X. *Experiments on the cooling of Water below its freezing Point. By* Charles Blagden, *M. D. Sec. R. S. and F. A. S.*

Read January 31, 1788.

WHEN the experiments for determining the degree of cold at which quickfilver becomes folid, related in the Philofophical Tranfactions for 1783, were under confideration, no difficulty occurred in explaining the phænomena that had been obferved, except in the few inftances where the mercury in the thermometer congealed, whilft it was furrounded with fome of the fame metal in a fluid ftate. The well-known property of water, that under different circumftances it will bear to be cooled feveral degrees below its freezing point without congealing, afforded from analogy the moft probable folution of this difficulty; but as neither the caufe of that property had been inveftigated, nor the circumftances by which it is modified had been afcertained, I was led to attempt fome expements on the fubject; not only in hopes of elucidating the above-mentioned phænomenon of the quickfilver, but alfo becaufe this very quality in water was itfelf a curious fubject of refearch.

I began with endeavouring to determine, whether this property belongs to it as pure water, or depends upon extraneous admixtures. For that purpofe I poured fome clean diftilled water into a common tumbler glafs, till it reached two or three inches above the bottom, and then fet the glafs in a

frigorific

frigorific mixture, made with ſnow and common ſalt. This was the method I uſed in moſt of the following experiments, ſometimes employing ice inſtead of ſnow, ſubſtituting a glaſs jar or cylinder inſtead of a tumbler, and filling the veſſel to a greater or leſs height above the bottom. I found that, in the frigoric mixture, the diſtilled water readily ſunk many degrees below 32°, ſtill continuing fluid; and by repeating the experiment with care, I ſeveral times cooled it to 24°, 23°½, and even almoſt to 23°. The temperature was aſcertained by means of a ſmall thermometer with a ſliding ſcale; and though the water was not of the ſame degree of cold throughout, yet the difference, when the experiment had been well conducted, was not conſiderable; and I was particularly careful that the thermometer ſhould not touch the ſides or bottom of the glaſs, ſo as to be affected immediately by the cold of the mixture. From theſe experiments therefore it ſeemed evident, that the property of being cooled below the freezing point did not depend on extraneous admixture, eſpecially as I found, by comparative trials, that common pump-water would ſcarcely ever bear to be cooled ſo much. An ambiguity, however, ſtill remained, on account of the air which is always mixed with water that has lain expoſed to the atmoſphere. In order to determine what might be aſcribed to this circumſtance, I put ſome of the ſame diſtilled water over the fire to boil, in a clean ſilver veſſel, and kept it in violent ebullition for a conſiderable time. In a few minutes after it had been taken off the fire, and before it was nearly cold, I ſet it in the frigorific mixture after the uſual manner; when, inſtead of freezing more readily, it bore to be cooled two degrees lower than I had ever been able to reduce the unboiled water, not congealing till the thermometer in it had ſunk to 21°. Subſequent experiments were attended

attended with a fimilar refult, and have fufficiently convinced me, that, other things equal, boiled water may be cooled a greater number of degrees below the freezing point, without congealing, than water which, not having undergone that operation, retains the air it naturally imbibes.

As a further proof that the prefence of an aërial fluid in water rather leffens than increafes its quality of being cooled below the freezing point, I found that diftilled water, which had been for that purpofe impregnated with fixed air, generally fhot into ice at a lefs degree of cold than the fame water in its ordinary ftate. I fufpect, however, that it is ufually by the admixture of other aërial fubftances, fuch as dephlogifticated air, phlogifticated air, or perhaps both, and not of fixed air, that water is inclined to congeal foon after it has paffed the freezing point; for, as will be feen hereafter, *acids* rather improve than diminifh the quality in water of refifting congelation.

