\phi(\gamma_{-s})}^{\phi(m)}\frac{z^s\psi(t)}{t^{s+1}}\,dt\right].\end{aligned}$$

Now, where $\psi(t)$ is a given form, and such that we can integrate expressions like $\psi(t)\, t^{s-1}\, dt$ (s positive or negative, but integral) we need only carry out this process and "sum" the ensuing series of positive and negative powers of z to obtain the dominant term of the asymptotic expansion of $\log \mathrm{F}(z)$. If, however, $\psi(t)$ is not thus formally given, we have to face the difficulty that the lower limits of the definite integrals are different quantities. The lower limits, however, corresponding to negative values of s, are such as to give rise to zero terms. If, then, we consider only indefinite integrals of the type $\int^{\phi(m)} \psi(t)\, t^s \frac{dt}{t}$, and take care that in any transformation of these we do not introduce arbitrary additive constants, we may take the asymptotic expansion in the form

$$\log \mathrm{F}(z) = -\tfrac{1}{2} \log z + \int^{\gamma_0} \log \phi(n)\, dn - \sum_{s=1}^{k} \frac{(-)^{s-1}}{s z^s} \int^{\gamma_s} \phi^s(n)\, dn$$
$$+ \int^{\phi(m)} \frac{\psi(t)\, dt}{t} \left\{1 + \sum_{s=1}^{k} \left(\frac{(-)^s}{z^s} t^s + \frac{(-)^s z^s}{t^s} \right)\right\}.$$

§ 55. It is the integral

$$\mathrm{I} = \underset{k=\infty}{\mathrm{L}t} \int^{\phi(m)} \frac{\psi(t)\, dt}{t} \left[1 + \sum_{s=-k}^{k}{}' \left(\frac{-t}{z}\right)^s\right]$$

which gives rise to the dominant term of the asymptotic expansion of $\log \mathrm{F}(z)$.

This integral is evidently equal to $\underset{k=\infty}{\mathrm{L}t} \int^{\phi(m)} \frac{\psi(t)\, dt}{t} \left[\frac{\left(\frac{-t}{z}\right)^{-k} - \left(\frac{-t}{z}\right)^{k+1}}{1 + \frac{t}{z}}\right]$.

Suppose now that $z = re^{\iota\theta}$ and take $\iota\mu = \log\left(-\frac{t}{z}\right)$, the logarithm, when $t = r$, having a cross-cut along the negative half of the real axis, so that

$$\iota\mu = \log \frac{t}{r} + \pi\iota - \iota\theta, \text{ where } \log \frac{t}{r} \text{ is arithmetic.}$$

Then

$$\mathrm{I} = \underset{k=\infty}{\mathrm{L}t}\ \iota \int^{\frac{1}{2}\log\left\{\frac{\phi(m)}{r}\right\} + \pi - \theta} \psi\left(z\, e^{\iota(\mu - \pi)}\right) \frac{\sin(k + \frac{1}{2})\mu}{\sin \frac{1}{2}\mu}\, d\mu.$$

Now the form of the dominant term I does not depend on the quantity $\log \frac{\psi(m)}{r}$ which vanishes when r is sufficiently large. We have then

$$\mathrm{I} = \underset{k=\infty}{\mathrm{L}t} \int^{\pi - \theta} \iota\psi\left\{z\, e^{\iota(\mu - \pi)}\right\} \frac{\sin(k + \frac{1}{2})\mu}{\sin \frac{1}{2}\mu}\, d\mu,$$

an integral of the type first considered by DIRICHLET.*

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* v. 'Crelle,' vol. 4, pp. 157, *et seq.*

The theory previously developed in Part II. tells us that this integral must, *quâ* function of z, be independent of θ; in other words, when $-\pi < \theta < \pi$, that

$$\underset{k=\infty}{\mathrm{Lt}} \int_{\pi-\theta}^{\pi} \iota\psi\left\{z\, e^{\iota(\mu-\pi)}\right\} \frac{\sin(k+\frac{1}{2})\mu}{\sin\frac{1}{2}\mu}\, d\mu = 0.$$

But this is precisely DIRICHLET'S result: we thus have a valuable verification of our theory.

Finally, then, the dominant term of the asymptotic expansion of $\log \mathrm{F}(z)$ is the function

$$f(z) = \underset{k=\infty}{\mathrm{Lt}} \int^{\pi} \iota\psi\left\{z\, e^{\iota(\mu-\pi)}\right\} \frac{\sin(k+\frac{1}{2})\mu}{\sin\frac{1}{2}\mu}\, d\mu.$$

Since we may evidently change the sign of ι without altering the value of $f(z)$ we have

$$f(z) = \underset{k=\infty}{\mathrm{Lt}} \int^{\pi} \frac{\psi\left\{z\, e^{\iota(\pi-\mu)}\right\} - \psi\left\{z\, e^{-\iota(\pi-\mu)}\right\}}{2\iota} \frac{\sin(k+\frac{1}{2})\mu}{\sin\frac{1}{2}\mu}\, d\mu.$$

Now ψ is the function inverse to ϕ. If, then, we suppose that ζ and η are determined from the relation $ze^{\iota(\pi-\mu)} = \phi(\zeta + \iota\eta)$, principal values of inverse expressions being taken, and ζ and η being functions of z and μ, we shall have finally $f(z) = \underset{k=\infty}{\mathrm{Lt}} \int^{\pi} \eta \frac{\sin(k+\frac{1}{2})\mu}{\sin\frac{1}{2}\mu}\, d\mu$, as the simplest form in which we may write $f(z)$.

There is no doubt that it is possible to construct functions $\phi(n)$ for which the preceding analysis will not hold good.* It would appear, however, to be applicable to most of the types of functions which would ordinarily arise, and a more accurate investigation will need the exquisite *finesse* of certain developments of the theory of functions of a real variable.

Note that, for the case in which $ze^{\iota(\pi-\mu)} = (\zeta - \iota\eta)^{\rho}$, we have established that $f(z) = \dfrac{\pi}{\sin\dfrac{\pi}{\rho}} z^{\frac{1}{\rho}}$.

§ 56. The dominant term $f(z)$ of the asymptotic expansion of $\log \prod_{n=1}^{\infty}\left[1 + \dfrac{z}{\phi(n)}\right]$ takes a very simple form for the case in which $\psi(t)$ can, when t is large, be expanded in descending powers of t in the form

$$\psi(t) = t^{\frac{1}{\rho}}\left[a_0 + \frac{a_1}{t} + \frac{a_2}{t^2} + \ldots\right], \text{ where } \rho > 1.$$

We have the asymptotic expansion

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* We have assumed, for instance, that we can apply the Maclaurin sum formula to $\sum_{n=1}^{m-1} \phi(n)$, and, therefore, that the conditions of § 41 are satisfied.

$$-\tfrac{1}{2}\log z+\int^{\gamma_0}\log\phi(n)\,dn-\sum_{s=1}^{k}\frac{(-)^{s-1}}{sz^s}\int^{\gamma_s}\phi^s(n)\,dn$$

$$+\int^{\phi(m)}\frac{\psi(t)\,dt}{t}\left\{1+\sum_{s=1}^{k}\left(\frac{(-)^s t^s}{z^s}+\frac{(-)^s z^s}{t^s}\right)\right\}.$$

Since $\phi(m)$ is a very large quantity we may utilise the expansion of $\psi(t)$. The integral last written is, therefore, equal to

$$\sum_{r=0} a_r\int^{\phi(m)}\frac{dt}{t^{r+1-\frac{1}{\rho}}}\left\{1+\sum_{s=1}^{k}\left(\frac{(-)^s t^s}{z^s}+\frac{(-)^s z^s}{t^s}\right)\right\}$$

$$=\sum_{r=0}\frac{a_r}{\phi^{r-\frac{1}{\rho}}(m)}\left[-\frac{1}{r-\frac{1}{\rho}}+\sideset{}{'}\sum_{s=-k}^{k}\frac{(-)^s}{z^s}\frac{\phi^s(m)}{s-r+\frac{1}{\rho}}\right]$$

$$=\sum_{r=0}\frac{a_r}{\phi^{r-\frac{1}{\rho}}(m)}\left[\frac{\pi}{\sin^{\pi}\left(\frac{1}{\rho}-r\right)}\left\{\frac{z}{\phi(m)}\right\}^{\frac{1}{\rho}-r}\right]$$

$$=\sum_{r=0}\left[(-)^r a_r\frac{\pi}{\sin\frac{\pi}{\rho}}z^{\frac{1}{\rho}-r}\right]$$

$$=\frac{\pi}{\sin\frac{\pi}{\rho}}z^{\frac{1}{\rho}}\left[\frac{\psi(-z)}{(-z)^{\frac{1}{\rho}}}\right].$$

If, then, we introduce the Maclaurin constants, $\log F_0=\int^{\gamma_0}\log\phi(n)\,dn$, $-F_s=\int^{\gamma_s}\phi^s(n)\,dn$, we shall obtain the asymptotic expansion

$$\prod_{n=1}^{\infty}\left[1+\frac{z}{\phi(n)}\right]=F_0 z^{-\frac{1}{2}}\exp\left\{\frac{\pi z^{\frac{1}{\rho}}}{\sin\frac{\pi}{\rho}}\left[\frac{\psi(-z)}{(-z)^{1/\rho}}\right]+\sum_{s=1}^{\infty}\frac{(-)^{s-1}F_s}{sz^s}\right\}.$$

Such values of the many-valued functions introduced are to be taken as would be indicated by the analysis.

§ 57. It is evident that the investigation of § 54 applies to all simple integral functions whose primary factors need no exponential to ensure convergency. Thus it includes all simple functions of order $\frac{1}{\rho}$, where ρ is real positive and >1 with algebraic zeros. It includes all simple functions with non-algebraic zeros of the type given by $a_n=[an^\rho+bn^{\rho_1}+\ldots](l^\tau n)^\sigma$, where τ and ρ are both real positive and >1, σ is positive or negative; where $l^\tau(n)$ denotes $\log\{\log\{\ldots n\}\}\ldots\}$, these being τ repetitions of the logarithm, and where ρ, ρ_1, . . are decreasing quantities tending to $-\infty$ as a limit.

But, because of the validity of the Maclaurin sum formula, it includes simple functions with very rapid convergence—such as those for which

$$a_n = e^{e^{\cdot^{\cdot^{\cdot^{e^n}}}}} \times \left(\text{function of } n \text{ of lower order than } e^{e^{\cdot^{\cdot^{\cdot^{e^n}}}}}\right).$$

§ 58. We can now extend the result which was obtained in § 52, and find an asymptotic approximation for a simple integral function with an algebraic sequence of zeros, that is to say, of a function of which the n^{th} zero, $-a_n$, admits, when n is large, an expansion of the form $a_n = n^\rho + b_1 n^{\rho-\epsilon_1} + b_2 n^{\rho-\epsilon_2} + \ldots$, where ρ is greater than unity and the quantities $\epsilon_1, \epsilon_2, \ldots$ are real positive and in ascending order of magnitude.

We take $a_n = \phi(n) = r$ so that, by reversion of series,

$$n = r^{\frac{1}{\rho}} - \frac{b_1}{\rho} r^{\frac{1-\epsilon_1}{\rho}} + \frac{\rho + 1 - 2\epsilon_1}{\rho^2} \cdot \frac{b_1^{\,2}}{2} r^{\frac{1-2\epsilon_1}{\rho}} - \frac{b_2}{\rho} r^{\frac{1-\epsilon_2}{\rho}} + \ldots = \psi(r) \text{ (say).}$$

Since, when s is positive, we may expand $a_n^{\,s}$ directly by the binomial theorem, we have, when m is large,

$$\sum_{n=1}^{m-1} a_n^{\,s} = \sum_{n=1}^{m-1} \left[n^{\rho s} + s b_1 n^{\rho s - \epsilon_1} + \frac{s \,.\, s-1}{1 \,.\, 2} n^{\rho s - 2\epsilon_1} + s b_2 n^{\rho s - \epsilon_2} + \ldots \right]$$

$$= \int^m \phi^s(n)\, dn + \mathrm{F}(\rho s) + s b_1 \mathrm{F}(\rho s - \epsilon_1) + \frac{s \,.\, s-1}{2} b_1^{\,2} \mathrm{F}(\rho s - 2\epsilon_1) + s b_2 \mathrm{F}(\rho s - \epsilon_2) + \ldots$$

$$- \frac{\phi^s(m)}{2} + \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t + 2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \phi^s(m)$$

$$= \int^m \phi^s(n)\, dn + \mathrm{F}(\rho s) + \mathrm{Z}\left(\rho, s\, ;\, \begin{matrix} \epsilon_1, \epsilon_2 \ldots \\ b_1, b_2 \ldots \end{matrix}\right) - \frac{\phi^s(m)}{2} + \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t + 2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \phi^s(m),$$

where $\mathrm{Z}\left(\rho.\, s\, ;\, \begin{matrix} \epsilon_1, \epsilon_2 \ldots \\ b_1, b_2 \ldots \end{matrix}\right)$ is a definite finite quantity vanishing with the quantities b, which can be expressed in terms of a series of Riemann ζ functions.

Again, when s is positive,

$$\sum_{n=m}^{\infty} \frac{1}{\phi^s(n)} = - \int^m \phi^{-s}(n)\, dn - \frac{\phi^{-s}(m)}{2} - \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t + 2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \phi^{-s}(m).$$

And $$\sum_{n=1}^{m-1} \log \phi(n) = \sum_{n=1}^{m-1} \left[\rho \log n + \frac{b_1}{n^{\epsilon_1}} - \frac{b_1^{\,2}}{2n^{2\epsilon_1}} + \frac{b_2}{2n^{\epsilon_2}} + \ldots \right]$$

$$= \int^m \log \phi(n)\, dn + \frac{\rho}{2} \log 2\pi + b_1 \mathrm{F}(-\epsilon_1) - \frac{b_1^{\,2}}{2} \mathrm{F}(-2\epsilon_1) + b_2 \mathrm{F}(-\epsilon_2)$$

$$- \frac{\log \phi(m)}{2} + \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{(2t + 2)\,!} \frac{d^{2t+1}}{dm^{2t+1}} \log \phi(m)\, ;$$

and we shall put $\mathrm{Z}\left(0\, ;\, \begin{matrix} \epsilon_1, \epsilon_2, \ldots \\ b_1, b_2, \ldots \end{matrix}\right) = b_1 \mathrm{F}(-\epsilon_1) - \frac{b_1^{\,2}}{2} \mathrm{F}(-2\epsilon_1) + b_2 \mathrm{F}(-\epsilon_2) + \ldots$

If now we substitute in the general formula

$$\log F(z) = -\tfrac{1}{2}\log z + \int^{\gamma_0} \log \phi(n)\, dn - \sum_{s=1}^{k} \frac{(-)^{s-1}}{sz^s} \int^{\gamma_s} \phi^s(n)\, dn$$

$$+ \int^{\phi(m)} \frac{\psi(t)\, dt}{t} \left\{1 - \sum_{s=1}^{k} (-)^s \left(\frac{t^s}{z^s} + \frac{z^s}{t^s}\right)\right\},$$

we shall obtain $\log F(z) = -\tfrac{1}{2}\log z - \dfrac{\rho}{2}\log 2\pi - Z\left(0\,;\begin{matrix}\epsilon_1, \epsilon_2, \ldots \\ b_1, b_2, \ldots\end{matrix}\right)$

$$+ \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{sz^s} F(\rho s) + \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{sz^s} Z\left(\rho,\ s\,;\begin{matrix}\epsilon_1, \epsilon_2, \ldots \\ b_1, b_2, \ldots\end{matrix}\right)$$

$$+ \int^{\phi(m)} \left(t^{\frac{1}{\rho}} - \frac{b_1}{\rho}\, t^{\frac{1-\epsilon_1}{\rho}} + \frac{\rho - \epsilon_1}{\rho^2}\frac{b_1^2}{2}\, t^{\frac{1-2\epsilon_1}{\rho}} - \frac{b_2}{\rho}\, t^{\frac{1-\epsilon_2}{\rho}} \ldots\right) \frac{dt}{t} \left\{1 + \sum_{s=-k}^{k}{}' \frac{(-t)^s}{z^s}\right\}.$$

And when we sum the Fourier series which result from the last integral, we find

$$\log F(z) = -\tfrac{1}{2}\log z - \frac{\rho}{2}\log 2\pi - Z\left(0\,;\begin{matrix}\epsilon_1, \epsilon_2, \ldots \\ b_1, b_2, \ldots\end{matrix}\right)$$

$$+ \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{sz^s} F(\rho s) + \sum_{s=1}^{\infty} \frac{(-)^{s-1}}{sz^s} Z\left(\rho,\ s\,;\begin{matrix}\epsilon_1, \epsilon_2, \ldots \\ b_1, b_2, \ldots\end{matrix}\right)$$

$$+ \frac{\pi}{\sin\dfrac{\pi}{\rho}}\, z^{\frac{1}{\rho}} - \frac{b_1\pi}{\rho}\, \frac{z^{\frac{1-\epsilon_1}{\rho}}}{\sin\pi\dfrac{1-\epsilon_1}{\rho}} + \frac{\pi b_1^2}{2}\cdot\frac{\rho + 1 - 2\epsilon_1}{\rho^2}\cdot\frac{z^{\frac{1-2\epsilon_1}{\rho}}}{\sin\pi\dfrac{1-2\epsilon_1}{\rho}} - \frac{b_2\pi}{\rho}\, \frac{z^{\frac{1-\epsilon_2}{\rho}}}{\sin\pi\dfrac{1-\epsilon_2}{\rho}} - \ldots$$

§ 59. This expansion is valid for all values of any z which lie between $-\pi$ and π. It is arithmetically asymptotic in the same way as the expansion from which it is derived.

