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# THE ABSORPTION OF LIGHT BY INORGANIC SALTS

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DISSERTATION

Presented In Partial Fulfillment of the Requirements for  
the Degree of Doctor of Philosophy In the Graduate  
School of the Ohio State University.

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BY

ENOCH FRANKLIN GEORGE



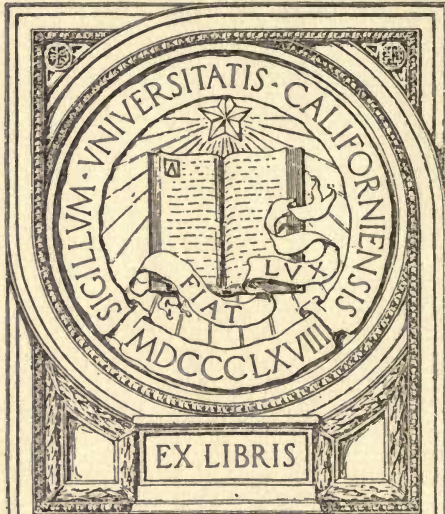
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The Ohio State University

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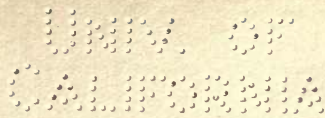
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## INTRODUCTION.

The mechanism of the absorption of light is one of the least understood of physical phenomena. The literature upon the subject is voluminous, but not always illuminating. The matter has been dealt with by theoretical and experimental physicists and chemists. On the experimental side there has, in general, been no attempt to distinguish between absorption, scattering, and reflection. In dealing with solutions, especially, the difference between the intensity of the incident light and that transmitted has been taken as a measure of the absorption, although the decrease in intensity is due to all three factors. This seems to be unavoidable. Certainly it is not easy to differentiate between them experimentally. But in any theoretical investigation or discussion, some attempt should be made to distinguish between them.

When an electromagnetic wave, as a light wave, is incident upon a material dielectric, there is set up in the medium, in addition to the displacement current in the ether, a polarization current due to the periodic displacement of the electrons in the atoms or molecules of the medium, and the magnitude of this current will be proportional to the time rate of change of the electric intensity. If the displacement of the electrons is resisted by some force similar to that of friction, energy will be absorbed from the waves and converted into heat, as when a condenser is heated by a rapidly alternating current. If in addition to the bound electrons of a dielectric there are also free electrons, as in a metal, there will be conduction currents proportional to the electric intensity. Thus again we will have heat generated at the expense of the radiant energy.

The chief difficulty with the foregoing explanation of light absorption is, that it does not fit in with observed facts. The reason is obvious. We have neglected the inertia of the electrons. True, the inertia of an electron, when compared with that of familiar things, is small. But when acted upon by a force whose direction changes through  $180^\circ$  a million billion times per second, the inertia becomes very considerable.

The reduction in the intensity of light in passing through material media is generally thought of as a resonance effect. Resonance is a phenomenon encountered in every branch of physics. A massive pendulum can be set into violent motion by a tiny force if applied

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periodically at the proper time—that is, if the frequency of the applied force is made exactly equal to that of the natural frequency of oscillation of the pendulum. This process of adjusting one frequency to that of another is known as “tuning”. If one tuning fork is set vibrating, another of **exactly** the same frequency will take up the vibration and thus absorb some of the energy of the first fork, while a third fork that is not so tuned will not be disturbed. The wireless operator adjusts the capacity and inductance of his sending apparatus until it oscillates with a certain frequency, which is the frequency of the radio waves transmitted through the ether. At the other end the operator must adjust the capacity and inductance of his receiving set until its frequency of oscillation is exactly equal to that of the oncoming radio waves; that is, he must tune his receiving set until its frequency of oscillation is equal to that of the electromagnetic waves propagated through space. When properly tuned it responds to the signals and absorbs energy from the ethereal waves. In light we have many examples of this effect. The characteristic lines of metallic vapors may be “reversed”, that is, the bright emission lines of a glowing vapor are reversed and become dark absorption lines when the vapor is placed in the path of a more intense light that gives a continuous spectrum. Certain phenomena, however, are not easily explained by resonance.