To determine the effect of other extraneous fubftances, I took fome very hard pump-water, fuch as is found in the northern parts of London, and fet it in the frigorific mixture. In general it congealed fooner by one or two degrees than unboiled diftilled water; that is, at 25° or 24° of the thermometer; and as there was fome variation in this refpect, I was led to remark, that the greateft cooling ufually took place when the water was moft clear and tranfparent. With a view to this circumftance I took fome New-River water, which happened at that time to be confiderably turbid, and tried it in the frigorific mixture; when I found, very unexpectedly, that it was not in my power to cool any of it below the freezing point; a cruft of ice always forming round the fides and at the bottom of the veffel, whilft the thermometer, fufpended about the

 middle

middle of the water, was two or three degrees above 32°. To try how far this depended on the foulneſs of the water, I collected ſome of the muddy ſediment which had been depoſited from the New-River water, and added it to the pump-water, which had before born to be cooled to 24° or 25°, ſo as to render it turbid; when it congealed, in the ſame manner as the New-River water had done, before the thermometer in the middle of it came to the freezing point. It muſt not however be imagined, that water thus made turbid is incapable of being cooled below 32°, without freezing: I have ſince repeated the experiments, with more caution in conducting them, and reduced it two or three degrees below the point of congelation. But ſtill they have all confirmed the general fact, that ſubſtances which leſſen the tranſparency of water, render it at the ſame time much more difficult to be cooled below the freezing point, and diſpoſe it to ſhoot into ice more readily, after it has paſſed that point, than pure water would do. It ſeems to be of little conſequence what the ſubſtance is that renders the water turbid: ſmall particles of any kind floating through it, I believe, have this effect, which does not take place, or at leaſt to the ſame degree, when the extraneous ſubſtance has ſubſided to the bottom.

It is this circumſtance, I ſuppoſe, which gave riſe to the opinion, that boiled water freezes ſooner than unboiled: for if the water contain calcareous earth, held in ſolution by means of fixed air, as is the caſe with moſt kinds of ſpring-water, this will be precipitated by the boiling, and will ſenſibly trouble the tranſparency of the water; which, if expoſed to the cold in that ſtate, will be liable to freeze ſooner than the ſame kind of water unboiled and tranſparent *.

* See Philoſophical Tranſactions, Vol. LXV. p. 124.

The

The effect of this want of transparency was very different from that of chemical mixture, as appeared by subsequent experiments.

Though the property of being cooled below the freezing point appeared to belong essentially to water in it's pure state, it was probable that it would be in some measure altered or modified by the various substances which are capable of being dissolved in, or chemically combining with, the water. But here a further circumstance came to be considered. It is well known, that such substances, uniting with water, have a power of lowering its point of congelation a greater or less number of degrees, according to the nature and quantity of the substance employed. The first object, therefore, was to determine in what manner the property of bearing to be cooled would be affected with regard to that new point of congelation. For this purpose I made many experiments with several different substances, which it would be too long to relate in detail, but the principal were as follows.

Having dissolved in distilled water as much common salt as lowered its freezing point to 28°, I cooled it to 18°½ before it congealed. Another solution of the same salt, whose freezing point was 16°, bore to be cooled to 9°; and a stronger solution, whose freezing point was 13°½, cooled to 5° before it shot. A solution of nitre, whose freezing point was 27°, cooled to 16°, that is, eleven degrees below its new freezing point; a solution of sal ammoniac, whose freezing point was 12°, cooled to 3°; and one of Rochelle salt, freezing point 27°½, suffered the thermometer to sink in it to 16° before it froze; a cooling equal to the greatest I ever obtained with the purest distilled water boiled. A solution of green vitriol, whose freezing point was near 30°, cooled below 19°: and, of salts with an

 earthy

earthy bafis, a folution of the common bitter purging falt, whofe freezing point was at 25°½, bore to be cooled to 19°.