We see from the results just obtained that the asymptotic approximation for $\log \prod_{n=1}^{\infty}\left[1 + \dfrac{z}{a_n}\right]$, where $a_n = n^\rho + b_1 n^{\rho-\epsilon_1} + \ldots$ exceeds that for $\log \prod_{n=1}^{\infty}\left[1 + \dfrac{z}{n^\rho}\right]$ by a quantity whose first term is $-Z\left(0\,;\begin{matrix}\epsilon_1, \epsilon_2, \ldots \\ b_1, b_2, \ldots\end{matrix}\right)$ when $\epsilon_1 > 1$, and by a quantity whose first term is

$$-\frac{b_1\pi}{\rho}\, \frac{z^{\frac{1-\epsilon_1}{\rho}}}{\sin\pi\dfrac{1-\epsilon_1}{\rho}}, \text{ when } \epsilon_1 < 1.$$

When $\epsilon_1 = 1$, the difference of the two asymptotic approximations commences with the indeterminate form $-\dfrac{b_1\pi}{\rho}\left[\dfrac{z^\theta}{\sin\pi\theta}\right]_{\theta=0}$, which arises from the integral

$$\frac{b_1}{\rho}\int^{\phi(m)} \frac{dt}{t}\left\{1 + \sum_{s=-k}^{k}{}' \frac{(-t)^s}{z^s}\right\}.$$

But this integral is equal to

$$\log \phi(m) + \sum_{s=-k}^{k}{}' \frac{(-)^s \phi^s(m)}{s z^s} = \log \phi(m) - \log \left[1 + \frac{\phi(m)}{z}\right] + \log \left[1 + \frac{z}{\phi(m)}\right] = \log z.$$

Thus, where $\epsilon_1 = 1$, the difference of the two asymptotic approximations commences with the term $-b_1 \rho^{-1} \log z$, a result which may be obtained without much difficulty by elementary algebra.

Note that $-b_1 \rho^{-1} \log z$ is the expression obtained when we reject the infinite part of the function $\dfrac{-b_1 \pi}{\rho} \dfrac{z^{\theta}}{\sin \pi^{\theta}}$ for $\theta = 0$, when expanded in powers of θ.

Note also that the constant $Z\left(0\,;\, \begin{matrix} \epsilon_1, \epsilon_2 \ldots \\ b_1, b_2 \ldots \end{matrix}\right)$ which, when $\epsilon_1 > 1$ is the first term of the asymptotic expansion of the logarithm of the ratio of our two products is equal to $\sum\limits_{n=1}^{\infty} \log \dfrac{a_n}{n^{\rho}}$.

By means of the formula $x > \log(1 + x) > \dfrac{x}{1 + x}$, where x is a real quantity lying between ± 1, we may prove that this series is absolutely convergent when $\rho > 1$.

Application to Functions of Zero Order.

§ 60. Hitherto no example has been given of a function of zero order, although the general investigation of § 36 applies equally to functions of this nature. In such cases it becomes necessary to introduce Maclaurin constants of a complexity which seems, except in special cases, beyond the reach of present analytical processes. They can no longer, as for functions of finite order, be expressed in terms of RIEMANN'S ζ function nor, I believe, in terms of any functions which have so far been introduced into analysis. An example will now be given of a very rapidly converging integral function. It obviously would serve as the starting point of a series of interesting researches dealing with the classification of simple integral functions of zero order.

61. We propose to obtain the asymptotic expansion of the function $\prod\limits_{n=1}^{\infty} \left[1 + \dfrac{z}{e^n}\right]$. In the notation of the general theory we have now $\phi(n) = e^n$.

Therefore $\qquad \log \phi(n) = n\,; \quad \sum\limits_{n=1}^{m-1} \log \phi(n) = \dfrac{m^2}{2} - \dfrac{m}{2}$.

By the Maclaurin sum formula, if s be positive,

$$\sum_{n=1}^{m-1} e^{ns} = \int^{m} e^{ns} dn + C_s - \frac{e^{ms}}{2} + \frac{B_1}{2\,!} s e^{ms} - \ldots$$

where C_s is the Maclaurin constant corresponding to e^{ns}, which may be determined as in § 84. If we put $\int^{m} e^{ns} dn = e^{ms}/s$, we have $C_s = (1 - e^s)^{-1}$.

If then we carry out the general process, we shall obtain the asymptotic expansion

$$\log \prod_{n=1}^{\infty} \left[1 + \frac{z}{e^n}\right] = (m - 1) \log z - \left(\frac{m^2}{2} - \frac{m}{2}\right) + \sum_{s=1}^{k} \frac{(-)^{s-1}}{sz^s} \mathrm{C}_s$$

$$+ \sum_{s=-k}^{k}{}' \left\{\frac{(-)^{s-1}}{sz^s} \left[\int^m e^{ns}\, dn - \frac{e^{ms}}{2}\right]\right\}$$

$$= (m - 1) \log z - \frac{m^2}{2} + \frac{m}{2} + \sum_{s=1}^{k} \frac{(-)^{s-1}\mathrm{C}_s}{sz^s} + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{sz^s} \left(\frac{e^{ms}}{s} - \frac{e^{ms}}{2}\right).$$

As before, we have to "sum" the final divergent series. We take $|z|$ to be a large quantity such that $\left|\frac{e^m}{z}\right|$ is very nearly equal to unity, and then we consider the Fourier series $\sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s} \left\{\frac{e^{i\theta s}}{s} - \frac{e^{i\theta s}}{2}\right\}$.

But $\sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s^2} e^{i\theta s} = 2 \sum_{s=1}^{k} \frac{(-)^{s-1} \cos \theta s}{s^2} = -\frac{1}{2}\left(\theta^2 - \frac{\pi^2}{3}\right)$.

And $\sum_{s=-k}^{k}{}' \frac{(-)^s e^{i\theta s}}{2s} = -\frac{1}{2} i\theta$.

Therefore we have the asymptotic expansion

$$\log \prod_{n=1}^{\infty} \left[1 + \frac{z}{e^n}\right] = (m - 1) \log z - \frac{m^2}{2} + \frac{m}{2} + \sum_{s=1}^{k} \frac{(-)^{s-1}\mathrm{C}_s}{sz^s} + \frac{1}{2}\left[\log \frac{e^m}{z}\right]^2 + \frac{\pi^2}{6} - \frac{1}{2} \log \frac{e^m}{z},$$

or finally* $\log \prod_{n=1}^{\infty} \left[1 + \frac{z}{e^n}\right] = \frac{1}{2} (\log z)^2 - \frac{1}{2} \log z + \frac{\pi^2}{6} + \sum_{s=1}^{\infty} \frac{(-)^{s-1}\mathrm{C}_s}{sz^s}$.

§ 62. It should be noticed that if, in the function whose asymptotic expansion has thus been obtained, we substitute e^z for z, we shall obtain the function $\prod_{n=1}^{\infty} \left[1 + \frac{e^z}{e^n}\right]$. This is an integral function whose zeros are of the form

$$z = n + (2m - 1) \pi \iota \begin{cases} n = 1, 2, 3, \ldots \infty. \\ m = -\infty, \ldots, -1, 0, 1, \ldots \infty. \end{cases}$$

It is substantially what I propose to call LAMBERT's function. The function has properties which are a sort of mean between those of the elliptic and double gamma functions.

We can express LAMBERT's function as a product of two double gamma functions. It is closely connected with the well-known LAMBERT's series, and in terms of it we can express in a very elegant form the coefficients of capacity of two spheres.

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* The dominant terms of this result are equivalent to those given by MELLIN, 'Acta Societatis Fennicæ,' t. 24, p. 50.

§ 63. The reader will notice that in the preceding analysis we have used the methods and not the result of the general formula.

The reason is that with an exponential subject of integration we are unable to ensure that we do not introduce arbitrary additive constants when the indefinite integrals are transformed as formerly.

For in this case $\phi(n) = e^n$ and $\psi(n) = \log n$;

and we have to consider a series of integrals of which the first is $\int^{\phi(m)} \frac{\psi(t)\,dt}{t}$.

We are tempted to say that this integral is equal to

$$\int^1 \frac{\log[\phi(m)\,t]\,dt}{t} = \int^1 \Big[\log\phi(m) + \log t\Big]\frac{dt}{t} = 0,$$

whereas we only avoid introducing an additive constant by saying that

$$\int^1 \frac{\log[\phi(m)\,t]\,dt}{t} = \tfrac{1}{2}\left[\log^2(\phi(m)\,t)\right]^1 = \tfrac{1}{2}\left[\log\phi(m)\right]^2.$$

§ 64. The integral function just considered is the most simple function of zero order. In carrying out the algebraical analysis of a theory of such functions, it would be necessary to consider the types

$$\prod_{n=1}^{\infty}\left[1 + \frac{z}{e^{e^n}}\right], \qquad \prod_{n=1}^{\infty}\left[1 + \frac{z}{e^{e^{e^n}}}\right] \text{ \&c.}$$

The asymptotic expansions for these successive functions are of successively lower orders of greatness—they are never, however, of so low an order as z^n, where n is finite. This agrees with the known theorem that an algebraical polynomial is the only uniforn function of such an order. Unfortunately, unless we introduce new analytical functions defined by definite integrals, we cannot investigate formally asymptotic approximations for such types; and until the properties of such new functions are investigated, we but express one unknown form in terms of another.

Simple Integral Functions of Finite Non-integral Order Greater than Unity.

§ 65. In the investigations to which we now proceed of simple integral functions of finite non-integral order greater than unity, the theoretical considerations which have been given in detail for functions of order less than unity will for the most part be suppressed, and for brevity only the bare analysis will be written down.

We consider first the standard function $Q_\rho(z) = \prod_1^\infty \left[\left(1 + \frac{z}{n^{1/\rho}}\right) e^{-\frac{z}{n^{1/\rho}} + \dots + \frac{(-)^p z^p}{p n^{p/\rho}}}\right]$,

where $\rho > 1$ and p is an integer such that $p + 1 > \rho > p$.

Let $z = Re^{i\theta}$, and suppose that R is very large.

Take m an integer such that $m - 1 < R^\rho \leqq m$.

Then
$$Q_\rho(z) = \prod_{n=1}^{m-1}\left[\left(1 + \frac{z}{n^{1/\rho}}\right) e^{-\frac{z}{n^{1/\rho}} + \dots + \frac{(-)^p z^p}{pn^{p/\rho}}}\right]$$
$$\times \prod_{n=m}^{\infty}\left[\left(1 + \frac{z}{n^{1/\rho}}\right) e^{-\frac{z}{n^{1/\rho}} + \dots + \frac{(-)^p z^p}{pn^{p/\rho}}}\right],$$

so that
$$Q_\rho(z) = \prod_{n=1}^{m-1}\left[1 + \frac{z}{n^{1/\rho}}\right] \times \prod_{n=1}^{m-1}\left[e^{-\frac{z}{n^{1/\rho}} + \dots + \frac{(-z)^p}{pn^{p/\rho}}}\right]$$
$$\times \prod_{n=m}^{\infty}\left[e^{\frac{(-)^p z^{p+1}}{(p+1)n^{\frac{p+1}{\rho}}} + \frac{(-)^{p+1} z^{p+2}}{(p+2)n^{\frac{p+2}{\rho}}} + \dots}\right];$$

and hence
$$\log Q_\rho(z) = (m - 1)\log z - \frac{1}{\rho}\sum_{n=1}^{m-1}\log n$$
$$+ \sum_{n=1}^{m-1}\left[\frac{n^{1/\rho}}{z} + \dots + \frac{(-)^{s-1} n^{s/\rho}}{sz^s} + \dots\right]$$
$$+ \sum_{n=1}^{m-1}\left[-\frac{z}{n^{1/\rho}} + \dots + \frac{(-z)^p}{pn^{p/\rho}}\right]$$
$$+ \sum_{n=m}^{\infty}\left[\frac{(-)^p z^{p+1}}{(p+1)n^{\frac{p+1}{\rho}}} + \frac{(-)^{p+1} z^{p+2}}{(p+2)n^{\frac{p+2}{\rho}}} + \dots\right].$$

Now, when m is a very large integer,

$$\sum_{n=1}^{m-1}\frac{1}{n^{s/\rho}} = \frac{m^{1-s/\rho}}{1 - \frac{s}{\rho}} - \frac{m^{-s/\rho}}{2} + \dots + \frac{(-)^t}{\frac{-s}{\rho} - 2t - 1}\binom{\frac{-s}{\rho}}{2t+2}\frac{B_{t+1}}{m^{2t - \frac{s}{\rho} + 1}} + \dots + F\left(\frac{-s}{\rho}\right).$$

And, when s is positive and greater than ρ,

$$-\sum_{n=m}^{\infty}\frac{1}{n^{s/\rho}} = \frac{m^{1-s/\rho}}{1 - \frac{s}{\rho}} - \frac{m^{-s/\rho}}{2} + \dots + \frac{(-)^t}{\frac{-s}{\rho} - 2t - 1}\binom{\frac{-s}{\rho}}{2t+2}\frac{B_{t+1}}{m^{2t - \frac{s}{\rho} + 1}} + \dots$$

We use these Maclaurin approximations and rearrange the double series which results as the arithmetically asymptotic approximation for $\log Q_\rho(z)$. We obtain, in the limit, when the limits of the summable divergent series are taken for k infinite, the asymptotic expansion

$$\log Q_\rho(z) = (m-1)\log z - \frac{1}{\rho}(m-\tfrac{1}{2})\log m - \frac{m}{\rho} - \frac{1}{2\rho}\log 2\pi$$

$$+ \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} F\left(\frac{s}{\rho}\right)$$

$$+ m\rho \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s\,.\,\rho + s}\left(\frac{m^{1/\rho}}{z}\right)^s - \tfrac{1}{2}\sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s}\left(\frac{m^{1/\rho}}{z}\right)^s$$

$$+ \sum_{t=0}^{\infty} \frac{(-)^t}{\overline{2t+2}\,!}\frac{B_{t+1}}{m^{2t+1}}\left\{\frac{-(2t)\,!}{\rho} + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s}\left(\frac{m^{1/\rho}}{z}\right)^s \left[\frac{d^{2t+1}x^{s/\rho}}{dx^{2t+1}}\right]_{x=1}\right\}.$$

We suppose now that $\frac{|z|}{m^{1/\rho}}$ is a quantity which, when m is very large, is ultimately equal to unity. Then we may "sum," as before (§ 52), the Fourier series, which are the various coefficients in the preceding expansion.

We have $\rho \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s\,.\,\rho+s}\left(\frac{m^{1/\rho}}{z}\right)^s = \frac{\pi}{\sin\pi\rho}\frac{z^\rho}{m} + \log\frac{m^{1/\rho}}{z} - \frac{1}{\rho}$, provided ρ is not integral, and provided $-\pi < \theta < \pi$. And $-\tfrac{1}{2}\sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s}\left(\frac{m^{1/\rho}}{z}\right)^s = -\tfrac{1}{2}\log\frac{m^{1/\rho}}{z}$.