Vapors of sodium, potassium, iodine, oxides of nitrogen, etc., show thousands of very fine absorption lines, whose spectral distribution follows more or less definite laws, as observed by Deslandres and others, and the emission spectrum is, broadly speaking, the complement of the absorption spectrum. It is easy to assume that for each line there is a set of resonators or oscillators whose frequency is identical with that of the spectral line, and that they remove from the incident radiation, the frequency corresponding to their own. But this explanation is not quite sufficient. Iodine vapor illuminated with monochromatic light emits a series of isolated bright lines, spaced at nearly equal distances throughout the spectrum. Only one frequency can be absorbed, since monochromatic light is used. According to Wood the absorbed energy is then re-distributed among other frequencies by some mechanism within the molecule. Another stumbling block in the path of the resonance theory is found in the behavior of Roentgen rays. According to this theory any substance should be



opaque to a radiation whose frequency is the same as that of one of its characteristic emission lines. It is well known, however, that any substance is unusually transparent to X-rays whose frequency is identical with that of one of its own characteristic radiations. Thus the behavior of X-rays is diametrically opposite to that which the phenomenon of resonance would lead us to expect.

Assuming the validity of the resonance theory, and certainly none better has been advanced, just how does it account for the reduction in the intensity of light? Presumably the vibrating electron extracts from the incident radiation the energy of that frequency corresponding to its own, and re-radiates it in all directions. But this is scattering, and not absorption. If this energy is re-radiated in all directions there will be one beam in the direction of the incident beam, but, according to Planck, in the re-radiated waves there will be a lag in phase of 180 degrees and consequently destructive interference. There is also a beam in the opposite direction, and since there is no other wave in this direction, there is no destructive interference. Consequently we should expect to find a beam traveling backward from the medium. But this is only selective reflection.

Does an electron absorb energy in quanta? Is this absorption accompanied by a shift to an orbit of greater radius, with its attendant increase in potential energy? Absorption, when strictly defined, means a conversion of a part of the radiant energy into heat energy, with its consequent increase in temperature. But temperature is a function of molecular velocity, that is, of the kinetic energy of the molecules. How does increase in electronic energy, that is, intra-atomic energy, increase the velocity of molecules? How does transference of energy between electrons and molecules take place? Apparently it does not take place unless it occurs during molecular collision. Just what the process of transfer is, no one seems to know. According to Schuster and Nagaoki, absorption is probably due to sudden changes in vibration caused by molecular impacts.

According to most of the current theories of atomic structure the atom consists of a number of electrons equal to the atomic number of the atom, revolving in elliptic orbits about a positive nucleus. The number and position of electronic orbits for a given atom under given conditions is perfectly definite, but the number of orbits may be exceedingly large in comparison with the number of electrons. That is, an electron may shift from one orbit to another, radiating energy

in definite quanta if the shift is inward, and absorbing energy if the shift is outward. The shift of an electron from one orbit to the nearest orbit on either side is characterized by the absorption or emission of one quantum of energy.

An electron in motion is, by definition, an electric current. A number of electrons revolving in coplanar orbits about a common center is essentially an electromagnet. Two atoms would naturally attract or repel each other depending upon their orientation. If two or more atoms combine there will certainly be a rearrangement of the magnetic lines of force. According to Humphreys, the electromagnetic "force fields" of the individual atoms "condense" with the emission of energy, to form the force fields of the resultant molecule.