Acids, as I have already had occafion to remark, rather augment this quality of being cooled below the freezing point. A combination of nitrous acid with diftilled water, in fuch proportions that the new freezing point was between 18° and 19°, funk down to 6° before it congealed; which being fully 12 degrees of cooling, is greater than I have been able to produce with pure water. Another mixture of the fame kind, fo ftrong as to have its freezing point about 11°, cooled down to 1°. A mixture of vitriolic acid and diftilled water, whofe freezing point was 24°½, cooled to 14°; and one with the acid of falt, having its freezing point at 25°, funk to 16° before it froze. It is here to be obferved, that thefe acid mixtures were rather remarkable for the fteadinefs with which they bore to be cooled, and the little tendency they fhewed to fhoot before they were funk much below the freezing point, than for exceeding the number of degrees which pure water might be cooled. Of the alkalies, a folution of tartar, whofe freezing point was 25°½, cooled to 18°; and another, with the freezing point at 15°, funk to 8°. A folution of cryftallifed foda, freezing point 30°, cooled to 21°; and a folution of mild volatile alkali, freezing point 19°, to 11°. A mixture of rectified fpirit of wine and water, whofe freezing point was 12°, cooled to 5°; and another, with the freezing point at 8°½, to 2°.

All thefe facts, with many others of the fame nature which I obferved, fufficiently fhew, that foreign fubftances, chemically combined with or diffolved in water, do not take away its property of being cooled below its point of congelation; though, by depreffing that point, they alter the degree of cold

at

at which the property commences. The experiments ſhew, that in ſome caſes the mixed water bore to be cooled as much below its new freezing point, as pure water below 32°; and with regard to the others, I think the variation was no greater than uſually takes place with different portions of common water. Scarcely any, perhaps none, of the above-mentioned points, were abſolutely the loweſt to which the ſolutions or mixtures could have been reduced, if the experiment had been conducted ſtill more ſlowly and cautiouſly. But however much they might all poſſibly have born to be cooled, a great difference occurred among them in the eaſe with which the operation ſucceeded. For inſtance, the ſolutions of nitre, and of Rochelle ſalt, would hardly ever ſhoot till they were cooled many degrees below their reſpective freezing points, however negligently the operation was conducted; whereas thoſe of common ſalt, ſalt of tartar, and ſome others, required conſtant attention to keep them from freezing, as ſoon as they were got four or five degrees below the point of congelation. Their difference in this reſpect may depend in part upon ſomething unknown in the nature of each particular ſalt; but there was one circumſtance to be diſtinctly traced, correſponding to what had been obſerved with pure water; namely, that the moſt tranſparent, moſt limpid ſolutions, were thoſe which admitted of being cooled with the greateſt eaſe and certainty. The ſame obſervation holds good with regard to the mixtures: thus the rectified ſpirit I employed aſſumed ſomething of an opaline tinge upon being mixed with the water (from the ſeparation of an oil it contained) and the compoſition bore to be cooled but ill, though a film of oil, regularly ſpread on its ſurface, would rather have retarded the freezing; and the acid mixtures, which cooled ſo remarkably well, ſtruck the eye parti-

 cularly

cularly on account of their very perfect and uniform transparency. In this last case, perhaps, another circumstance might contribute to the easy cooling, that the acids, by combining with the water, seemed to expel the air it contained more perfectly than most other substances, as appeared from the innumerable small bubbles that were almost immediately formed.

Want of transparency, however, is only one among several causes which impair the property water naturally possesses, of bearing to be cooled many degrees below its freezing point. M. MAIRAN, in his elaborate Treatise upon Ice, having occasion to examine this subject, was led by his experiments to conclude, that the cooling of water below its freezing point depends upon rest, and that agitation is the general cause by which it is brought to shoot into ice. In this opinion he has been almost implicitly followed by all the writers I have seen, excepting only Professor WILCKE, of Stockholm *. To bring it to the test of experiment, I set in the frigorific mixture some distilled water, which by boiling had been rendered capable of sustaining a cold of 21° before it froze. When this water was cooled to 22°, I agitated it, by moving the tumbler, by shaking a quill in it, and by blowing on it so as to ruffle the surface; but it supported all these trials without congealing, and did not shoot till a minute or two afterwards, when by continuance in the frigorific mixture it was cooled down to 21°. In other experiments, however, all the above-mentioned kinds of agitation made similar water instantly congeal, even when not cooled so low by several degrees. The congelation, therefore, must in these cases have depended on some further circumstance than the mere want of rest. One that I suspected is a sort of tremulation, rather agitating small portions of the

* Kongl. Vetensk. Acad. Handlingar, Vol. XXX. p. 103. 105.