Also, exactly as before, the coefficient of B_{t+1} in the asymptotic approximation for $\log Q_\rho(z)$ vanishes identically.

Therefore we have, provided $-\pi < \theta < \pi$, the asymptotic equality

$$\log Q_\rho(z) = (m-\tfrac{1}{2})\log\frac{z}{m^{1/\rho}} - m - \tfrac{1}{2}\log z - \frac{1}{2\rho}\log 2\pi + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{sz^s}F\left(\frac{s}{\rho}\right)$$

$$+ \frac{\pi z^\rho}{\sin\pi\rho} + m\log\frac{m^{1/\rho}}{z} - \frac{m}{\rho} - \tfrac{1}{2}\log\frac{m^{1/\rho}}{z}.$$

Thus, provided $-\pi < \arg z < \pi$, we have finally

$$\log Q_\rho(z) = \frac{\pi z^\rho}{\sin\pi\rho} - \frac{1}{2\rho}\log 2\pi - \tfrac{1}{2}\log z + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{sz^s}F\left(\frac{s}{\rho}\right).$$

This expansion is exactly analogous to the one previously obtained for $\log P_\rho(z)$ and is to be regarded in the same way. It must be borne in mind that $n^{1/\rho}$ has been assumed to be the arithmetic ρ^{th} root of n. Had any other root been taken—say the arithmetic root multiplied by $\omega = e^{\frac{2\pi\iota r}{\rho}}$, where r is an integer, we should have obtained the asymptotic expansion

$$Q_\rho(z) = e^{\frac{\pi\iota r}{\rho}}\frac{(2\pi)^{-\frac{1}{2}\rho}}{z^{1/2}}\exp\left\{\frac{\pi z^\rho}{\sin\pi\rho} + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}\omega^s}{sz^s}F\left(\frac{s}{\rho}\right)\right\}$$

valid, when $-\pi < \theta - \frac{2\pi r}{\rho} < \pi$, *i.e.*, when $-\pi + \frac{2\pi r}{\rho} < \theta < \pi + \frac{2\pi r}{\rho}$.

The expansion is thus valid everywhere except along the new line of zeros.

§ 66. We proceed now to investigate the asymptotic expansion for

$$\mathrm{F}(z) = \prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{a_n}\right) e^{\frac{-z}{a_n} + \ldots + \frac{(-z)^p}{p a_n{}^p}} \right],$$

where a_n is such a function of n, $\phi(n)$, let us say, that $\sum_{n=1}^{\infty} \frac{1}{a_n{}^{\rho+\epsilon}}$ converges, and $\sum_{n=1}^{\infty} \frac{1}{a_n{}^{\rho-\epsilon}}$ diverges, however small ϵ may be, ρ being real, finite, positive, non-integral, and greater than unity, while p is an integer such that $p + 1 > \rho > p$.

Suppose that the result of reversing the equality $r = \phi(n)$ is to give $n = \psi(r)$.

Let m be a very large integer, such that $m - 1 < \psi(|z|) \eqslantless m$.

As previously, we have

$$\begin{aligned}\log \mathrm{F}(z) = (m-1) \log z &- \sum_{n=1}^{m-1} \log \phi(n) \\ &+ \sum_{n=1}^{m-1} \left[\frac{\phi(n)}{z} + \ldots + \frac{(-)^{s-1} \phi^s(n)}{s z^s} + \ldots \right] \\ &+ \sum_{n=1}^{m-1} \left[-\frac{z}{\phi(n)} + \ldots + \frac{(-)^p z^p}{p \phi^p(n)} \right] \\ &+ \sum_{n=m}^{\infty} \left[\frac{(-)^p z^{p+1}}{(p+1)\, \phi^{p+1}(n)} + \frac{(-)^{p+1} z^{p+2}}{p+2\ \phi^{p+2}(n)} + \ldots \right].\end{aligned}$$

Substitute now the arithmetically asymptotic approximations given by the Maclaurin sum formula, and we have

$$\begin{aligned}\log \mathrm{F}(z) = (m-1) \log z &- \int_{\gamma_0}^{m} \log \phi(n)\, dn + \tfrac{1}{2} \log \phi(m) \\ &+ \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s z^s} \int_{\gamma_s}^{m} \phi^s(n)\, dn - \tfrac{1}{2} \sum_{s=-k}^{k}{}' \frac{(-)^{s-1} \phi^s(m)}{s z^s} \\ &+ \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{(2t+2)!} \left\{ -\frac{d^{2t+1}}{dm^{2t+1}} \log \phi(m) + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{s z^s} \frac{d^{2t+1}}{dm^{2t+1}} \phi^s(m) \right\}.\end{aligned}$$

In this expansion γ_{-s} is infinite, and there is no corresponding Maclaurin constant if, and only if, $s > \rho$.

Use indefinite integrals and transform by integrating by parts in the same way and under the same restrictions as in § 54, and we get

$$\begin{aligned}\log \mathrm{F}(z) = -\tfrac{1}{2} \log z &+ \int^{\gamma_0} \log \phi(n)\, dn + \sum_{s=-p}^{\infty}{}'' \frac{(-)^s}{s z^s} \int^{\gamma_s} \phi^s(n)\, dn \\ &+ \int^{\phi(m)} \frac{\psi(t)\, dt}{t} \left\{ 1 + \sum_{s=-k}^{k}{}' \frac{(-t)^s}{z^s} \right\}.\end{aligned}$$

The final integral gives rise to the dominant term of the asymptotic expansion. As formerly, it may be written

$$\underset{k=\infty}{Lt}\int^{\pi}\iota\psi\{z\,e^{\iota(\mu-\pi)}\}\,\frac{\sin(k+\frac{1}{2})\,\mu}{\sin\frac{1}{2}\mu}\,d\mu.$$

If we denote the value of this integral by $f(z)$, and if we put

$$\int^{\gamma_0}\log\phi(n)\,dn=\log F_0,\quad \int^{\gamma_s}\phi^s(n)\,dn=F_s,$$

we have the final asymptotic equality

$$\prod_{n=1}^{\infty}\left\{\left(1+\frac{z}{a_n}\right)e^{\frac{-z}{a_n}+\dots+\frac{(-z)^p}{pa_n{}^p}}\right\}=F_0\,z^{-\frac{1}{2}}\exp\left\{f(z)+\sum_{s=-p}^{\infty}{}'\,\frac{(-)^sF_s}{s\,z^s}\right\}.$$

§ 67. We notice the exact analogy between this expansion and the one previously obtained in the case when the order of the function is less than unity. The only difference arises from the Maclaurin constants. In the former case, all the constants corresponding to negative values of s were zero; in the present case, the first p of them are formed from asymptotic expansions like $\sum_{n=1}^{m-1}\frac{1}{a_n{}^s}=\int_{\gamma_{-s}}^{m}\phi^{-s}(n)\,dn+\dots$, and give rise consequently to finite constants; while only the remaining ones, formed from expansions like $-\sum_{n=m}^{\infty}\frac{1}{a_n{}^s}=\int_{r_{-s}}^{m}\phi^{-s}(n)\,dn+\dots$ are such that $\gamma_{-s}=\infty$.

We notice also the great elegance with which WEIERSTRASS' exponential factor enters to ensure the finiteness of the expressions obtained in the course of the analysis. Could we conceive an attempt to investigate, for functions of order greater than unity, the theory which we carried out for functions of order less than unity in the first paragraphs of this part of the present paper, we should at the outset be forced to invent again WEIERSTRASS' great theorem.

Application to Functions with Algebraic Sequence of Zeros.

§ 68. We will now evaluate the first few terms of the asymptotic expansion for $P(z)=\prod_{1}^{\infty}\left[\left(1+\frac{z}{a_n}\right)e^{-\frac{z}{a_n}+\dots+\frac{(-)^pz^p}{pa_n{}^p}}\right]$, where $a_n=n^{\frac{1}{\rho}}\left[1+\frac{b_1}{n^{\epsilon_1}}+\frac{b_2}{n^{\epsilon_2}}+\dots\right]$, and the ϵ's are positive real quantities arranged in ascending order of magnitude.

Let $r=a_n=\phi(n)$, then on reversion of series we find

$$n=\psi(r)=r^{\rho}-\rho b_1r^{\rho(1-\epsilon_1)}+\left\{\frac{\rho(\rho+1-2\rho\epsilon_1)}{2}\,b_1{}^2\right\}r^{\rho(1-2\epsilon_1)}-\rho b_{2r}{}^{\rho(1-\epsilon_2)}+\dots$$

When s is positive,

$$\sum_{n=1}^{m-1} a_n^s = \sum_{n=1}^{m-1} \left[n^{\frac{s}{\rho}} + sb_1 n^{\frac{s}{\rho} - \epsilon_1} + \frac{s(s-1)}{2} b_1^2 n^{\frac{s}{\rho} - 2\epsilon_1} + sb_2 n^{\frac{s}{\rho} - \epsilon_2} + \ldots \right]$$

$$= \int^m \phi^s(n)\, dn + \mathrm{F}\left(\frac{s}{\rho}\right) + sb_1 \mathrm{F}\left(\frac{s}{\rho} - \epsilon_1\right) + \frac{s(s-1)}{2} b_1^2 \mathrm{F}\left(\frac{s}{\rho} - 2\epsilon_1\right)$$

$$+ sb_2 \mathrm{F}\left(\frac{s}{\rho} - \epsilon_2\right) + \ldots$$

$$- \frac{\phi^s(m)}{2} + \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t+2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \phi^s(m);$$

and $$\sum_{n=1}^{m-1} \frac{1}{a_n^s} = \sum_{n=1}^{m-1} \left[n^{-\frac{s}{\rho}} - sb_1 n^{-\frac{s}{\rho} - \epsilon_1} + \frac{s(s+1)}{2} b_1^2 n^{-\frac{s}{\rho} - 2\epsilon_1} - sb_2 n^{-\frac{s}{\rho} - \epsilon_2} - \ldots \right]$$

$$= \int^m \phi^{-s}(n)\, dn + \mathrm{Z}\left(\rho, -s; \begin{matrix} \epsilon_1 & \epsilon_2 & \ldots \\ b_1 & b_2 & \ldots \end{matrix}\right) + \mathrm{F}\left(-\frac{s}{\rho}\right) - \frac{\phi^{-s}(m)}{2}$$

$$+ \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t+2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \phi^{-s}(m),$$

where $\mathrm{Z}\left(\rho, -s; \begin{matrix} \epsilon_1 & \epsilon_2 & \ldots \\ b_1 & b_2 & \ldots \end{matrix}\right)$ can be expressed in terms of Riemann ζ functions, or the equivalent Maclaurin constants F by the formula

$$\mathrm{Z}\left(\rho, -s; \begin{matrix} \epsilon_1 & \epsilon_2 & \ldots \\ b_1 & b_2 & \ldots \end{matrix}\right) = -sb_1 \mathrm{F}\left(-\frac{s}{\rho} - \epsilon_1\right) + \frac{s(s+1)}{2} b_1^2 \mathrm{F}\left(-\frac{s}{\rho} - 2\epsilon_1\right)$$

$$- sb_2 \mathrm{F}\left(-\frac{s}{\rho} - \epsilon_2\right) + \ldots$$

As formerly, we put

$$\mathrm{Z}\left(0; \begin{matrix} \epsilon_1, & \epsilon_2 & \ldots \\ b_1, & b_2 & \ldots \end{matrix}\right) = b_1 \mathrm{F}(-\epsilon_1) - \frac{b_1^2}{2} \mathrm{F}(-2\epsilon_1) + b_2 \mathrm{F}(-\epsilon_2) + \ldots,$$

so that $\frac{\rho}{2} \log 2\pi + \mathrm{Z}(0)$ arises as the Maclaurin constant corresponding to the asymptotic expansion for $\sum_{n=1}^{m-1} \log \phi(n)$.

Proceeding exactly as for the case when the order of the function is equal to unity we see that the asymptotic expansion of $\log \mathrm{P}(z)$ is

$$\frac{\pi}{\sin \pi\rho} z^\rho - \tfrac{1}{2} \log z - \frac{1}{2\rho} \log 2\pi + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{\rho}\right)$$

$$\frac{-\pi\rho b_1}{\sin \pi\rho(1-\epsilon_1)} z^{\rho(1-\epsilon_1)} + \frac{\rho(\rho+1-2\rho\epsilon_1)}{2} b_1^2 \frac{\pi}{\sin \pi\rho(1-2\epsilon_1)} z^{\rho(1-2\epsilon_1)}$$

$$\frac{-\pi\rho b_2}{\sin \pi\rho(1-\epsilon_2)} z^{\rho(1-\epsilon_2)} + \ldots + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{Z}\left(\rho, s; \begin{matrix} \epsilon_1, & \epsilon_2 & \ldots \\ b_1, & b_2 & \ldots \end{matrix}\right)$$

$$- \mathrm{Z}\left(0; \begin{matrix} \epsilon_1, & \epsilon_2 & \ldots \\ b_1, & b_2 & \ldots \end{matrix}\right),$$

this expansion being valid when $-\pi < \arg z < \pi$.

Thus, when $\rho - \epsilon_1\rho > p$, the first term of the expansion of the ratio

$$\log \frac{\prod\limits_{n=1}^{\infty}\left[\left(1+\frac{z}{a_n}\right)e^{-\frac{z}{a_n}+\ldots,+\frac{(-z)^p}{p a_n{}^p}}\right]}{\prod\limits_{n=1}^{\infty}\left[\left(1+\frac{z}{n^{1/\rho}}\right)e^{-\frac{z}{n^{1/\rho}}+\ldots+\frac{(-z)^p}{p n^{p/\rho}}}\right]} \quad \text{is} \quad \frac{-\pi\rho b_1}{\sin\pi\rho(1-\epsilon_1)}\, z^{\rho(1-\epsilon_1)}.$$

And, when $\rho - \epsilon_1\rho < p$, the first term is $\dfrac{(-)^p z^p}{p}\, Z\left(\rho, -p\,;\, \begin{matrix}\epsilon_1, \epsilon_2 \ldots \\ b_1, b_2 \ldots\end{matrix}\right)$, which is readily seen to be equal to $\dfrac{(-z)^p}{p}\sum\limits_{n=1}^{\infty}\left[\dfrac{1}{a_n{}^p} - \dfrac{1}{n^{p/\rho}}\right]$.

§ 69. The expansion which we have obtained is valid for all points except those near the line of zeros of the function and for all finite values of the quantities b and ϵ such that a_n has a finite value. It must be carefully noticed that when any term becomes infinite through the occurrence of sines of integral multiples of π, we must revert to the genesis of that term to find the true form of the expansion. Thus, when $\rho - \rho\epsilon_1 = p$, the first term of the ratio just considered is that which arises from

$$-b_1\rho\int^{\phi(m)} t^p\left\{1 + \sum_{s=-k}^{k}{}' \frac{(-t)^s}{z^s}\right\}\frac{dt}{t},$$

that is, from

$$-b_1\rho\left\{\frac{\phi^p(m)}{p} + \sum_{s=-k}^{k}{}'' \frac{(-)^s\phi^{s+p}(m)}{(s+p)z^s} + (-z)^p\log\phi(m)\right\},$$

where the double accent denotes that the terms corresponding to $s = 0$ and $s = -p$ are to be omitted from the summation.

Put now $\dfrac{\phi(m)}{z} = e^{-i\theta}$, then, with the argument previously used, we have to sum the series

$$-b_1\rho\phi^p(m)\left\{\frac{1}{p} + \sum_{s=-k}^{k}{}'' \frac{(-e^{-i\theta})^s}{s+p} + (-e^{+i\theta})^p\log\phi(m)\right\}.$$

Now, when ρ is not integral, we have seen that

$$\frac{1}{p} + \sum_{s=-k}^{k}{}' \frac{(-)^s}{s+\rho}e^{-si\theta} = \frac{\pi}{\sin\pi\rho}e^{\rho i\theta}, \quad \text{provided} \quad -\pi \lesseqgtr \theta \lesseqgtr \pi.$$

Let us put $\rho = p + \epsilon$, where p is a positive integer and ϵ is very small. Then we have, retaining only first powers of ϵ,

$$\frac{1}{p} + \sum_{s=-k}^{k}{}'' \frac{(-)^s e^{-si\theta}}{s+p} + \frac{(-)^p e^{pi\theta}}{\epsilon} = \frac{\pi}{(-)^p\pi\epsilon}e^{pi\theta}[1+\epsilon i\theta],$$

so that

$$\frac{1}{p} + \sum_{s=-k}^{k}{}'' \frac{(-)^s e^{-si\theta}}{s+p} = (-)^p e^{pi\theta} i\theta,$$

The term which we seek is then the value of

$$- b_1 \rho \phi^p (m) (-)^p \left\{ \frac{z}{\phi(m)} \right\}^p \log z = (-)^{p+1} b_1 \rho z^p \log z.$$

This is, of course, the term independent of θ in the expansion of $\frac{-\pi \rho b_1}{\sin \pi (p + \theta)} z^{p+\theta}$ in ascending powers of θ.