What effect does the union of two or more atoms in the formation of a molecule have upon the characteristic frequencies of the atoms? Perhaps the best answer has been given by Baly. According to him, when two atoms unite to form a molecule, the individual atoms may still vibrate with their characteristic frequencies, but added to these are frequencies which are characteristic of the molecules; these frequencies being the least common multiple of the atomic frequencies. In a more complex molecule we would have the frequencies characteristic of the individual atoms, frequencies characteristic of atomic groups within the molecule, and frequencies characteristic of the molecule.

The width of an absorption band is, according to Baly, due to subsidiary frequencies. According to Bjerrum (*Zeitsch. Electrochem.* 17, 731, (1911); *ibid*, 18, 101, (1912); Nernst, *Festschrift*, p. 90, (1912).) the subsidiary frequencies are due to the rotation of the molecules. If a molecule has a frequency of vibration  $v$ , and a frequency of rotation  $u$ , then it will exhibit frequencies  $v$  plus  $u$  and  $v$  minus  $u$  as well as  $v$ . Since the rotational frequencies of different molecules are naturally different, we should expect the absorption bands of any element to change with its chemical composition.

If an atom consists of a system of coplanar rings of electrons, each of definite mass, revolving in the same sense about a positive nucleus, then the atom, due to its configuration, will have a certain moment of inertia, and on account of the revolution of the electrons, will possess a certain angular momentum. It is easy to see that the atom will function as a gyroscope. Rotation of the atom, in the ordinary sense, will not occur. Molecular and atomic impacts will, in

general, be followed by precessional vibrations, or "wabbles", as when an ordinary gyroscope is struck a sharp blow. The frequencies of these vibrations will be a function of the moment of inertia of the atom, which, in turn, is a function of the number and distribution of the electrons in their orbits. The moment of inertia of a neutral atom will be different from that of an ionized atom, and the moment of inertia of a free atom will be quite different from that of the same atom in chemical combination, because the configuration of the electrons will be different.

If we assume the validity of the principle of equipartition of energy, then from a study of the experimental values of the molecular heats of gases, we must conclude that diatomic gas molecules possess only five degrees of freedom; that is, one degree of freedom is apparently missing. There are, of course, three degrees of freedom of translation, which leaves only two to be accounted for. Kruger has interpreted this fact as evidence in favor of his theory of precessional vibrations, which corresponds to two degrees of freedom. These precessional vibrations are, according to Kruger (*Annal. der Physik*. IV, 50, 346; *ibid*, 51, 450, 1916), responsible for the subsidiary frequencies.

According to Baly, the subsidiary frequencies associated with a given true molecular frequency may be represented by the expression  $M \pm nI \pm mA$ , where  $M$  is the particular molecular frequency concerned,  $I$  is one or the other of the intra-molecular frequencies,  $A$  stands for an atomic frequency, while  $m$  and  $n$  stand for the numbers 0, 1, 2, 3, 4, etc. The center of the band will be found by making  $m = 0$  and  $n = 0$ . This will result in the entire group of subsidiary frequencies which are associated with a given molecular frequency, being divided into sub-groups. Thus for a gas we should expect the absorption curve to consist of a series of isolated peaks arranged in groups, the whole being more or less symmetrically placed with respect to the molecular frequency  $M$ . The various peaks will decrease in height as they recede from the center of the band. If the envelope of the peaks is drawn, we should have a smooth curve falling off on either side of the frequency  $M$ . On account of the crowding of the molecules in a liquid, the vibrations and oscillations are more or less forced, so that absorption does not consist of sharp lines, but is more or less continuous. What we get, then, is a band whose curve is approximately that of the envelope mentioned above.

It is thus evident that chemical action—that is, regrouping of atoms—may exert a very great influence upon absorption of light if the atoms, either individually or in combination, have characteristic frequencies which fall within the visible spectrum. As an example of this effect, it is well known that the introduction of certain colorless compounds, known as chromophores, result in colored compounds.