water ſeparately, than moving the whole together. I have found, that ſtriking the bottom of the tumbler againſt a board would produce inſtant congelation, when ſtirring the water, or ſhaking the tumbler in the hand, would have no effect. In like manner, when in ſtirring the cooled water the quill, or ſtick of glaſs, employed for that purpoſe, ſtrikes againſt the ſide or bottom of the tumbler, the water, which had reſiſted the general ſtirring, is often by this percuſſion made to freeze. The ſame effect is produced, and with leſs uncertainty, if the quill, or ſtick of glaſs, be rubbed, and as it were ground, againſt the ſide of the tumbler. But of all ſuch methods of bringing on the congelation, that which I have found to fail the ſeldomeſt, is to rub a bit of wax againſt the ſide of the tumbler under the water; a particular roughneſs in the motion is felt, with ſome ſound, approaching to a muſical tremulation, and a cruſt of ice is immediately perceived under the wax upon the glaſs. This effect of the wax I take to be mechanical, depending on its particular ſtate of conſiſtence. Wood acts in the ſame manner, though with leſs certainty; ſo does a quill, and likewiſe glaſs; but the latter, being very hard, produces the effect with leaſt certainty. It is a mechanical action upon the water in contact with the rubbing ſubſtance and the glaſs: for if the outſide of the tumbler, or any part of the inſide above the water, be rubbed, even if it be wet ſo as to communicate a ſimilar feeling of tremulation, yet ſtill the congelation is not produced.

All theſe modes of bringing on the congelation ſucceed beſt, as might be expected, in proportion as the water is more cooled below the freezing point. Unleſs the cooling amount to four or five degrees, the friction with wax is often in vain.

From

From the above-mentioned facts it appears, that M. MAIRAN's position, though not destitute of foundation, was enounced by him too generally, and without sufficient precision. It is the natural property of water to bear to be cooled a certain number of degrees without freezing; rest favours this property negatively, by giving it no interruption; but most kinds of agitation interfere with its operation to a greater or less degree, and some perhaps would prevent it altogether; whilst others affect it so little, as not to superinduce the congelation, even when the cooling is brought within one degree of the greatest that the water will bear.

Whatever be the effect of agitation, there is another cause which much more powerfully hastens the congelation of water. It has been long known, that when water is cooled below its freezing point, the contact of the least particle of ice will instantly make it congeal, the glacial crystals shooting all through the liquor, from the spot where the ice touches it, till the whole comes up to the freezing point. Few experiments of the minute kind afford a more striking spectacle than this, especially when the water has been cooled nearly as much as possible below the freezing point; both from the beautiful manner in which the crystals shoot through it, and the rapidity with which the mercury in the thermometer immersed in it runs up through a space of 10 or 11 degrees, stopping and fixing always at 32 in pure water. If from any circumstance, however, as a less cooling, or the addition of a salt, the shooting of the ice proceed more slowly, the thermometer will often remain below the freezing point even after there is much ice in the liquor; and does not rise rapidly, or to its due height, till some of the ice is formed close to its bulb; which exemplifies the evolution of the latent heat from the very particles that congeal.

Many of the circumſtances attending the greater or leſs cooling of water below its freezing point depend upon this principle. In a calm day, when the temperature of the air was about 20°, I expoſed two veſſels with diſtilled water to the cold; one of them was ſlightly covered with paper, the other was left open: the former bore to be cooled many degrees below the freezing point, whilſt a cruſt of ice always formed on the ſurface of the other before the thermometer immerſed in the middle of it came to the freezing point. This phænomenon, which other obſervers have remarked without being able to account for it, appears to me clearly owing to frozen particles, which in froſty weather are almoſt always floating about in the air, often perceptibly to the ſenſes. They come moſt commonly either from clouds paſſing over head, or from ſnow or hoar-froſt lying upon the earth; and when they touch the cooled ſurface of the water, inſtantly make it freeze. That the effect does not depend ſimply on the contact of cold air, is plain from the following experiment. I expoſed to the cold a glaſs jar, with ſome diſtilled water, and placed in it two thermometers; one immerſed in the water, the other ſuſpended a little above its ſurface, in the empty part of the jar. The latter ſunk faſter than the former; but after a certain time, the thermometer above the ſurface was at 25°, and that in the water at 25°$\frac{1}{2}$, yet the water continued unfrozen. I perceive too by M. WILCKE's experiments, that in much more intenſe cold than we uſually experience in this country, veſſels of water ſtanding within doors in a laboratory are often cooled ſo far below the freezing point as to become almoſt full of ice upon being made to ſhoot, though the ſurface