In exactly the same manner, if $\rho - n\epsilon_s$ (say) is an integer, the corresponding term of our asymptotic expansion must undergo the same process of evaluation and will give rise to a logarithmic term. If one of the ϵ's, say ϵ_k, is equal to ρ, we obtain in the asymptotic expansion a corresponding logarithmic term

$$- \rho b_k \log z.$$

Simple Integral Functions of Finite Integral Order.

§ 70. We proceed now to consider the standard function

$$\mathrm{R}_\rho (z) = \prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{n^{1/\rho}} \right) e^{\frac{-z}{n^{1/\rho}} + \dots + \frac{(-z)^\rho}{\rho n^{\rho/\rho}}} \right], \text{ where } \rho \text{ is an integer} \geqq 1.$$

Let $z = re^{\iota\theta}$, where r is very large, and let m be a large integer such that $m - 1 < r^\rho \leqq m$.

Then, employing the same process and argument as before,

$$\begin{aligned} \log \mathrm{R}_\rho (z) = & \sum_{n=1}^{m-1} \left\{ \frac{n^{1/\rho}}{z} + \dots + \frac{(-)^{s-1} n^{s/\rho}}{s z^s} + \dots \right\} \\ & + (m - 1) \log z - \frac{1}{\rho} \sum_{n=1}^{m-1} \log n + \sum_{n=1}^{m-1} \left\{ \frac{-z}{n^{1/\rho}} + \dots + \frac{(-z)^\rho}{\rho n^{\rho/\rho}} \right\} \\ & - \sum_{n=m}^{\infty} \left\{ \frac{(-z)^{\rho+1}}{(\rho+1) n^{\frac{\rho+1}{\rho}}} + \frac{(-z)^{\rho+2}}{(\rho+2) n^{\frac{\rho+2}{\rho}}} + \dots \right\}. \end{aligned}$$

Now, when $\frac{s}{\rho} = 1$,

$$\sum_{n=1}^{m-1} \frac{m^{s/\rho}}{n^{s/\rho}} = \gamma m^{s/\rho} + m^{s/\rho} \log m - \tfrac{1}{2} + \dots + \frac{(-)^t}{-\frac{s}{\rho} - 2t - 1} \binom{-\frac{s}{\rho}}{2t+2} \frac{\mathrm{B}_{t+1}}{m^{2t+1}} + \dots,$$

and in accordance with the definition of § 49 we put $\gamma = \mathrm{F}(-1)$.

If, then, we suitably modify the analysis formerly employed we shall obtain, when the limits of the summable divergent series as k tends to infinity are taken, the arithmetically asymptotic expansion

$$\log \mathrm{R}_\rho(z) = (m-1)\log z - \frac{1}{\rho}\{(m-\tfrac{1}{2})\log m - m + \tfrac{1}{2}\log 2\pi\}$$

$$+ \sum_{s=-\rho}^{\infty}{}' \frac{(-)^{s-1}}{sz^s}\mathrm{F}\left(\frac{s}{\rho}\right) + m\sum_{s=-k}^{k}{}'' \left\{\frac{(-)^{s-1}}{sz^s}\frac{m^{s/\rho}}{\dfrac{s}{\rho}+1}\right\}$$

$$+ \frac{(-z)^{-\rho}}{\rho}\log m - \tfrac{1}{2}\sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{sz^s}m^{s/\rho}$$

$$+ \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t+2!}\frac{1}{m^{2t+1}}\left\{\frac{-(2t)!}{\rho} + \sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{sz^s}m^{s/\rho}\left[\frac{d^{2t+1}}{dx^{2t+1}}x^{s/\rho}\right]_{x=1}\right\};$$

where the double accent denotes that in the corresponding summation the terms for which $s = 0$ and $s = -\rho$ are to be omitted.

As before, the coefficient of B_{t+1} vanishes identically.

The series $\displaystyle\sum_{s=-k}^{k}{}' \frac{(-)^{s-1}}{sz^s}m^{s/\rho}$ is equal to $\log \dfrac{m^{1/\rho}}{z}$.

It is then only necessary for us to consider the series $\displaystyle\sum_{s=-k}^{k}{}'' \frac{(-)^{s-1}}{sz^s}\frac{m^{s/\rho}}{\dfrac{s}{\rho}+1}$.

If we put $t = \log \dfrac{m^{1/\rho}}{z}$, we may write this series in the form

$$f(t) = \sum_{s=-k}^{k}{}'' \frac{(-)^{s-1}e^{st}}{s\left(\dfrac{s}{\rho}+1\right)} = \sum_{s=-k}^{k}{}'' (-)^{s-1}e^{st}\left(\frac{1}{s} - \frac{1}{s+\rho}\right).$$

Remembering that a summable divergent series may be differentiated, we find

$$f(t) = -\frac{1}{\rho}f'(t) + \sum_{s=-k}^{k}{}'' \frac{(-)^{s-1}e^{st}}{s},$$

or

$$f'(t) + \rho f(t) = \rho t + (-)^{\rho-1}e^{-\rho t}.$$

Therefore

$$f(t) = \mathrm{A}e^{-\rho t} + t - \frac{1}{\rho} + (-)^{\rho-1}te^{-\rho t},$$

where A is a constant of integration.

Now when $t = 0$,

$$f(t) = \sum_{s=-k}^{k}{}'' \frac{(-)^{s-1}}{s\left(\dfrac{s}{\rho}+1\right)} = \sum_{s=-k}^{k}{}'' (-)^{s-1}\left(\frac{1}{s} - \frac{1}{s+\rho}\right),$$

and, by putting $\theta = 0$ in the FOURIER's series, which we considered in the preceding paragraph, we see that this is equal to $-\frac{1}{\rho} + \frac{(-)^{\rho-1}}{\rho}$.

Therefore

$$f(t) = (-)^{\rho-1} e^{-\rho t} \left[\frac{1}{\rho} + t\right] + t - \frac{1}{\rho},$$

so that

$$\sum_{s=-k}^{k}{}'' \frac{(-)^{s-1}}{sz^s} \frac{m^{s/\rho}}{\frac{s}{\rho} + 1} = (-)^{\rho-1} \frac{z^\rho}{m} \left[\frac{1}{\rho} + \log \frac{m^{1/\rho}}{z}\right] + \log \frac{m^{1/\rho}}{z} - \frac{1}{\rho}.$$

Revert now to the asymptotic expansion for $\log \mathrm{R}_\rho(z)$.

We find on substitution that

$$\begin{aligned}\log \mathrm{R}_\rho(z) = (m-1)\log z &- \frac{1}{\rho}\{(m-\tfrac{1}{2})\log m - m + \tfrac{1}{2}\log 2\pi\} \\ &+ \sum_{s=-\rho}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{\rho}\right) + (-)^{\rho-1} z^\rho \left\{\log \frac{m^{1/\rho}}{z} + \frac{1}{\rho}\right\} \\ &+ m\left(\log \frac{m^{1/\rho}}{z} - \frac{1}{\rho}\right) + \frac{(-z)^\rho}{\rho} \log m - \tfrac{1}{2} \log \frac{m^{1/\rho}}{z}.\end{aligned}$$

And thus, when ρ is an integer, $|z|$ very large, and $-\pi < \arg z < \pi$,

$$\log \mathrm{R}_\rho(z) = -\tfrac{1}{2}\log z + \sum_{s=-\rho}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{\rho}\right) - \frac{1}{2\rho}\log 2\pi + (-z)^\rho \log z + (-)^{\rho-1} \frac{z}{\rho}.$$

As formerly, this expansion is, in form, independent of the argument of z.

§ 71. We may easily deduce this theorem independently as the limit of our former results.

Take the asymptotic equality

$$\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{n^{1/\rho}}\right) e^{-\frac{z}{n^{1/\rho}} + \dots + \frac{(-z)^{p-1}}{\overline{p-1}\, n^{\frac{p-1}{\rho}}}}\right] = (2\pi)^{-\frac{1}{2\rho}} z^{-\frac{1}{2}} e^{\frac{\pi}{\sin \pi\rho} z^\rho + \sum_{s=-p+1}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{\rho}\right)},$$

where ρ lies between $p - 1$ and p.

Put now $\rho = p - \epsilon$; then $\mathrm{R}_p(z)$ is the limit, when ϵ vanishes, of

$$\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{n^{\frac{1}{p-\epsilon}}}\right) e^{-\frac{z}{n^{\frac{1}{p-\epsilon}}} + \dots + \frac{(-z)^{p-1}}{\overline{p-1}\, n^{\frac{p-1}{p-\epsilon}}}}\right] \times \prod_{n=1}^{\infty} e^{\frac{\frac{(-z)^p}{p}}{\rho\, n^{\frac{p}{p-\epsilon}}}}.$$

It therefore possesses an asymptotic expansion which is the limit, when ϵ vanishes, of

$$(2\pi)^{-\frac{1}{2p-\epsilon}} z^{-\frac{1}{2}} \exp\left\{\frac{\pi z^{p-\epsilon}}{\sin \pi (p-\epsilon)} + \frac{(-z)^p}{p} \zeta\left(\frac{p}{p-\epsilon}\right) + \sum_{s=-p+1}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{p-\epsilon}\right)\right\}$$

$$= (2\pi)^{-\frac{1}{2p}} z^{-\frac{1}{2}} \exp\left\{(-z)^p \log z + \frac{(-z)^p(\gamma-1)}{p} + \sum_{s=-p+1}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{p}\right)\right\}$$

$$= (2\pi)^{-\frac{1}{2p}} z^{-\frac{1}{2}} \exp\left\{(-z)^p \log z + (-)^{p-1}\frac{z^p}{p} + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{p}\right)\right\},$$

remembering that $\mathrm{F}(-1) = \gamma$, and that $\underset{s=1}{\mathrm{L}t}\left[\zeta(s) + \frac{1}{1-s}\right] = \gamma +$ terms which vanish when $s = 1$.

We thus obtain the same asymptotic expansion as in the previous paragraph.

Note that we have obtained our expansion by making ρ increase up to the nearest integer. If, on the contrary, we make ρ decrease *down* to the nearest integer, there is no breach of continuity in the introduction of an additional exponential factor. Thus we have

$$\mathrm{R}_p(z) = \underset{\epsilon=0}{\mathrm{L}t} \prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{n^{\frac{1}{p+\epsilon}}}\right) e^{-\frac{z}{n^{\frac{1}{p+\epsilon}}} + \ldots + \frac{(-z)^p}{pn^{\frac{p}{p+\epsilon}}}}\right],$$

and therefore we have the asymptotic expansion

$$\mathrm{R}_p(z) = \underset{\epsilon=0}{\mathrm{L}t}\,(2\pi)^{-\frac{1}{2p+\epsilon}} z^{-\frac{1}{2}} \exp\left\{\frac{\pi z^{p+\epsilon}}{\sin \pi (p+\epsilon)} + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{p+\epsilon}\right)\right\}.$$

Now, unless $s = -1$, $\mathrm{F}(s) = \zeta(-s)$; and therefore we have asymptotically

$$\mathrm{R}_p(z) = \underset{\epsilon=0}{\mathrm{L}t}\,(2\pi)^{-\frac{1}{2p+\epsilon}} z^{-\frac{1}{2}} \exp\left\{\frac{(-z)^p(1 + \epsilon \log z + \ldots)}{\epsilon} + \frac{(-z)^p}{p}\zeta\left(\frac{p}{p+\epsilon}\right) \right.$$

$$\left. + \sum_{s=-p+1}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{p+\epsilon}\right)\right\}$$

$$= (2\pi)^{-\frac{1}{2p}} z^{-\frac{1}{2}} \exp\left\{(-z)^p \log z + \frac{(-z)^p(\gamma-1)}{p} + \sum_{s=-p+1}^{\infty}{}' \frac{(-)^{s-1}}{sz^s} \mathrm{F}\left(\frac{s}{p}\right)\right\},$$

the same expansion as before.

This paragraph is instructive in that it shows how the asymptotic expansion calls for another exponential factor in each term of WEIERSTRASS' product as the order passes through an integral value.

§ 72. If now it is desired to construct a function which is the natural extension among simple integral functions of the ordinary gamma function, we take

$$\frac{1}{\Gamma(z|\rho)} = e^{\sum_{s=1}^{\rho}\frac{(-)^{s-1}}{s}z^s\,\mathrm{F}\left(-\frac{s}{\rho}\right)} \,.\, z \,.\, \prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{n^{1/\rho}}\right) e^{-\frac{z}{n^{1/\rho}} + \ldots + \frac{(-z)^\rho}{\rho n^{\rho/\rho}}}\right].$$

And now the asymptotic expansion of $\Gamma(z|\rho)$ when $|z|$ is very large and $-\pi < \arg z < \pi$ is given by

$$(2\pi)^{\frac{1}{2\rho}}\, z^{(-)^{\rho-1} z^{\rho} - \frac{1}{2}}\, e^{\sum\limits_{s=1}^{\infty} \frac{(-)^s}{s z^s} \mathrm{F}\left(\frac{s}{\rho}\right) + \frac{(-z)^{\rho}}{\rho}}.$$

When $\rho = 1$, this formula is exactly the asymptotic expansion of $\Gamma(z)$ for complex values of z, which, as stated in § 3, was first obtained by STIELTJES.

For, when s is an even positive integer, $\mathrm{F}(s) = 0$.

When s is an odd positive integer $= 2t + 1$, let us say, $\mathrm{F}(s) = \frac{(-)^{t-1}\mathrm{B}_{t+1}}{2t+2}$. $t \geqq 0$. And $\mathrm{F}(-1) = \gamma$.

Thus, when $\rho = 1$, $\Gamma(z|\rho)$ becomes $\Gamma(z)$, and the series $\sum\limits_{s=1}^{\infty} \frac{(-)^s}{s z^s} \mathrm{F}\left(\frac{s}{\rho}\right)$ becomes $\sum\limits_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t+1\,.\,2t+2} \cdot \frac{1}{z^{2t+1}}$, which accords with the usual result.

§ 73. It is obvious that we can now at once write down the asymptotic expansion for $\mathrm{G}(z) = \prod\limits_{1}^{\infty} \left[\left(1 + \frac{z}{a_n}\right) e^{-\frac{z}{a_n} + \ldots + \frac{(-)^p z^p}{a_n{}^p}}\right]$, where $a_n = n^{\frac{1}{p}} \left[1 + \frac{b_1}{n^{\epsilon_1}} + \frac{b_2}{n^{\epsilon_2}} + \ldots\right]$ and p is an integer, from the corresponding expansion for the function in which $a_n = n^{\frac{1}{\rho}} \left[1 + \frac{b_1}{n^{\epsilon_1}} + \ldots\right]$ and ρ is not integral. The ϵ's, of course, are assumed to be positive and in ascending order of magnitude.

The result is

$$\begin{aligned}
&\log \prod_{1}^{\infty} \left[\left(1 + \frac{z}{a_n}\right) e^{-\frac{z}{a_n} + \ldots + \frac{(-)^p z^p}{a_n{}^p}}\right] \\
&= (-)^p z^p \log z + (-)^{p-1} \frac{z^p}{p} - \tfrac{1}{2} \log z - \frac{1}{2p} \log 2\pi + \sum_{s=-p}^{\infty}{}' \frac{(-)^s}{s z^s} \mathrm{F}\left(\frac{s}{p}\right) \\
&+ (-)^p \frac{\pi p b_1}{\sin \pi p \epsilon_1} z^{p-\epsilon_1 p} + (-)^{p-1} \frac{p(p+1-2p\epsilon_1)}{2} b_1{}^2 \frac{\pi}{\sin 2\pi p \epsilon_1} z^{p-2\epsilon_1 p} \\
&+ (-)^p \frac{\pi \rho b_2}{\sin \pi p \epsilon_2} z^{p-\epsilon_2 p} + \ldots + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{s z^s} \mathrm{Z}\left(p, s\,;\, \begin{matrix}\epsilon_1, \epsilon_2 \ldots \\ b_1, b_2 \ldots\end{matrix}\right) - \mathrm{Z}\left(p, 0\,;\, \begin{matrix}\epsilon_1, \epsilon_2 \ldots \\ b_1, b_2 \ldots\end{matrix}\right),
\end{aligned}$$

provided $\frac{p\epsilon_1}{n}, \frac{p\epsilon_2}{n} \ldots$ be not integral ($n = 1, 2, \ldots \infty$).