One quantum of energy absorbed at the higher frequency might be re-radiated at the same frequency (resonance radiation), or as a whole number of quanta at the lower frequencies. It seems reasonable to suppose that the reverse process might also take place; that is, several quanta absorbed at the lower frequencies might combine according to the principle of the least common multiple and be given out again as a single quantum at a higher frequency. The true molecular frequency is the convergence frequency of the atomic frequency series. By means of this principle of the combination and resolution of frequencies, Baly has apparently offered a simple explanation of fluorescence and phosphorescence. It is apparently similar to the analysis of a wave by means of a Fourier's series.

According to Lambert's law, which holds strictly within the limit of experimental error for monochromatic light of any wave-length, layers of any homogeneous substance of equal thickness absorb the same fraction of the light incident upon them. In other words, there is an exponential relation between the intensity of the transmitted light and the thickness of the absorbing medium. According to Beer's law the absorption of light by a fluid of definite thickness is directly proportional to the concentration, or, stated another way, the absorption is constant so long as the product of the concentration and thickness is kept constant. Beer's law holds approximately in a large number of cases and fails completely in perhaps a larger number. It is well known that the position, intensity and width of the absorption bands of many solutions vary greatly with the concentration as well as with the nature of the solvent, even when the product of concentration and thickness is kept constant. In other words, the so-called extinction coefficient is not independent of the concentration. And further, if to a solution of a colored salt, say ferric chloride, a solution of a colorless salt, as ammonium chloride, is added, a profound change in the absorption takes place.

Jones has explained these changes in terms of his "Solvate Theory"; or, rather, he has interpreted these phenomena as one link

in the long chain of evidence in favor of his solvate theory. According to this theory when a salt goes into solution, both the ions and the molecules of the salt become "solvated", that is, form loose aggregates with the solvent. When copper chloride, for instance, is dissolved in water, both the copper ions and the molecules of copper chloride are attached to large numbers of molecules of water. The frequency of vibration of the resonators of these aggregates is naturally different from that of the free molecule of the salt or of the copper ion. The number and size of these aggregates depend upon the concentration, consequently the extinction coefficient is not independent of the concentration. According to this conception, if a colorless salt, as calcium chloride, is now added, it proceeds to form aggregates with the molecules of the water, and, in general, will rob the copper ions and molecules of some of their water of solvation. The resultant effect, of course, will be a change in absorption.

Since our knowledge of the many variables, both physical and chemical, which enter into this problem is so slight, and since the investigations of Jones and his co-workers were so extensive, the writer has no desire to seriously question the validity of the solvate theory as applied to absorption phenomena, but should like to venture an alternative explanation which seems more simple and perhaps clearer. It is well-known that the degree of dissociation of an electrolyte is a function of the concentration; the more dilute the solution, the more nearly complete is the dissociation. We might well expect, also, that the absorption of light by a salt in the ionic state is, or may be, quite different from what it is in the molecular state; whether the reason for it is that given by Baly, by Bjerrum, by Kruger, or some other. If we cannot accept this assumption, we can see no reason for accepting Jones's assumption that the absorption is influenced by the state of aggregation. On the assumption, then, that the absorption is a function of the dissociation, it is easy to see why Beer's law does not hold.

If to an aqueous solution of a colored salt, as copper chloride, in a definite state of dissociation, we add a certain amount of sodium chloride, keeping the concentration of the copper chloride, in gram molecules per liter, constant, we should naturally expect that some of the copper ions would be driven back into the molecular state, because of the increase in concentration of the chlorine ions. This statement may be justified by the law of mass action of Guldberg and

Waage, or by the principle of van't Hoff that molecules and ions in solution behave as gases and obey all the gas laws. This seems to explain, at least as well as the solvate theory, the changes in absorption which take place when a colorless salt is added to a colored one in a binary solution.