ſurface of the water be in no wiſe defended from the cold air of the laboratory. Oil ſpread over the ſurface of water has been found to prevent it from freezing, when other water ſimilarly expoſed has had a cruſt of ice formed upon it. This I aſcribe entirely to the prevention of frozen particles from coming in contact with the water: for in experiments with frigorific mixtures, in a room of moderate temperature, I do not find that oil on the ſurface has any ſenſible effect in enabling water to ſupport more cold, unleſs, indeed, where the operation is otherwiſe too much precipitated. Alſo a crack in the tumbler containing the water prevents it from cooling below the point of congelation, a thin film of ice inſinuating itſelf through the crack into contact with the water. And often, in experiments with frigorific mixtures, the congelation is brought on by raiſing the immerſed thermometer a little out of the water, and lowering it down again; ſome of the adhering water having frozen upon its ſtem.

Several other circumſtances, though not ſo diſtinctly aſcertained as the preceding, appear to facilitate the congelation of cooled water. For inſtance, in experiments with frigorific mixtures, if the cold be very intenſe, the water freezes almoſt immediately round the ſides of the veſſel, as if ſomething depended on too ſudden a change of temperature. Accordingly, the only way of inſuring the greateſt degree of cold in water without freezing, is to cool it in a very gradual manner, keeping the cold of the frigorific mixture regularly only two or three degrees below that of the water. Sudden cooling, therefore, may be conſidered as one of the cauſes which haſten congelation. No doubt this will ſometimes depend on ſuch a cold as water cannot reſiſt without freezing, being propagated through the glaſs to the neareſt part of the water, quicker than it can be be diftributed to the reft of the water; but, I think, the above-mentioned effect takes place when no part of the fluid can be fuppofed to be many degrees below the freezing point.

It has been alledged, that metal in contact, either with the outfide of the veffel containing the water, or with the water itfelf, difpofes it to freeze fooner after it is cooled below 32°. Though upon repeating this experiment I have found it poffible to cool water in a metal veffel many degrees below its freezing point, and even to touch it, when fo cooled, with metal equally cold, without producing congelation; yet the metal certainly tends to haften the freezing, and, I believe, on the above-mentioned principle of too quick a change of temperature, occafioned by its quality as a good conductor of heat. For the fame reafon it is more difficult to cool water much below the freezing point in thin veffels than in thofe whofe bottom and fides are of confiderable thicknefs; the latter tranfmitting the heat more flowly, and allowing it thereby to be diffufed more equably.

In cooling water below its freezing point by frigorific mixtures, it is of confequence to keep the mixture fome way below the upper edge of the water within the tumbler, otherwife the congelation quickly begins at that place. This very likely depends on the principle laft mentioned, that the thin edge of water rifing up againft the fide of the glafs, being more in contact with air than with the general mafs of water, does not fo eafily diftribute its cold, and therefore fuffers a more rapid change of temperature by the action of the mixture. Hence one of the moft effential precautions for cooling water to the utmoft without congelation, is to perform the experiment in a warm room, that the air in contact with the edges

 and

and furface of the water may prevent their fudden cooling. And one of the moft convenient veffels for the purpofe is a round body terminating in a neck, the body to be furrounded with the frigorific mixture, whilft the water in the neck is kept above the freezing point.