Thus, ϵ_1 not being integral, the first term of the asymptotic expansion of the quotient

$$\log \frac{\prod\limits_{1}^{\infty} \left\{\left(1 + \frac{z}{a_n}\right) e^{-\frac{z}{a_n} + \ldots + \frac{(-)^p z^p}{a_n{}^p}}\right\}}{\prod\limits_{1}^{\infty} \left\{\left(1 + \frac{z}{n^{\frac{1}{p}}}\right) e^{-\frac{z}{n^{1/p}} + \ldots + \frac{(-)^p z^p}{n}}\right\}} \quad \text{is} \quad \frac{(-)^p}{p} z^p \mathrm{Z}\left(p, p\,;\, \begin{matrix}\epsilon_1, \epsilon_2 \ldots \\ b_1, b_2 \ldots\end{matrix}\right).$$

We note that $\mathrm{Z}\left(p, p\,;\, \begin{matrix}\epsilon_1, \epsilon_2, \ldots \\ b_1, b_2, \ldots\end{matrix}\right) = \sum\limits_{n=1}^{\infty} \left[\frac{1}{a_n{}^p} - \frac{1}{n}\right]$.

When $p\epsilon_1$ is an integer, we see on evaluating the limit which arises, that the dominant term of the asymptotic expansion is still the one just written down. For, in this case, the only other term which might be considered first in the asymptotic expansion of the quotient is $(-)^{p+1} pb_1 z^{p-\epsilon_1 p} \log z$, which, since ϵ_1 is positive, is of lower order than

$$\frac{(-)^p}{p} z^p \, Z\left(p, p\,;\, \begin{matrix}\epsilon_1, \epsilon_2, \ldots \\ b_1, b_2, \ldots\end{matrix}\right).$$

§ 74. It is now evident that, if we are given any simple function of finite integral order, we can find its asymptotic expansion. The analysis just given solves completely the case of algebraical zeros. When the zeros are not algebraic we may, and, in fact, we shall have to introduce new analytical functions defined as indefinite integrals; but there will be no essential difference in the theory.

It should be noticed that just as we have to take the principal values of the algebraically many-valued expressions which occur in the asymptotic approximation for functions of non-integral order, so we must assign principal values to the logarithms which occur when the functions are of integral order.

Part IV.

The Asymptotic Expansion of Repeated Integral Functions.

§ 75. As has been stated in the general classification of Part I., an integral function, which is such that its n^{th} zero is repeated a number of times dependent upon n, is called a *repeated* function.

If the number of sequences of zeros be not infinite, the function is called a *simple* repeated function; and it is obvious that such a function may be built up of functions, each of which possesses a single sequence of zeros. We shall limit ourselves to the consideration of such functions. The order of simple repeated functions with a single sequence of zeros has been previously defined. Taking this definition, we consider, in turn, in the ensuing paragraphs, functions

(1) of finite (non-zero or zero) order less than unity,
(2) of finite non-integral order greater than unity,
(3) of finite integral order greater than or equal to unity.

And, finally, an example is given of the asymptotic expansion of a repeated function with a transcendental index.

Inasmuch as the principles which underlie the analysis are exactly the same as those which have been previously discussed, we shall give but a bare outline of the methods by which the results are obtained.

Simple Repeated Functions of Finite Order less than Unity.

§ 76. The most general function of this type may be written

$$\mathrm{F}(z) = \prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{a_n}\right)^{\mu_n} \right],$$

where the principal value of each term is taken when μ_n is any function of n; and where a_n is a function of n which increases without limit as n increases, and which is such that $\sum_{n=1}^{\infty} \mu_n/a_n$ is absolutely convergent. The function is of finite (or zero) order less than unity; and, when μ_n is an integer, its n^{th} zero is repeated μ_n times.

We take

$$a_n = \phi(n).$$

When $r = \phi(n)$ we suppose that inversely $n = \psi(r)$. Suppose that $z = \mathrm{R}e^{i\theta}$, then if we take m to be a large integer such that $m - 1 < \psi(\mathrm{R}) \eqslantless m$, we have

$$\log \mathrm{F}(z) = \sum_{n=1}^{m-1} \mu_n \log z - \sum_{n=1}^{m-1} \mu_n \log \phi(n) + \sum_{n=1}^{m-1} \mu_n \log \left(1 + \frac{a_n}{z}\right) + \sum_{n=m}^{\infty} \mu_n \log \left(1 + \frac{z}{a_n}\right).$$

We carry out our analysis in a manner which depends exactly upon the argument previously employed in the corresponding case for non-repeated functions.

We have at once, in the limit when $k = \infty$,

$$\log \mathrm{F}(z) = \log z \sum_{n=1}^{m-1} \mu_n - \sum_{n=1}^{m-1} \mu_n \log \phi(n) + \sum_{n=1}^{m-1} \sum_{s=1}^{k} \frac{(-)^{s-1} \mu_n \phi^s(n)}{s z^s} + \sum_{n=m}^{\infty} \sum_{s=1}^{k} \frac{(-)^{s-1} \mu_n z^s}{s \phi^s(n)}.$$

Now, if s be positive,

$$\sum_{n=1}^{m-1} \mu_n \phi^s(n) = \int_{\gamma_s}^{m} \mu_n \phi^s(n)\, dn - \tfrac{1}{2}\mu_m \phi^s(m) \ldots + (-)^t \frac{\mathrm{B}_{t+1}}{2t+2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \mu_m \phi^s(m) + \ldots$$

where γ_s is a constant depending on s and on the forms of μ_n and $\phi(n)$.

We call γ_s the s^{th} Maclaurin integral limit for μ_n and $\phi(n)$. If s be negative, the previous expansion will hold, but in this case $\gamma_{-s} = \infty$, and the constant term vanishes. Again we have

$$\sum_{n=1}^{m-1} \mu_n \log \phi(n) = \int_{\gamma_0}^{m} \mu_n \log \phi(n)\, dn - \tfrac{1}{2}\mu_m \log \phi(m) + \ldots$$
$$+ (-)^t \frac{\mathrm{B}_{t+1}}{2t+2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \mu_m \log \phi(m) + \ldots$$

and

$$\sum_{n=1}^{m-1} \mu_n = \int_{g_0}^{m} \mu_n\, dn - \tfrac{1}{2}\mu_m + \ldots + (-)^t \frac{\mathrm{B}_{t+1}}{2t+2\,!} \frac{d^{2t+1}}{dm^{2t+1}} \mu_m + \ldots$$

We shall find it convenient to put

$$\int^{m} \mu_n \, dn = \chi(m), \quad \text{so that} \quad \int^{g_0} \mu_n \, dn = \chi(g_0) = -\,\mathrm{M} \text{ (say).}$$

And now, if the limiting values when $k = \infty$ of the summable divergent series be taken,

$$\begin{aligned}
\log \mathrm{F}(z) = \log z \left[\int^{m} \mu_n \, dn + \mathrm{M} - \tfrac{1}{2}\mu_m \right] \\
- \int_{\gamma_0}^{m} \mu_n \log \phi(n) \, dn + \frac{\mu_m}{2} \log \phi(m) \\
- \sum_{s=1}^{k} \frac{(-)^s}{s z^s} \left[\int_{\gamma_s}^{m} \mu_n \phi^s(n) \, dn - \tfrac{1}{2} \mu_m \phi^s(m) \right] \\
+ \sum_{s=1}^{k} \frac{(-)^s}{s} z^s \left[\int_{\gamma_{-s}}^{m} \frac{\mu_n \, dn}{\phi^s(n)} - \frac{\mu_m}{2\phi^s(m)} \right] \\
+ \sum_{t=0}^{\infty} \frac{(-)^{t-1} \mathrm{B}_{t+1}}{\overline{2t+2}\,!} \frac{d^{2t+1}}{dm^{2t+1}} \left[\mu_m \log \phi(m) - \mu_m \log z + \sum_{s=1}^{k} \frac{(-)^s}{s} \left\{ \frac{\mu_m \phi^s(m)}{z^s} - \frac{\mu_m z^s}{\phi^s(m)} \right\} \right].
\end{aligned}$$

The last term vanishes as for the corresponding case of non-repeated functions. After reduction, we have

$$\begin{aligned}
\log \mathrm{F}(z) = \log z \left[\int^{m} \mu_n \, dn + \mathrm{M} \right] - \int_{\gamma_0}^{m} \mu_n \log \phi(n) \, dn \\
+ \sum_{s=1}^{k} \frac{(-)^{s-1}}{s} \left\{ \int_{\gamma_s}^{m} \frac{\mu_n \phi^s(n)}{z^s} \, dn - \int_{\gamma_{-s}}^{m} \frac{\mu_n z^s}{\phi^s(n)} \, dn \right\} \\
= \mathrm{M} \log z + \int^{\gamma_0} \mu_n \log \phi(n) \, dn + \sum_{s=1}^{k} \frac{(-)^s}{s z^s} \int^{\gamma_s} \mu_n \phi^s(n) \, dn \\
+ \int^{\phi(m)} \chi[\psi(t)] \frac{dt}{t} \left[1 + \sum_{s=-k}^{k}{}' \frac{(-)^s t^s}{z^s} \right].
\end{aligned}$$

The last integral

$$= \underset{k=\infty}{\mathrm{L}t} \int^{\pi} \chi[\psi(-z e^{i\phi})] \, i \, d\phi \, \frac{\sin(k + \frac{1}{2})\phi}{\sin \frac{1}{2}\phi} = f(z) \text{ say.}$$

If then we put $\log \mathrm{F}_0 = \int^{\gamma_0} \mu_n \log \phi(n) \, dn$, $\mathrm{F}_s = -\int^{\gamma_s} \mu_n \phi^s(n) \, dn$, so that F_0 and F_s may be called the zero and s^{th} Maclaurin constants for μ_n and $\phi(n)$, we shall have the asymptotic approximation

$$\prod_{n=1}^{\infty} \left\{ \left(1 + \frac{z}{a_n} \right)^{\mu_n} \right\} = \mathrm{F}_0 z^{\mathrm{M}} e^{f(z) + \sum_{s=1}^{\infty} \frac{(-)^{s-1} \mathrm{F}_s}{s z^s}}.$$

§ 77. Consider now, as an application of the general formula just obtained, the asymptotic expansion of $\prod_{n=1}^{\infty}\left[\left(1+\frac{z}{n^{\rho}}\right)^{n^{\sigma}}\right]$, where σ and ρ are real positive quantities such that $\sum_{n=1}^{\infty} n^{\sigma-\rho}$ is convergent, and, therefore, such that $\rho > \sigma + 1$.

With our former notation

$$\mu_n = n^{\sigma},$$

$$\chi(m) = \int^{m} \mu_n \, dn = \frac{m^{\sigma+1}}{\sigma+1},$$

$$\psi(t) = t^{1/\rho},$$

$$\chi[\psi(t)] = \frac{t^{\frac{\sigma+1}{\rho}}}{\sigma+1}.$$

The constant g_0 arises from the asymptotic equality

$$\sum_{n=1}^{m-1} n^{\sigma} = \int_{g_0}^{m} n^{\sigma}\, dn - \frac{m^{\sigma}}{2} + \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{(2t+2)!} \frac{d^{2t+1}}{dm^{2t+1}} m^{\sigma},$$

and, therefore, $\mathrm{M} = -\chi(g_0) = \zeta(-\sigma)$.

Similarly $\int^{\gamma_s} \mu_n \phi^s(n)\, dn = -\zeta(-\overline{\rho s + \sigma})$.

The constant γ_0 arises from the asymptotic equality

$$\sum_{n=1}^{m-1} n^{\sigma} \log n = \int_{\gamma_0}^{m} n^{\sigma} \log n \, dn - \frac{m^{\sigma}}{2} \log m + \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t+2!} \frac{d^{2t+1}}{dm^{2t+1}} (m^{\sigma} \log m).$$

We may readily show that $\int^{\gamma_0} n^{\sigma} \log n \, dn = \zeta'(-\sigma)$.

For, as has been stated, for all values of s,

$$\zeta(s) = \sum_{n=1}^{m-1} \frac{1}{n^s} - \frac{1}{1-s} \frac{1}{m^{s-1}} + \frac{1}{2m^s} + \sum_{t=1}^{\infty} \binom{-s}{2t} \frac{(-)^{t-1} \mathrm{B}_t}{(s+2t-1)\, m^{s+2t-1}}.$$

If, then, we put $s = \sigma + t$, and expand each term in powers of t, we may equate coefficients of similar powers in the identity.*

If we equate coefficients of the first power, we find

$$\zeta'(\sigma) = -\sum_{n=1}^{m-1} \frac{\log n}{n^{\sigma}} - \frac{1}{m^{\sigma-1}} \left[\frac{1}{(1-\sigma)^2} - \frac{\log m}{1-\sigma}\right] - \frac{1}{2m^{\sigma}} \log m + \sum_{t=0}^{\infty} \frac{(-)^t \mathrm{B}_{t+1}}{2t+2!} \frac{d^{2t+1}}{dm^{2t+1}} \frac{\log m}{m^{\sigma}},$$

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* Compare the process carried out in §§ 27 and 30 of the "Theory of the Gamma Function."

or, changing σ into $-\sigma_1$,

$$\sum_{n=1}^{m-1} n^\sigma \log n = \int^m n^\sigma \log n \, dn - \zeta'(-\sigma) - \frac{m^\sigma}{2} \log m + \sum_{t=0}^{\infty} \frac{(-)^t B_{t+1}}{2t+2!} \frac{d^{2t+1}}{dm^{2t+1}} m^\sigma \log m.$$

Thus

$$\int^{\gamma_0} n^\sigma \log n \, dn = \zeta'(-\sigma).$$

We have, therefore,

$$\log \prod_{n=1}^{\infty} \left(1 + \frac{z}{n^\rho}\right)^{n^\sigma} = \zeta(-\sigma) \log z + \rho\zeta'(-\sigma) + \sum_{s=1}^{k} \frac{(-)^{s-1}}{sz^s} \zeta(-\rho s + \sigma)$$

$$+ \frac{1}{\sigma+1} \int^{\frac{\phi(m)}{z}} z^{\frac{\sigma+1}{\rho}} t^{\frac{\sigma+1}{\rho}-1} dt \left[1 + \sum_{s=-k}^{k}{}' (-)^s t^s\right].$$

The last integral is equal to

$$\frac{[\phi(m)]^{\frac{\sigma+1}{\rho}}}{\sigma+1} \left[\frac{\rho}{\sigma+1} + \sum_{s=-k}^{k}{}' \left\{\frac{-\phi(m)}{z}\right\}^s \frac{1}{s + \frac{\sigma+1}{\rho}}\right]$$

$$= \frac{[\phi(m)]^{\frac{\sigma+1}{\rho}}}{\sigma+1} \frac{\pi}{\sin \frac{\pi \cdot \sigma+1}{\rho}} \left[\frac{z}{\phi(m)}\right]^{\frac{\sigma+1}{\rho}} = \frac{\pi}{\sin \pi \cdot \frac{\sigma+1}{\rho}} \frac{z^{\frac{\sigma+1}{\rho}}}{\sigma+1}.$$

Thus we have the asymptotic expansion

$$\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{n^\rho}\right)^{n^\sigma}\right] = z^{\zeta(-\sigma)} e^{\rho\zeta'(-\sigma) + \sum\limits_{s=1}^{\infty} \frac{(-)^{s-1}}{sz^s} \zeta(-\rho \overline{s+\sigma}) + \frac{\pi}{\sin \frac{\pi \cdot \sigma+1}{\rho}} \cdot \frac{z^{\frac{\sigma+1}{\rho}}}{\sigma+1}}.$$

We note that the first term of this product vanishes when σ is an even integer.