It is well known that increase in temperature is generally accompanied by marked changes in the absorption of light. The absorption band usually broadens and deepens and sometimes shifts to the right. Jones attributes this to the splitting up of the molecular aggregates and the formation of simpler complexes. It seems that this effect could be readily explained by changes in ionization with changes in temperature. Bohr, in order to explain the fact that many lines of the Balmer series of hydrogen are observed in the spectra of the heavenly bodies which are not found in the laboratory, advanced the hypothesis that the electrons do not occupy the outer orbits except when the pressure is vanishingly small; in other words, the pressure exerted by neighboring molecules restrain the electrons from occupying the outermost orbits. This explanation is accepted as rational by several subsequent writers. Now if the pressure of the other molecules exerts an inward force on the electronic orbits, then, since action and reaction are equal and opposite, it is reasonable to suppose that the electrons exert a pressure tending to keep the molecules, and in many cases the atoms of the molecules apart. If the absorption of energy by the electrons is accompanied by shifts to orbits of greater radii, we might well expect that, in general, the absorption of energy by the electrons would tend to increase dissociation in those molecules where the electrons of all the atoms are not revolving in orbits about a single axis. According to this line of reasoning, increase in temperature would probably be accompanied by increased dissociation. Very often, however, other forces may be brought into play which tend to accelerate the reverse process.

According to Jones, however, the above conclusions are wrong.

In discussing this phase of the subject he says: "Rise in temperature not only does not increase the number of ions present, but, as is well known, diminishes dissociation." It is doubtful, however, if this sweeping statement can be justified. Walker says, for instance: "Since the heat of dissociation into ions is sometimes positive, sometimes negative, a rise of temperature may in some cases be accomp-

anied by increased dissociation, in others by diminished dissociation." This seems to be in accordance with Le Chatelier's theorem.

It seems quite probable, however, that some of the changes which take place are far too complex to be explained either by the solvate theory of Jones or by the changes in ionization. There are probably secondary reactions which play an important role. For instance, Baly (*Phil. Mag.* 27, p 632, 1914) found that in certain reactions the solutions passed through intermediate phases which could be traced by means of changes in the absorption bands. A great many electrolytes, on going into solution, react chemically with water. For instance, when ferric chloride goes into aqueous solution, one or more of the chlorine atoms may be replaced by OH radicals from the water with the formation of a basic ferric salt or the ferric hydroxide and hydrochloric acid. The ferric hydroxide is brick red in color. A colorless salt, as aluminum chloride, when added to the above solution, may have a catalytic effect in bringing about these reactions. Furthermore, the effect would undoubtedly be increased by heating, as hydrolysis is promoted by rise of temperature.

Jones's work in the visible and ultra-violet was done by the method of spectro-photography. This method, while possessing many advantages, has the disadvantage that the results are qualitative only. Changes in the width and position of an absorption band can be measured, and some notion of the relative intensities of different bands can be obtained from the blackness of the photographs, but no information concerning the shape of the absorption curve is possible.

The plan of the present work was to repeat some of the work of Jones, making use of the method of spectro-photometry, thus making the results quantitative, and to extend the work to other salts. In particular it was desired to study the effect of those colorless salts which do not form hydrates, upon the absorption of colored salts, and the effect of one colored salt upon another. It was also planned to study the effect of temperature on solutions of certain salts and mixtures of different salts. In addition, it was desired to measure the absorption of certain organic compounds. No attempt has been made to investigate Beer's law.

## APPARATUS AND METHOD.

The method of the present work was that of spectro-photometry. The results are quantitative, although the method does not adapt itself to a high degree of precision. The instrument consists of a Hilger spectrometer with a Nutting photometer box. A sketch of the apparatus, showing in detail the optical parts of the photometer box, is given in plate 1. The light source is at S. A 40 watt tungsten lamp was used. A Nernst glower or other line source might have been better, but the lamp used gave very good results. In the earlier part of the work direct current from the storage battery was used for illumination, but later on ordinary A. C. power was used. The apparatus functioned about as well in the latter case as in the former. Two beams of light, rendered parallel by the wedge-shaped prisms, pass through the photometer box. E is a glass cell about 1 cm. thick, 2 cms. wide by  $2\frac{1}{2}$  cms. deep which contained the solution whose absorption was to be measured. D is an exactly similar cell which in general contained either distilled water or an aqueous solution of a colorless salt.