Thefe are the principal facts with which my experiments have furnifhed me relative to the cooling of water below its point of congelation. I fee no general circumftance that applies to them all. At one time I thought that much depended on reducing the water into thin plates; an idea which was principally fuggefted by the more ready congelation of the edges of the water where it rifes up as a thin film on the fides, and by the effect of extraneous fubftances floating in the water to haften its freezing, which might be fuppofed frequently in their motions to intercept fmall portions of the fluid, and form it into thin plates. Agitation likewife might act by reducing the water in fome part or another into fimilar plates. And as water impregnated with air appeared lefs capable of being cooled than the fame water deprived of its air, it feemed not impoffible that the air might act likewife by producing thin plates in different parts of the fluid. With a view to this hypothefis I made feveral experiments. Into a tumbler with diftilled water I put a quantity of fand, which fettled loofely to the bottom, and left the water above as tranfparent as before. This tumbler being placed in the frigorific mixture, the water bore to be cooled as well as it had done without this addition. Laying thin bits of glafs upon one another at the bottom of the tumbler, in place of the fand, I found no difference in the effect. By this latter experiment it was moreover proved, that points in the water do not perceptibly facilitate its cryftallifation into ice. Now the thin plates or wedges of of water, which muſt be intercepted by the bits of ſand or glaſs, ſeem very analogous to ſuch as may be produced by floating particles of extraneous matter; and therefore the effect of the latter is probably to be aſcribed to ſome other cauſe, ſuch as haſtening the cooling, or rendering it leſs uniform, or, perhaps, communicating motion to the fluid.

In the preceding inſtances, however, the water may be conſidered as conſtituting, by its adheſion, a ſort of continued body with the ſubſtance it touches; and it might be ſuppoſed that, if one or both ſurfaces of the thin plate were in contact with air only, the congelation would take place. I therefore put down ſome air, retained by a ſmall diſh of wax, into the water to be cooled, and let it ſtay there till the whole was reduced many degrees below the freezing point; but no congelation enſued: I then contrived to turn up the diſh of wax in the water, ſo that the air it had carried down, eſcaping from under it, aſcended as a bubble to the top of the water, and there burſt: ſtill the water retained its fluidity, notwithſtanding the contact of a looſe bubble of ſuch cold air, and the motion produced by its exploſion on the ſurface. In other experiments, I have indeed ſeen the burſting of a bubble on the ſurface apparently bring on the congelation; but ſeemingly from the agitation it occaſioned. And though a wetted ſurface, or a ſmall thin portion of water, freeze in general more readily than a larger maſs, yet I have ſeen inſtances of a jar cooled many degrees below the freezing point, and the water and air in it equally cold, which had, notwithſtanding, upon its inſide, from the ſurface of the water to an inch or more above it, an evident dew that remained quite fluid, and rendered the ſurface of the glaſs wet. Under the ſame circumſtances alſo, I have raiſed the thermometer out of the cooled water, without occaſioning any congelation in the adhering thin film of that fluid.

fluid. These facts, though they do not shew but that a film of water, in contact on both sides with air below its freezing point, would at once congeal, yet, I think, are sufficient to prove, that its formation into thin plates is not a general cause of its early freezing.

From a consideration of the above-mentioned causes of freezing, and their various exceptions, I am led to think, that the matter in question depends upon some circumstance of the more intimate nature or composition of the water; for instance, the arrangement, attractions, and perhaps shape, of its particles. If we suppose the particles of water to possess a kind of polarity, that is, to have particular attracting points or surfaces, properly arranged, not only its crystallisation in regular angles, but likewise most of the above-mentioned phænomena, admit of some kind of explanation. For latent heat, be it a matter or motion, may be considered as a cause either lessening the power or impeding the operation of this polarity; the effect of which is gradually diminished by external cold, till at length the polarity entirely overcomes the resistance it occasions, and the attracting points or surfaces rush together. Whatever tends, therefore, to bring these particles into a state more advantageous for their junction, as by presenting their attracting surfaces more directly to one another, forcing them nearer together, or removing attractions of a contrary tendency, and allowing the particles free scope to follow the impulse of their polarity, must tend to hasten the congelation. When particles of water, already frozen, are presented to other fluid water of a proper degree of coldness, not only the attracting surfaces will be in the most favourable position from the arrangement they have taken in the freezing, but very possibly their power may be stronger from their union with one another; and hence ſuch water is inſtantly brought to freeze. Indeed it is this circumſtance which conſtitutes the freezing point; for that point is evidently nothing elſe but the degree of cold which renders the particles of any fluid incapable of reſiſting the attractive power of other particles of the ſame fluid, already reduced into a ſolid form: and the fact, that the cold of the freezing point is leſs than the fluid will otherwiſe bear, ſeems a proof that when the particles have acquired this arrangement of ſolidity, their attractive powers are the ſtrongeſt; ſo that the difference between the freezing point, and the greateſt cold the fluid will bear, may be conſidered as the meaſure of this additional attractive force.