§ 78. It is now possible to write down the expansion of

$$\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{n^\rho}\right)^{\mu_n}\right],$$

where μ_n is algebraic and of the form $a_0 n^\sigma + a_1 n^{\sigma_1} + a_2 n^{\sigma_2} + \ldots$, in which $\sigma > \sigma_1 > \sigma_2 > \ldots$

For such a function is merely the product of the

a_0th power of $\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{n^\rho}\right)^{n^\sigma}\right]$,

the a_1th power of $\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{n^\rho}\right)^{n^{\sigma_1}}\right]$, and so on.

We note that the constants which enter will be expressible in terms of the coefficients of μ_n and values of the Riemann ζ function.

We might now investigate the asymptotic expansion of a repeated function of finite order less than unity with algebraic sequence of zeros of the type

$$a_n = n^\rho \left[1 + \frac{b_1}{n^{\epsilon_1}} + \frac{b_2}{n^{\epsilon_2}} + \ldots\right]$$

where the quantities $\epsilon_1, \epsilon_2, \ldots$ are real, positive, and in ascending order of magnitude.

The analysis is, however, such an obvious extension of the corresponding result of Part III. that it may be at once supplied by the reader.

Repeated Simple Functions of Finite Non-integral Order greater than Unity.

§ 79. We next consider the asymptotic expansion of the function

$$\mathrm{F}(z) = \prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{a_n}\right)^{\mu_n} e^{\mu_n \sum\limits_{m=1}^{p} \frac{1}{m}\left(-\frac{z}{a_n}\right)^m}\right],$$

where $p < \rho < p + 1$, and ρ is such that

$$\Sigma \frac{\mu_n}{a_n^{\rho+\epsilon}} \text{ is convergent, and } \Sigma \frac{\mu_n}{a_n^{\rho-\epsilon}} \text{ divergent,}$$

when ϵ is a small real positive quantity.

The analysis is an obvious modification of that employed in § 66.

We find $\mathrm{F}(z) = \mathrm{F}_0 z^{\mathrm{M}} e^{f(z) + \sum\limits_{s=-p}^{\infty}{}' \frac{(-)^{s-1}\mathrm{F}_s}{s z^s}}$, where $a_n = \phi(n)$, $\chi(m) = \int^m \mu_n \, dn$,

$$\sum_{n=1}^{m-1} \mu_n = \int^m \mu_n \, dn + \mathrm{M} - \tfrac{1}{2}\mu_m + \ldots,$$

$$\sum_{n=1}^{m-1} \mu_n \log \phi(n) = \int^m \mu_n \log \phi(n) \, dn - \log \mathrm{F}_0 - \tfrac{1}{2}\mu_m \log \phi(m) + \ldots,$$

$$\sum_{n=1}^{m-1} \mu_n \phi^s(n) = \int^m \mu_n \phi^s(n) \, dn + \mathrm{F}_s - \tfrac{1}{2}\mu_m \phi^s(m) + \ldots (s = -p, -(p-1), \ldots -1, 1, 2, \ldots \infty),$$

and

$$f(z) = \underset{k=\infty}{\mathrm{Lt}}\; i \int^{\pi} \chi[\psi(-z e^{i\phi})] \frac{\sin(k + \frac{1}{2})\phi}{\sin \frac{1}{2}\phi} \, d\phi.$$

§ 80. As an example, we may consider the function

$$\mathrm{F}(z) = \prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{n^\tau}\right)^{n^\sigma} e^{n^\sigma \sum\limits_{m=1}^{p} \frac{1}{m}\left(-\frac{z}{n^\tau}\right)^m}\right], \text{ where } \frac{\sigma+1}{\tau} \text{ is not integral, and } p < \frac{\sigma+1}{\tau} < p+1.$$

The order of the function is $\dfrac{\sigma+1}{\tau}$.

We have

$$-\chi(g_0) = \zeta(-\sigma),$$

$$\log \mathrm{F}_0 = -\sum_{n=1}^{m-1} \tau n^\sigma \log n + \int^m \tau n^\sigma \log n \, dn - \frac{\tau}{2} n^\sigma \log n + \ldots = \tau \zeta'(\sigma),$$

$$-\mathrm{F}_s = -\zeta(-\overline{\tau s + \sigma}).$$

And, as in § 77, $f(z) = \dfrac{\pi}{\sin \dfrac{\pi(\sigma+1)}{\tau}} \cdot \dfrac{z^{\frac{\sigma+1}{\tau}}}{(\sigma+1)}$.

Thus the asymptotic expansion of F (z) may be written

$$z^{\zeta(-\sigma)} e^{\frac{\pi}{\sin \pi \left(\frac{\sigma+1}{\tau}\right)} \frac{z^{\frac{\sigma+1}{\tau}}}{\sigma+1} + \tau \zeta'(-\sigma) + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1} \zeta(-\sigma-\tau s)}{s z^s}}.$$

Note that $\zeta(0)$* $= -\frac{1}{2}$, $\zeta'(0)$† $= -\frac{1}{2} \log 2\pi$.

Hence, when $\sigma = 0$, $\tau = \dfrac{1}{\rho}$, we get the asymptotic expansion

$$\prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{n^{\frac{1}{\rho}}}\right) e^{\sum_{m=1}^{p} \frac{1}{m}\left(-\frac{z}{n^{1/\rho}}\right)^m}\right] = z^{-\frac{1}{2}} e^{\frac{\pi}{\sin \pi\rho} z^\rho - \frac{1}{2\rho} \log 2\pi + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1} \zeta\left(-\frac{s}{\rho}\right)}{s z^s}},$$

which agrees with the expansion of § 65.

Simple Repeated Functions of Finite Integral Order.

§ 81. It is obvious from the investigations of §§ 70–73 that the asymptotic expansion obtained in § 79 for $\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{a_n}\right)^{\mu_n} e^{\mu_n \sum_{m=1}^{p} \frac{1}{m}\left(-\frac{z}{a_n}\right)^m}\right]$, where $p < \rho < p + 1$ and ρ is such that $\Sigma \frac{\mu_n}{a_n^{\rho+\epsilon}}$ is convergent, and $\Sigma \frac{\mu_n}{a_n^{\rho-\epsilon}}$ divergent, will hold in the limit when $\rho = p$, provided that in any terms which become infinite we reject the infinite part and keep only the corresponding finite expression found by applying the usual methods of the calculus of limits to the subsidiary Fourier and Maclaurin series. Consider, for example, the function

$$\prod_{n=1}^{\infty} \left\{\left(1 + \frac{z}{n^\tau}\right)^{n^\sigma} e^{n^\sigma \sum_{m=1}^{p} \frac{1}{m}\left(-\frac{z}{n^\tau}\right)^m}\right\}, \quad \text{where} \quad \frac{\sigma+1}{\tau} = p.$$

The asymptotic expansion obtained previously was

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* "Theory of the Gamma Function," § 27.

† *Ibid.*, § 30.

$$z^{\zeta(-\sigma)}\, e^{\frac{\pi}{\sin\frac{\pi(\sigma+1)}{\tau}} \frac{z^{\frac{\sigma+1}{\tau}}}{(1+\sigma)} + \tau\zeta'(-\sigma) + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}\zeta(-\sigma-\tau s)}{sz^{s}}}.$$

Now, when $\frac{\sigma+1}{\tau} = p =$ an integer, $\frac{\pi}{\sin\frac{\pi(\sigma+1)}{\tau}} z^{\frac{\sigma+1}{\tau}}$ becomes infinite.

We have then to substitute a corresponding finite expression derived by proceeding to the limit in the infinite terms of the subsidiary Fourier series. When $\frac{1}{\tau}$ is not integral, the series and its equivalent value are given by

$$\sum_{s=1}^{\infty} \frac{(-)^{s-1}e^{-si\theta}}{s\left(1+\frac{s\tau}{1+\sigma}\right)} + \sum_{s=1}^{\infty} \frac{(-)^{s}e^{si\theta}}{s\left(1-\frac{s\tau}{1+\sigma}\right)} = \frac{\pi e^{i\theta\frac{\sigma+1}{\tau}}}{\sin\pi\frac{\sigma+1}{\tau}} - \frac{\tau}{1+\sigma} - i\theta.$$

When $\frac{1}{\tau}$ is integral, this series, omitting the term for which $s = \frac{1+\sigma}{\tau}$ in the second summation, is equal to the finite part of

$$\frac{e^{i\theta\frac{\sigma+1}{\tau}}(1+\epsilon i\theta+\ldots)}{(-)^{\frac{1+\sigma}{\tau}}\epsilon} - \frac{\tau}{1+\sigma} - i\theta - \frac{\tau(-)^{\frac{1+\sigma}{\tau}}}{1+\sigma} e^{i\theta\frac{\sigma+1}{\tau}},$$

when $\epsilon = 0$; that is to say, it is equal to

$$(-)^{\frac{\sigma+1}{\tau}-1} e^{i\theta\frac{\sigma+1}{\tau}}\left(-i\theta+\frac{\tau}{1+\sigma}\right) - \frac{\tau}{1+\sigma} - i\theta.$$

We thus replace

$$\frac{\pi}{\sin\frac{\pi(\sigma+1)}{\tau}} \cdot \frac{z^{\frac{\sigma+1}{\tau}}}{\sigma+1} \quad \text{by} \quad \frac{(-z)^{\frac{\sigma+1}{\tau}}}{1+\sigma}\left\{\log z - \frac{\tau}{1+\sigma}\right\}.$$

Again, since σ is a positive integer, the only term of the form

$$\zeta(-\sigma-\tau s)\; s = -p, \ldots -1, 1, 2, \ldots \infty$$

which becomes infinite is that for which $s = -p$.

This term is $\zeta(+1)$, which arises from the Maclaurin series

$$\sum_{n=1}^{m-1} \frac{1}{n} = \left[\zeta(s) + \frac{1}{1-s}\cdot\frac{1}{m^{s-1}}\right]_{s=1} - \frac{1}{2m} + \ldots = \log m + \gamma - \frac{1}{2m} +$$

We have already taken account of the substitution of $\log m$ for $\frac{1}{1-s}\cdot\frac{1}{m^{s-1}}$; we need, therefore, only replace $\zeta(+1)$ by γ.

We have then the asymptotic expansion

$$\prod_{n=1}^{\infty} \left\{ \left(1 + \frac{z}{n^\tau}\right)^{n^\sigma} e^{n^\sigma \sum_{s=1}^{\frac{\sigma+1}{\tau}} \frac{1}{\sigma} \left(\frac{-z}{n^\tau}\right)^s} \right\}$$

$$= z^{\zeta(-\sigma)} \exp\left[\tau\zeta'(-\sigma) + \frac{(-z)^{\frac{\sigma+1}{\tau}}}{\sigma+1}\left\{\log z + \gamma\tau - \frac{\tau}{1+\sigma}\right\}\right.$$

$$\left. + \sum_{s=1-\frac{\sigma+1}{\tau}}^{\infty}{}' \frac{(-)^{s-1}\zeta(-\sigma-\tau s)}{sz^s}\right],$$

in which $\frac{1}{\tau}$ and σ are both integers, and $\frac{\sigma+1}{\tau}$ is the "genre" of the function.

It is interesting to notice that the constants which enter into the asymptotic expansion of this very general function are all values of the Riemann ζ function.

§ 82. When $\tau = 1$, the function is to an exponential factor an important function which I have proposed to call the σ-ple G function. These G functions are derived from the multiple Gamma functions by the coalescence of the parameters. The theory of the simple G function has been developed elsewhere* in the second of a series of papers on Gamma functions.

In that development I took

$$G(z+1) = (2\pi)^{\frac{z}{2}} e^{-\frac{z.z+1}{2} - \gamma\frac{z^2}{2}} \prod_{n=1}^{\infty}\left[\left(1+\frac{z}{n}\right)^n e^{-z+\frac{z^2}{2n}}\right]$$

and obtained† the asymptotic expansion

$$\log G(z+1) = \tfrac{1}{12} - \log A + \frac{z}{2}\log 2\pi + \left(\frac{z^2}{2} - \tfrac{1}{12}\right)\log z - \frac{3z^2}{4} + \sum_{s=1}^{\infty} \frac{(-)^s B_{s+1}}{2s\,.\,2s+2\,z^{2s}},$$

where A is the Glaisher-Kinkelin constant.

Putting $\sigma = \tau = 1$, the asymptotic expansion which we have obtained for the same function in the present paragraph is

$$\frac{z}{2}\log 2\pi - \frac{z(z+1)}{2} - \frac{\gamma z^2}{2} + \zeta(-1)\log z + \frac{z^2}{2}\log z + \frac{\gamma z^2}{2} - \frac{z^2}{4}$$

$$+ \zeta'(-1) + \sum_{s=-1}^{\infty}{}' \frac{(-)^{s-1}\zeta(-s-1)}{sz^s}.$$

Now‡

$$\zeta(-1) = -\tfrac{1}{12}, \quad \zeta(0) = -\tfrac{1}{2},$$

$$\zeta(-s-1) = 0, \text{ when } s \text{ is odd},$$

and

$$= \frac{(-)^{t-1}B_{t+1}}{(2t+2)}, \text{ when } s = 2t.$$

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* 'Quarterly Journal of Mathematics,' vol. 31, pp. 264 *et seq.*

† *Ibid.*, § 15.

‡ *Ibid.*, § 23.

And, since A is given by the identity,

$$\sum_{n=1}^{m-1} n \log n = \log A + \left(\frac{m^2}{2} - \frac{m}{2} + \tfrac{1}{12}\right) \log m - \frac{m^2}{4} + \text{terms which vanish when } m \text{ is}$$

infinite, we have $\log A = - \zeta' (-1) + \frac{1}{12}$.

Thus the asymptotic expansion of the present paragraph may be written

$$\tfrac{1}{12} - \log A + \frac{z}{2} \log 2\pi + \left(\frac{z^2}{2} - \tfrac{1}{12}\right) \log z - \frac{3z^2}{4}$$
$$+ \sum_{s=1}^{\infty} \frac{(-)^s B_{s+1}}{2s \,.\, \overline{2s+2}\, z^{2s}}.$$

We thus obtain a valuable verification of our results.

Repeated Simple Integral Functions of Transcendental Index.

§ 83. It is obvious that such a function as

$$\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{a_n}\right)^{e^n} e^{e^n \sum\limits_{m=1}^{p} \left(-\frac{z}{a_n}\right)^m}\right]$$

is of infinite order when a_n is algebraic.

If, however, a_n is of the same order as e^n, the order of the function is finite, and can therefore be expanded in the neighbourhood of infinity by our methods.

We shall take, as an example of repeated functions of transcendental index, the product

$$\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{e^{qn}}\right)^{e^{pqn}} e^{e^{pqn} \sum\limits_{m=1}^{\rho} \left(-\frac{z}{e^{qn}}\right)^m}\right].$$

This function is of order ρ, greater than or equal to unity.

Suppose first that p is not an integer, so that ρ is the integer next greater than p. Then without former notation

$$\sum_{n=1}^{m-1} e^{pqn} = \int^m e^{pqn}\, dn + M - \frac{e^{pqn}}{2} + \ldots$$

$$\sum_{p=1}^{m-1} e^{pqn}\, qn = \int^m e^{pqn}\, qn\, dn - \log F_0 - \tfrac{1}{2} e^{pqm}\, qm + \ldots$$

$$\sum_{n=1}^{m-1} e^{pqn + sqn} = \int^m e^{(p+s)qn}\, dn - F_s - \frac{e^{\overline{p+s}\, qm}}{2} + \ldots$$

And

$$f(z) = \frac{\log z}{pq} e^{pqm} - \frac{m}{p} e^{pqm} + \frac{1}{p^2 q} e^{pqm} + \sum_{s=-k}^{k}{}' \frac{1}{q} \left[\frac{(-)^{s-1}}{s z^s} \frac{e^{\overline{p+s}\, qm}}{p+s}\right],$$

where we take the limit when $k = \infty$ of the summable divergent series.

Thus

$$p\frac{f(z)}{e^{pqm}} = \frac{\log z}{q} - m + \frac{1}{pq} + \frac{1}{q}\sum_{=-k}^{k}{}' \left[\frac{(-)^{s-1}}{s}\left(\frac{e^{qm}}{z}\right)^s\right] - \frac{1}{q}\sum_{s=-k}^{k}{}' \left[\frac{(-)^{s-1}}{p+s}\cdot\left(\frac{e^{qm}}{z}\right)^s\right]$$

$$= \frac{\log z}{q} - m + \frac{1}{pq} + \frac{1}{q}\left\{\frac{\pi\left(\frac{z}{e^{qm}}\right)^p}{\sin \pi p} - \frac{1}{p} - \log\frac{z}{e^{qm}}\right\}.$$

Therefore

$$f(z) = \frac{\pi z^p}{pq \sin \pi p}.$$

Again, M is given by

$$\frac{e^{\alpha} - e^{\alpha m}}{1 - e^{\alpha}} = \mu + \underset{k=\infty}{\mathrm{Lt}}\ \frac{e^{\alpha m}}{\alpha}\left[1 - \frac{\alpha}{2} + \sum_{t=0}^{k}\frac{(-)^t B_{t+1}\,\alpha^{2t+2}}{2t+2!}\right] \quad . \quad . \quad . \quad . \quad . \quad (1),$$

$$= \mathrm{M} + \frac{e^{\alpha m}}{\alpha}\cdot\frac{\alpha}{1-e^{\alpha}}, \text{ when } \alpha = pq.$$

Thus

$$\mathrm{M} = \frac{e^{pq}}{1 - e^{pq}}.$$

Also $-\mathrm{F}_s$ is given by putting $\alpha = \overline{p+s}\,q$ in this same expansion.

Thus

$$-\mathrm{F}_s = \frac{e^{q\,.\,\overline{p+s}}}{1 - e^{q\,.\,\overline{p+s}}}.$$

Again, by substituting $\alpha + \epsilon$ for α, expanding in power of ϵ, and equating coefficients of the first power of ϵ in the asymptotic identity (1), we readily find

$$-\log \mathrm{F}_0 = q\frac{e^{pq}}{(1 - e^{pq})^2}.$$

If, then, p is not an integer, we have the asymptotic expansion

$$\prod_{n=1}^{\infty}\left[\left(1 + \frac{z}{e^{qn}}\right)^{e^{pqn}} e^{e^{pqn}\sum_{m=1}^{\rho}\left(\frac{-z}{e^{qn}}\right)^m}\right] = z^{-(1-e^{-pq})^{-1}}\, e^{\frac{\pi z^p}{pq \sin \pi p} - \frac{q e^{pq}}{(1-e^{pq})^2} + \sum_{s=-\rho}^{\infty}{}' \frac{(-)^{s-1} e^{q\overline{p+s}}}{s(1-e^{q\overline{p+s}})z^s}}.$$

§ 84. Suppose next that p is an integer—so that $\rho = p$. The analysis will, of course, be slightly more complicated.

The constant F_{-p} will be given by

$$\underset{s=p}{\mathrm{Lt}}\left\{\sum_{n=1}^{m-1} e^{qn(p-s)}\right\} = \int^{m} dn - \mathrm{F}_{-p} - \tfrac{1}{2}$$

or

$$m - 1 = m - \tfrac{1}{2} - \mathrm{F}_{-p}, \text{ so that } \mathrm{F}_{-p} = \tfrac{1}{2}.$$

And we shall have

$$\frac{p\,f(z)}{e^{pqm}} = \frac{\log z}{q} - m + \frac{1}{pq} + (-)^p \frac{mz^p}{e^{pqm}} + \frac{1}{q} \sum_{s=-k}^{k}{}'' \left[\frac{(-)^{s-1}}{s} \left(\frac{e^{qm}}{z} \right)^s \right] - \frac{1}{q} \sum_{s=-k}^{k}{}'' \left[\frac{(-)^{s-1}}{p+s} \cdot \left(\frac{e^{qm}}{z} \right)^s \right],$$

the double dash denoting that the terms for which $\left. \begin{array}{l} s = 0 \\ s = -p \end{array} \right\}$ are to be omitted.

We therefore have

$$\frac{p\,f(z)}{e^{pqm}} = \frac{\log z}{q} - m + \frac{1}{pq} + (-)^p \frac{mz^p}{e^{pqm}} - \frac{(-)^p}{pq} \left(\frac{z}{e^{qm}} \right)^p$$
$$+ \frac{1}{q} \left[(-)^p \left(\frac{z}{e^{qm}} \right)^p \log \left(\frac{z}{e^{qm}} \right) - \frac{1}{p} - \log \left(\frac{z}{e^{qm}} \right) \right].$$

Therefore
$$f(z) = \frac{(-)^p}{pq} z^p \log z - \frac{(-)^p}{p^2 q} z^p.$$

We thus have the asymptotic expansion

$$\prod_{n=1}^{\infty} \left[\left(1 + \frac{z}{e^{qn}} \right)^{e^{pqn}} e^{e^{pqn} \cdot \sum_{m=1}^{p} \left(\frac{-z}{e^{qn}} \right)^m} \right] = z^{-(1-e^{-pq})^{-1}} e^{\frac{(-z)^p \log z}{pq} - \frac{(-z)^p}{p^2 q} - q \frac{e^{pq}}{(1-e^{pq})^2} + \frac{(-)^{p-1} z^p}{2p}}$$
$$\times e^{\sum_{s=-p+1}^{\infty}{}' \frac{(-)^{s-1} e^{q(p+s)}}{s\left(1-e^{q(p+s)}\right) z^s}}.$$

We have now given examples of the asymptotic expansions of repeated simple functions with transcendental index in the cases when the order is or is not integral. And it is evident that such examples might be multiplied indefinitely. In the more complex cases the difficulties of the analysis will, no doubt, be very great; but such difficulties in no way invalidate the theory which has been developed.

PART V.

Applications of the Previous Asymptotic Expansions.

§ 85. We proceed now to consider some applications of the previous theorems to such questions concerning integral functions as have been raised in the Introduction to the present paper.

In the first place, a knowledge of the asymptotic expansion of a function serves to determine the number of roots which it possesses inside a circle of given large radius.

Let us consider the simple example of the Gamma function, for which we have the asymptotic equality

$$\frac{1}{\Gamma(z)} = (2\pi)^{-\frac{1}{2}} z^{z-\frac{1}{2}} \exp \left\{ \gamma z + \sum_{t=0}^{\infty} \frac{(-)^t B_{t+1}}{2t+1 . 2t+2} \frac{1}{z^{2t+1}} \right\},$$

in which the terms neglected on the right-hand side are of lower exponential order than those retained.

By CAUCHY's theorem the number of roots N within a circle of given large radius r is determined by

$$N = \frac{1}{2\pi\iota}\int \frac{d}{dz} \log \Gamma(z)\, dz,$$

the integral being taken round the circle in question.

Now we may, to terms which vanish exponentially with $\frac{1}{r}$, substitute for $\Gamma(z)$ its value given by the asymptotic expansion. And this expansion is valid for all values of z for which $-\pi < \arg z < \pi$. It is also valid right up to the two limits of $\arg z$, provided the circle on which z lies passes between two consecutive zeros of $\frac{1}{\Gamma(z)}\cdot$

If, now, $z = re^{\iota\theta}$, we have, to terms which vanish exponentially with $\frac{1}{r}$,

$$N = \frac{1}{2\pi}\int_{-\pi}^{\pi}\left[-1 + \frac{e^{-\iota\theta}}{2r} - \log r - \iota\theta - \gamma + \sum_{t=0}^{\infty}\frac{(-)^t B_{t+1}}{2t+2}\frac{e^{-(2t+2)\iota\theta}}{r^{2t+2}}\right] re^{\iota\theta}\, d\theta.$$

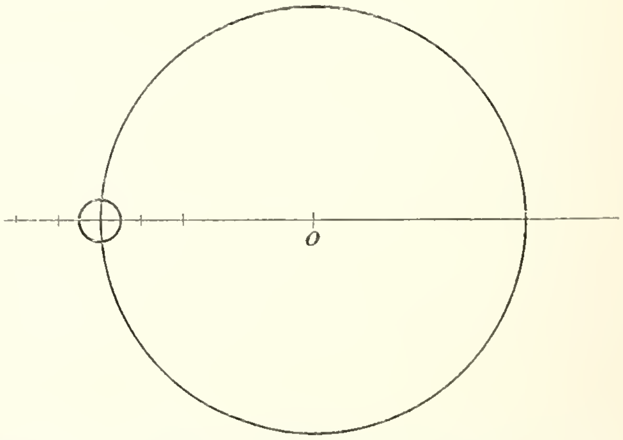
Now

$$\begin{aligned} \frac{-\iota r}{2\pi}\int_{-\pi}^{\pi}\theta e^{\iota\theta}\, d\theta &= \frac{-\iota r}{2\pi}\left\{\left[\frac{1}{\iota}\theta e^{-\iota\theta}\right]_{-\pi}^{\pi} - \frac{1}{\iota}\int_{-\pi}^{\pi} e^{\iota\theta}\, d\theta\right\} \\ &= \frac{-r}{2\pi}\{\pi e^{\iota\pi} + \pi e^{-\iota\pi}\} \\ &= r. \end{aligned}$$

Therefore, to terms which are ultimately exponentially small,

$$N = r + \tfrac{1}{2}.$$

Of course we know independently that the number of roots is the greatest integer less than r. And the entrance of the term $\frac{1}{2}$ might have been predicted *à priori*, for when the circle of radius r passes through a zero of $\frac{1}{\Gamma(z)}$ we jump from $-\frac{1}{2}$ to $+\frac{1}{2}$ as we integrate round a small circle enclosing this zero.



§ 86. It is interesting to notice that the analysis verifies itself in the same way for the function $F(z) = \prod_{n=1}^{\infty} \left[1 + \frac{z}{e^n}\right]$, which, by a change of the independent variable, reduces to LAMBERT'S function.

For this function we have obtained the asymptotic expansion

$$\log F(z) = \tfrac{1}{2}(\log z)^2 - \tfrac{1}{2}\log z + \frac{\pi^2}{6} + \sum_{s=1}^{\infty} \frac{(-)^{s-1} C_s}{s z^s}.$$

Therefore $\frac{d}{dz} \log F(z) = \frac{\log z}{z} - \frac{1}{2z} + \sum_{s=1}^{\infty} \frac{(-)^s C_s}{z^{s+1}}$.

The number of roots within a circle of radius r is, therefore, to terms which are exponentially small when r is large

$$\frac{1}{2\pi\iota}\int_{-\pi}^{\pi} \left\{\frac{\log r}{r} e^{-\iota\theta} + \frac{e^{-\iota\theta}}{r}(\iota\theta - \tfrac{1}{2})\right\} re^{\iota\theta}\, \iota d\theta = \log r - \tfrac{1}{2}.$$

Since the function has no zero at the origin, we should have predicted the occurrence of the term $-\frac{1}{2}$.

§ 87. We may now prove that, if the dominant term of the zero of an integral function is algebraic and such that the zero is of non-integral order ρ (where ρ is neither zero nor infinite, but greater or less than unity), then the number of roots of the function within a circle of large radius r is to a first approximation

$$\frac{\sin \pi\rho}{\pi} \log \phi(r),$$

where $\phi(r)$ is the maximum value of the modulus of the function on the circle in question.

There are two cases to be considered according as ρ is greater or less than unity. We take the former, the argument will hold in detail for the latter by changing ρ into $\frac{1}{\rho}$.

Let $F(z)$ be the function in question; then, under the conditions enunciated, $\log F(z)$ is equal to $\frac{\pi}{\sin \pi\rho} z^\rho$ + terms of lower order.

Hence N, the number of roots required is, to a first approximation, given by

$$N = \int_{-\pi}^{\pi} \frac{\pi\rho}{\sin \pi\rho} r^\rho e^{\rho\iota\theta}\, \iota d\theta = r^\rho = \frac{\sin \pi\rho}{\pi} \log \phi(r).$$

We thus complete and prove BOREL'S intuition.

§ 88. When ρ is an integer, the preceding theorem ceases to be valid. But we can now prove that the number of roots to a first approximation is $\frac{\log \phi(r)}{\log r}$.

For, the same conditions still being supposed to hold good, log F (z) has to a first approximation been proved to be equal to

$$(-z)^p \log z + (-)^{p-1}\frac{z^p}{p} + \frac{(-)^{p-1}\gamma}{p} z^p + \text{lower terms.}$$

And therefore

$$\frac{d}{dz}\log \mathrm{F}(z) = (-)^p\, p z^{p-1}\log z + \text{lower terms.}$$

Hence, to a first approximation,

$$\begin{aligned}\mathrm{N} &= \frac{1}{2\pi\iota}\int_{-\pi}^{\pi} p\,(-)^p\, e^{p\iota\theta}\, r^p\,[\log r + \iota\theta]\,\iota\, d\theta \\ &= (-r)^p\,\frac{\iota p}{2\pi}\int_{-\pi}^{\pi} e^{p\iota\theta}\,\theta\, d\theta = r^p = \frac{\log\phi(r)}{\log r},\end{aligned}$$

which establishes the theorem in question.

§ 89. In the two preceding paragraphs we have assumed that we were dealing with non-repeated functions.

From the analysis of Part IV. it is, however, evident that the theorems hold *in toto* for repeated functions, the order being that which has been assigned to such functions.

We cannot, of course, attempt to prove the theorems for functions of multiple sequence until we have investigated the corresponding asymptotic expansions.

§ 90. We may next write down a number of theorems relating to two or more integral functions.

It is obvious that the sum of two or more integral functions of simple sequence is an integral function of order equal to the largest order of the component integral functions. We may replace additive signs by those of subtraction if the two component functions of largest order are not identically equal. The large zeros of the compound expression are to the first order of approximation equal to the large corresponding zeros of the component function of largest order.

The product of two or more integral functions of simple sequence is an integral function of order equal to the largest order of the component integral functions.

The number of zeros of the equation

$$h_1(z)\,\mathrm{F}_1(z) + h_2(z)\,\mathrm{F}_2(z) + \ldots \qquad + h_n(z)\,\mathrm{F}_n(z) = 0,$$

where the F's are integral functions of simple sequence and the *h's* algebraic polynomials, within a circle of large radius is ultimately to a first approximation equal to the number of zeros within that circle of the function of largest order.

§ 91. The expansions which have been obtained may be utilised to give a proof of BOREL's extension of a theorem due to PICARD.*

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* PICARD, 'Annales de l'École Normale Supérieure,' 2 ser., t. 9 (1880). BOREL, 'Acta Mathematica,' t. 20, pp. 382–388.

The identity

$$\sum_{\iota=1}^{n} G_\iota(z)\, e^{H_\iota(z)} = 0,$$

in which the G's are integral functions of simple sequence of any finite or zero order not greater than some number ρ, and the functions $H_\iota - H_k$ are polynomials of order greater than ρ or transcendental integral functions, necessarily involves

$$G_1(z) = G_2(z) = \ldots \qquad = G_n(z) = 0.$$

Since the identity holds for all points in the plane of the complex variable z, we may consider it in the neighbourhood of $z = \infty$.

Suppose first that the G's are functions of simple sequence of non-integral finite order.

If ρ_ι be the order of $G_\iota(z)$, we shall have near $z = \infty$ the identity

$$\sum_{\iota=1}^{n} e^{\frac{\pi}{\sin \pi\rho_\iota} z^{\rho_\iota} + \ldots + H_\iota(z)} = 0,$$

where we have neglected in each term terms of lower exponential order than those retained.

The identity will hold for all values of arg z such that z is not within a finite distance of the zeros of the G's.

The functions H (z) by hypothesis cannot be equal to one another. As z tends to infinity, one of them must become infinite to an order which exceeds the order to which all the others become infinite by a quantity of order greater than z^ρ.

The corresponding term (say) $G_1(z)\, e^{H_1(z)}$ is then infinite to an order greater than the order of any other term of the identity $\sum_{\iota=1}^{n} G_\iota(z)\, e^{H_\iota(z)} = 0$.

Since $e^{H(z)}$ cannot vanish, we must then have $G_1(z) = 0$.

The same argument may now be applied to the identity $\sum_{\iota=2}^{n} G_\iota(z)\, e^{H_\iota(z)} = 0$, and it may be proved successively that all the functions G vanish.

And thus the theorem will be proved.

When any of the quantities ρ are integral, a suitable modification of the formulæ in accordance with § 73 shows that the theorem is still true. When the G's are repeated functions, a corresponding modification again establishes the theorem. When the functions G's reduce to constants c_ι, so that $\rho = 0$, the theorem is still true, the functions H being unequal.

§ 92. We pass now to the consideration of the resemblance between an integral function of simple sequence and its derivative.