Agitation may be eaſily conceived, by the various motions impreſſed upon the particles, to occaſion ſome of them to apply their polar points in a more advantageous poſition, or even to force them nearer together; and theſe effects are more likely to be produced by an intimate agitation, than by a general motion of the whole maſs. The want of tranſparency, in certain caſes, as in ſome ſolutions of ſalts, ſeems not owing to the preſence of foreign matters, but rather to depend upon a particular arrangement of the combined particles, which may diſpoſe thoſe of the water to join more readily, and detach thoſe of the ſalt. Extraneous ſubſtances, beſides their indirect effect, may, by various chances attending their floating in the water, throw the particles into favourable ſituations; and if thin plates are more diſpoſed to freeze, it may be, that the particles of water in ſuch are more free from counteracting attractions.

Sudden cooling may promote congelation ſimply by occaſioning the water at the bottom and ſides of the veſſel to acquire a greater degree of cold than the reſt. But perhaps it may have alſo another effect, admitting of a particular expla-

nation.

nation. Water in freezing undergoes a confiderable expanfion. This may be afcribed to fuch a form of its particles, and pofition of their poles, as fhall make them, when touching and adhering by thofe poles alone, intercept very large interftices, which may be confidered as the *pores* of the ice. Various pofitions of the poles and figures of the particles may be conceived, which fhould caufe them to occupy more fpace, when touching in certain points only, than they filled when lying near without any contact. But in whatever way the expanfion is produced, experiment hath fhewn that it begins fome time before congelation; fo that when water is cooled down to 32°, it is already fenfibly expanded; and if the congelation does not take place here, this expanfion augments, in proportion as the water is further cooled*. The expanfion, therefore, being fo evidently an approach to freezing, may be confidered as an indication that the polarity already prevails fo far as to draw the particles fomewhat out of the fituation they naturally affume in the higher temperatures. And it is conceivable, that if this operation go on very quick, and the confequent change of pofition in the particles be made with fome degree of velocity, they may acquire a fmall momentum of motion, enabling them to overcome a refiftance which would otherwife prevent their junction.

* In experiments where the water has cooled much below its freezing point, I have feen the expanfion fo great as to bear a confiderable proportion to the whole expanfion produced by freezing, which laft, I believe, is more than one-feventh of the volume of the water. It feemed to me as if the expanfion proceeded in an increafing ratio, being much greater upon the laft degrees of cooling than it was upon the firft. The difficulty of procuring a proper apparatus for thefe experiments has hitherto prevented me from afcertaining the quantities with precifion.

As

As chemical combinations all depend upon attractions between the subſtances which unite, it is not difficult to conceive, that a particle of ſalt, an acid, or the like, may attract a particle of water in ſuch a manner as ſhall oppoſe or diminiſh its attraction for the other particles of water. Hence the polarity may be ſo much weakened, as not to bear the ſame proportion to the reſiſting power of the latent heat, till this alſo is diminiſhed by a greater degree of cold, which conſtitutes the new freezing point. But when, by increaſing the cold, all the powers are reduced to a ſimilar ſtate of equilibrium, exactly the ſame phænomena take place as belong to the natural freezing point of the water.

To aſſiſt the conception, I have here reaſoned upon the particles of water as ſolid, and of a determinate ſhape. But it ſeems moſt probable, that the particles of matter in general are nothing more than centres to certain attractive and repulſive powers; on which hypotheſis it may be underſtood, that if two or more of theſe central points are brought much within the limits of their reſpective attractions and repulſions, theſe powers will no longer be equal at equal diſtances from their common centre. Now ſuch a combination of central points may be conſidered as one particle of any particular matter; and the unequal diſtances from the common centre at which the attractions and repulſions are equal will define what may be called the ſhape of that particle. And if, at equal diſtances, the attraction or repulſion is much greater at one point than at another, that will conſtitute a polarity.

The greateſt cold I have been able to make water acquire without freezing, is near 12 degrees of FAHRENHEIT's ſcale below its common freezing point. Some diſtilled water was boiled about a quarter of an hour in a tin cup, and placed in the fame veffel, whilft ftill warm, in the frigorific mixture. The mixture was made to act very flowly, fo that the operation continued more than an hour. When the immerfed thermometer had funk to 20°⅓, the water was ftill fluid: I then fhook it confiderably, but no ice formed. After waiting fome time, and finding the thermometer would fink no lower, becaufe by the length of the procefs the fnow of the mixture was almoft confumed, I added fome frefh materials, which could not be done without fhaking the tin cup. Still, however, the water did not freeze inftantly, though it fhot as foon after as it can be fuppofed to have felt the influence of the new frigorific mixture. When this water was cooled to 24°, I tried the temperature of the air near its furface, and found it 34° or 35°, the experiment being performed in a room with a fire.

Another time I cooled fome diftilled water, covered with oil, below 21°, by fimilar precautions.

This, however, is by no means the greateft cooling of which water is fufceptible. In FAHRENHEIT's experiment, with an exhaufted globe half full of boiled rain water, it feems to have been cooled to 15° *. M. DE LUC likewife informs us, † that having filled a thermometer with fome water he had purged of air by the means defcribed in his great work upon the atmofphere, he expofed it to a cold which funk a mercurial thermometer to 14° of FAHRENHEIT's fcale. The water in the thermometer continued tranfparent, and upon breaking the ball was found to be liquid, but froze that inftant. In fome of my experiments too with mixtures of nitrous acid and water, the liquor bore to be cooled as much as 13 degrees

* Philofophical Tranfactions, Vol. XXXIII. p. 81.

† Idées fur la Météorologie, Tom, II. p. 105.

below

below its new freezing point; and it has been already obſerved, that the addition of an acid always expelled much air from the water. It is not improbable, therefore, that if water could be thoroughly purged of air, it would readily bear to be cooled 18 degrees, or more, below its freezing point, without congelation; though the deprivation of air, obtained by boiling it, is ſuch only as will barely enable it to admit a cooling of 12 degrees.

Other fluids may bear to be cooled much more below their proper point of conſolidation. This is evidently the caſe in what Mr. CAVENDISH calls * the ſpirituous congelation of acids. Mr. M^c NAB's nitrous acid bore to be cooled from 30 to near 40 degrees below its freezing point †; and Mr. KEIR's vitriolic acid at the ſtrength of eaſieſt freezing continued fluid at 29°, though its heat became 46°½ when it began to congeal ‡. How low quickſilver may be cooled has not yet been aſcertained, but probably many degrees below – 40°.

So many of the above-mentioned facts were obſerved in the year 1783, that I then ventured to remark, that "independently of theſe circumſtances, neither ſtirring, agitation, a current of freſh air on the ſurface, nor the contact of any extraneous body not colder, would [neceſſarily] cauſe the water to ſhoot into ice, notwithſtanding the repeated aſſertions of authors to the contrary **." Similar experiments, made in the courſe of the ſucceeding winters, have confirmed in general the former reſults, and furniſhed the materials of the preceding ſheets. I am very ſenſible, that the

* Philoſophical Tranſactions, Vol. LXXVI. p. 261.

† Ibid. p. 252.

‡ Ibid. Vol. LXXVII. p. 279.

** Ibid. Vol. LXXIII. p. 358.

ſubject ſtill remains involved in great obſcurity; nor ſhould I have troubled the Society with an account of experiments which leave ſo much uncertainty, had I not thought that they tended to elucidate a few points, and to correct ſome erroneous opinions. I hope that perſons inhabiting a climate more advantageous for the purpoſe, will be induced to undertake ſuch experiments in another, and probably a more ſucceſsful way, by expoſure to *natural* cold.