And I would remark that, in the same manner as Rolle's theorem is proved, it may be established that the real zeros of such a function with real coefficients are separated by zeros of its derivative. [It cannot, however, be proved that the derived function has not other real or a (necessarily even) number of other imaginary zeros.] This theorem I shall not prove, as it is not connected with the main developments of the present paper. We proceed, however, to show that such developments complete and to some extent verify this extension of ROLLE's theorem, and that incidentally they furnish many criteria as to the nature of the derivative of a given integral function.

§ 93. Let us consider, as an elementary example, the function of genre zero and order $\frac{1}{\rho}$,

$$P_\rho(z) = \prod_{n=1}^{\infty} \left[1 + \frac{z}{n^\rho}\right], \text{ where } \rho > 1.$$

We have the asymptotic equality

$$P_\rho(z) = (2\pi)^{-\frac{\rho}{2}} z^{-\frac{1}{2}} \exp. \left[\frac{\pi}{\sin\frac{\pi}{\rho}} z^{\frac{1}{\rho}} + \sum_{s=1}^{\infty} \frac{(-)^{s-1} F(\rho s)}{z^s}\right].$$

Remember, now, that it has been proved in Part II. that we may differentiate an asymptotic equality of this type, and we obtain

$$\frac{d}{dz} P_\rho(z) = (2\pi)^{-\frac{\rho}{2}} z^{-\frac{1}{2}} \exp \left\{\frac{\pi}{\sin\frac{\pi}{\rho}} z^{\frac{1}{\rho}} + \ldots\right\} \left\{\frac{\pi}{\sin\frac{\pi}{\rho}} z^{\frac{1-\rho}{\rho}} - \frac{1}{2z} + \ldots\right\}$$

$= (2\pi)^{-\frac{\rho}{2}} \frac{\pi}{\sin\frac{\pi}{\rho}} z^{\frac{1+\rho}{\rho}} \exp \left\{\frac{\pi}{\sin\frac{\pi}{\rho}} z^{\frac{1}{\rho}} + \ldots\right\}$ together with terms whose ratio to the terms retained tends to zero as $|z|$ tends to infinity.

From this expansion we see that

(1) $P_\rho'(z)$ is of the same order as $P_\rho(z)$,

(2) The zeros of $P_\rho'(z)$ are such that, when n is large, we have with the usua notation $a_n = n^\rho + (\rho - 1) n^{\rho-1} +$ lower terms.

Not only so, but theoretically, by finding successive terms in the expansion for $P_\rho'(z)$, we ought to be able to determine the form of its n^{th} zero as nearly as we please. Practical difficulties will, of course, arise when we come, in the asymptotic expansion, to a term which arises from a transcendental term in the n^{th} zero of $P_\rho'(z)$.

Note that the formula for a_n may be readily verified when $\rho = z$.

For
$$\prod_{n=1}^{\infty} \left[1 + \frac{z}{n^2}\right] = \frac{\sinh \pi\sqrt{z}}{\pi\sqrt{z}},$$

and, therefore,
$$P_2'(z) = \frac{1}{2} \frac{\cosh \pi\sqrt{z}}{z} - \frac{1}{2} \frac{\sinh \pi\sqrt{z}}{z^{3/2}} = \frac{e^{\pi\sqrt{z}}}{4z} - \frac{e^{\pi\sqrt{z}}}{4\pi z^{3/2}} \text{ asymptotically.}$$

The large zeros of $\mathrm{P}_z'(z)$ are approximately those of $\cosh \pi\sqrt{z}$, and the latter are such that, with the usual notation, $a_n = n^2 + n + \frac{1}{4}$.

We notice that the general form of a_n given above shows that the large zeros of $\mathrm{P}_\rho(z)$ separate and are separated by those of $\mathrm{P}_\rho'(z)$, a fact which agrees with the extension of ROLLE's theorem.

§ 94. From the preceding example it is now evident that we are in a position to prove that, for all the types of integral functions of which asymptotic expansions have been obtained in this memoir, the order of the function is equal to the order of its derivative. And not only so, but we are theoretically in a position to determine as nearly as we please a formula for the (large) n^{th} zero of the derivative. It would be tedious to consider in turn all cases which can arise.: we will take one or two as typical of the rest.

As an immediate corollary of the preceding example it may be seen that the derivative of a simple non-repeated function of order $\frac{1}{\rho}$ less than unity with algebraic zeros of the type $a_n = n^\rho + \theta n^{\rho-1} + \ldots$ is a similar function of equal order, whose zeros are typified by $b_n = n^\rho + (\theta + \rho - 1)\, n^{\rho-1} + \ldots$

§ 95. As a suggestion of the possibility of extending the expansions of Parts III. and IV. let us next write down the first few terms of the asymptotic expansion of

$\dot{\mathrm{P}}(a + z) = \log \prod_1^\infty \left[\left(1 + \frac{z + a}{a_n}\right) e^{-\frac{z+a}{a_n} + \ldots + \frac{(-)^p (z+a)^p}{p a_n^p}}\right]$, where a is any quantity of finite modulus, and $a_n = n^{1/\rho}\left[1 + \frac{b_1}{n^{\epsilon_1}} + \frac{b_2}{n^{\epsilon_2}} + \ldots\right]$.

The expansion will be (§ 68)

$$\frac{\pi}{\sin \pi\rho}(z + a)^\rho - \tfrac{1}{2}\log(z + a) - \frac{1}{2\rho}\log 2\pi + \sideset{}{'}\sum_{s=-p}^{\infty} \frac{(-)^{s-1}}{s\,(z + a)^s}\,\mathrm{F}\left(\frac{s}{\rho}\right)$$
$$- \frac{\sin \pi\rho b_1}{\sin \pi\rho\,(1 - \epsilon_1)}(z + a)^{\rho(1-\epsilon_1)} + \frac{\rho\,(\rho + 1 - 2\rho\epsilon_1)}{2}\,{b_1}^2\,\frac{\pi}{\sin \pi\rho\,(1 - 2\epsilon_1)}(z + a)^{\rho(1-2\epsilon_1)}$$
$$- \frac{\sin \pi\rho b_2}{\sin \pi\rho\,(1 - \epsilon_2)}(z + a)^{\rho(1-\epsilon_2)} + \ldots + \sideset{}{'}\sum_{s=-p}^{\infty} \frac{(-)^{s-1}}{s\,(z + a)^s}\,\mathrm{Z}\left(\rho,\, s\,;\, \begin{matrix}\epsilon_1,\, \epsilon_2\, .\;\;.\\ b_1,\, b_2\, .\, .\, .\end{matrix}\right)$$
$$- \mathrm{Z}\left(0\,;\, \begin{matrix}\epsilon_1,\, \epsilon_2\, .\, .\, .\\ b_1,\, b_2\, .\, .\, .\end{matrix}\right),$$

and may be transformed into

$$\frac{\pi}{\sin \pi\rho} z^\rho - \tfrac{1}{2}\log z - \frac{1}{2\rho}\log 2\pi + \sideset{}{'}\sum_{s=-p}^{\infty} \frac{(-)^{s-1}}{s\, z^s}\,\mathrm{F}\left(\frac{s}{\rho}\right) + \frac{a\rho\pi}{\sin \pi\rho} z^{\rho-1}$$
$$+ \frac{\rho\,(\rho - 1)\,\pi}{\sin \pi\rho}\, a^2 z^{\rho-2} + \ldots - \tfrac{1}{2}\,\frac{a}{z} \ldots + (-)^p\, z^{p-1}\, a\mathrm{F}\left(-\,\frac{p}{\rho}\right)$$
$$+ \left[(-)^p\,\frac{p - 1}{2}\,a^2\mathrm{F}\left(\frac{p}{\rho}\right) + (-)^{p-1}\, a\mathrm{F}\left(\frac{p - 1}{\rho}\right)\right] z^{p-2} + \ldots$$

[OVER.

$$- \frac{\pi\rho b_1}{\sin\pi\rho(1-\epsilon_1)} z^{\rho(1-\epsilon_1)} - \frac{\pi\rho^2 b_1(1-\epsilon_1)}{\sin\pi\rho(-\epsilon_1)} a z^{\rho(1-\epsilon_1)-1} + \dots$$

$$+ \frac{\rho(\rho+1-2\epsilon_1)}{2} {b_1}^2 \frac{\pi}{\sin\pi\rho(1-2\epsilon_1)} z^{\rho(1-2\epsilon_1)} + \frac{\rho^2(\rho+1-2\epsilon_1)(1-2\epsilon_1)}{2} \frac{\pi a z^{\rho(1-2\epsilon_1)-1}}{\sin\pi\rho(1-2\epsilon_1)} + \dots$$

$$- \frac{\pi\rho b_2}{\sin\pi\rho(1-\epsilon_2)} z^{\rho(1-\epsilon_2)} + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{s z^s} Z\left(\rho, s; \begin{matrix}\epsilon_1, \epsilon_2 \dots \\ b_1, b_2 \dots\end{matrix}\right)$$

$$- Z\left(0; \begin{matrix}\epsilon_1, \epsilon_2 \dots \\ b_1, b_2 \dots\end{matrix}\right) + (-)^p z^{p-1} a Z\left(\rho, -p; \begin{matrix}\epsilon_1, \epsilon_2 \dots \\ b_1, b_2 \dots\end{matrix}\right) + \dots .$$

By the employment of extended Riemann ζ functions of parameter a, it is impossible to give a form of this expansion which shall include all powers of a, analogous to the expansion of $\log \Gamma(z+a)$, which involves BERNOULLIAN functions of a as coefficients. For brevity we content ourselves with the preceding first approximation.

§ 96. By differentiating the expansion for $\log P(z)$, given in § 68, we have at once, as is evident by the preceding paragraph,

$$\frac{P'(z)}{P(z)} = \frac{\pi\rho}{\sin\pi\rho} z^{\rho-1} - \frac{1}{2z} \dots \qquad + (-)^p z^{p-1} F\left(\frac{-p}{\rho}\right) + \dots$$

$$- \frac{\pi\rho^2 b_1(1-\epsilon_1)}{\sin\pi\rho(1-\epsilon_1)} z^{\rho(1-\epsilon_1)-1} - \frac{\pi\rho^2 b_2(1-\epsilon_2)}{\sin\pi\rho(1-\epsilon_2)} z^{\rho(1-\epsilon_2)-1} - \dots$$

$$+ (-)^p z^{p-1} Z\left(p, -\rho; \begin{matrix}\epsilon_1, \epsilon_2, \dots \\ b_1, b_2, \dots\end{matrix}\right).$$

Thus the asymptotic expansion for $\log P'(z)$ is given by

$$\frac{\pi}{\sin\pi\rho} z^\rho + \left(\rho - \frac{3}{2}\right)\log z - \frac{1}{2\rho}\log 2\pi + \log\frac{\pi\rho}{\sin\pi\rho} + \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{s z^s} F\left(\frac{s}{\rho}\right)$$

$$- \frac{\pi\rho b_1}{\sin\pi\rho(1-\epsilon_1)} z^{\rho(1-\epsilon_1)} + \frac{\rho(\rho+1-2\rho\epsilon_1)}{2} {b_1}^2 \frac{\pi}{\sin\pi\rho(1-\epsilon_1)} z^{\rho(1-2\epsilon_1)} - \dots$$

$+ \sum_{s=-p}^{\infty}{}' \frac{(-)^{s-1}}{s z^s} Z\left(\rho, s; \begin{matrix}\epsilon_1, \epsilon_2 \dots \\ b_1, b_2 \dots\end{matrix}\right) - Z\left(0; \begin{matrix}\epsilon_1, \epsilon_2 \dots \\ b_1, b_2 \dots\end{matrix}\right)$ + terms involving positive (fractional) powers of $1/z$.

Thus $\frac{d}{dz} P(z)$ is a function of the type

$$\prod_{n=1}^{\infty}\left[\left(1+\frac{z}{b_n}\right)e^{-\frac{z}{b_n}+\dots+\frac{(-)^p z^p}{p {b_n}^p}}\right],$$

where $b_n = n^{1/\rho}\left[1 + \frac{b_1}{n^{\epsilon_1}} + \frac{b_2}{n^{\epsilon_2}} + \dots\right] - n^{1/\rho}\left[\frac{\rho-1}{\rho n} + \text{higher powers of } \frac{1}{n}\right]$.

Thus the differential of an integral function of order ρ (> 1), where ρ is not integral, is itself an integral function of order ρ whose n^{th} zero, when n is large, will differ from the corresponding zero of the original function by the term $-\frac{\rho - 1}{\rho n^{1-1/\rho}}$, together with terms involving lower powers of n.

In an exactly similar manner it may be proved that the function $R'_\rho(z)$ admits an asymptotic expansion of which the dominant term is

$$(-)^\rho \rho z^{(-z)^\rho + \rho - 3/2} \exp. \left\{(-)^{\rho-1} \frac{z^\rho}{\rho} + \log\log z - \frac{1}{2\rho} \log 2\pi + \sum_{s=-\rho}^{\infty}{}' \frac{(-)^{s-1}}{s z^s} F\left(\frac{s}{\rho}\right)\right\},$$

so that $R'_\rho(z)$ is of integral order ρ.

The term $\log\log z$ in the exponential just written down shows that we shall come, sooner or later, to a transcendental term in the expansion of the n^{th} zero of $R'_\rho(z)$.

Similarly the theorem may be established for the general simple non-repeated function of finite integral order.

As regards the application of the same methods to simple repeated functions it is only necessary to notice that corresponding to a zero k times repeated of the original function there will be a zero $(k - 1)$ times repeated of its derivative.

§ 97. We have now to consider whether the derivative of an integral function, all of whose roots are real, can have zeros other than the real zeros which by the extension of ROLLE's theorem separate the roots of the original function.

For this purpose let us consider the difference between the number of roots of $P(z)$ and of $P'(z)$ within a circle of very large radius r.

This number will be $N = \frac{1}{2\pi\iota} \int \left\{\frac{d}{dz} \log P'(z) - \frac{d}{dz} \log P(z)\right\} dz$

$= \frac{1}{2\pi\iota} \int \frac{d}{dz} \log \frac{P'(z)}{P(z)} dz$, where the integral is taken round the circle in question.

Now by examining the various cases which can arise, it may at once be seen that the asymptotic expansion of $\frac{d}{dz} \log \frac{P'(z)}{P(z)}$ is given by $(\rho - 1) \log z +$ terms which vanish when $|z| = \infty$. Therefore to a first approximation we have $N = \rho - 1$.

If then the function $P(z)$ is of genre p, its derivative can at most have only p zeros besides those demanded by the extension of ROLLE's theorem.

And therefore when p is odd, $P'(z)$ can at most have only $(p - 1)$ imaginary roots.[*] In particular when $P(z)$ is of genre 0 or 1, $P'(z)$ can have no imaginary roots.[†]

From this theorem coupled with the expansion given in § 5 and the equality

$$\frac{d}{dz} \frac{J_n(z)}{z^n} = -\frac{J_{n+1}(z)}{z^n},$$

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[*] BOREL, 'Fonctions Entières,' p. 44.

[†] LAGUERRE, 'Œuvres,' t. 1, pp. 167 *et seq.*

we see that all the zeros of $\frac{J_{n+1}(z)}{z^{n+1}}$ are real if the zeros of $\frac{J_n(z)}{z^n}$ are real—a theorem due to MACDONALD.[*]

If the function $P(z)$ be multiplied by an algebraic polynomial with real coefficients whose degree is q, the derivative of the product can at most have only $p+q$ imaginary roots.

§ 98. So far we have only considered integral functions whose roots are all real and negative. If, however, we have an integral function all of whose roots lie along a line other than the negative half of the real axis, a change of the independent variable will at once reduce it to an integral function all of whose roots are real and negative.

If then an integral function of genre p have all its roots but q lying in a sequence along a straight line through the origin, its derivative will at most have $p+q$ roots which do not lie along this line.

§ 99. We now conclude for the present the applications of the expansions which have been obtained. There are many questions which are still to be discussed—for instance :—

(1) Functions of infinite order ;
(2) Functions of multiple sequence ;
(3) Asymptotic expansions deducible from linear differential equations ;
(4) The rate of increase of the coefficients of the TAYLOR'S series expansion of an integral function ; and so on.

Investigations in connection with each of these questions have been tentatively undertaken—notably by BOREL, HORN, HADAMARD and POINCARÉ. And I find it possible to extend, by the methods of this memoir, many of the results which have hitherto been obtained. But such investigations I leave for future publication.

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[*] MACDONALD, "Zeros of the Bessel Functions," 'Proc. Lond. Math. Soc.,' vol. 29, p. 575.

INDEX

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