In order to obtain even fair results, certain precautions were found to be necessary. The illumination must be neither too faint nor too brilliant. At either extremity of the spectrum the illumination was too feeble for good results. Where the illumination was too intense, it was cut down by means of a variable resistance. The best results were obtained with a rather faintly illuminated field. The eye should be in good condition, rested, and not recently exposed to a strong light. It is useless to try to take readings immediately after a walk in the bright sunlight. As far as possible all light was eliminated except that passing through the telescope. The heating effect from the lamp was largely eliminated by placing a large cell full of water in front of the cells D and E. This cell was broad and deep and about 3cms. thick. Considerable care was taken to keep the solution free from undissolved particles in suspension. If, on close inspection, there was the slightest indication of murkiness, the solution was filtered. In the case of the salts of chromium, the filtration was repeated many times. The wave-length readings on the drum was occasionally checked against a known wave-length, as the prism P sometimes became slightly displaced.

To obtain the absorption of a simple solution the following



method was used: a definite weighed quantity of the salt was dissolved in distilled water and then water added to make a definite volume of the solution. This same concentration was always used when dealing with the same colored salt. The cell E was filled with the colored solution. The cell D was filled with distilled water. The interval between the readings ordinarily varied from 50 to 200 Å. U. The number of readings for any given wave length varied from three to eight.

To measure the absorption of a mixed solution of a colored salt with a colorless one, the following plan was used: the two salts, after having been weighed, were mixed together. Sufficient distilled water was added to dissolve both salts. Then water was added in sufficient quantity to make the desired volume of solution. The cell E was filled with this solution. An aqueous solution of the colorless salt was then made by dissolving the same quantity of the colorless salt in the same volume of solution. This solution was placed in the Cell D.

In the case of two colored salts, as for instance cobalt chloride and copper chloride, the procedure was as follows: the solution of the two salts, each having the same concentration as when its absorption was determined alone (that is, the same number of molecules per unit volume), was placed in the cell E. In the cell D was placed an aqueous solution of copper chloride of the same concentration as that in the cell E. The absorption of the copper chloride in the cell D should balance that of the same salt in the cell E. The readings should then indicate only the absorption of the cobalt chloride plus whatever change was brought about by the influence of the one salt upon the other.

When dealing with a mixture of three colored salts, still another plan was followed. The solution of the three salts, each having the same concentration as before, was placed in the cell E. In D was placed distilled water. The absorption was measured throughout the visible spectrum and the curve plotted. But in this case the extinction coefficient was not determined, the extinction coefficient of a mixture apparently having no meaning. The curve was plotted in instrument readings; that is, in terms of the logarithm of the reciprocal of the square of the cosine of the angle of rotation of the analyser. The comparison curve was obtained by adding together the absorption curves of the three salts as determined separately. The difference

between these two curves shows the changes due to the influence of the different salts on each other. Two sets of readings are given in Table I, copied directly from the original records. In the first column are recorded wave-lengths in millimicrons and in the second the corresponding readings of the instrument. It may be observed that where the solution is nearly transparent, and therefore the readings very small, the percentage of error is liable to be quite large.

### CONCENTRATIONS.

In this series of experiments the same concentration was always used with the same colored salt. In preparing the solution, the salt was always weighed to within one tenth of one per cent. Considerable care was taken to free the salt from excess moisture. The concentration was determined in gram molecules per liter, and are as follows: Copper chloride, .2742; copper nitrate, .1645; copper sulphate, .1720; nickel chloride, .342; nickel nitrate, .2286; nickel sulphate, .3202; cobalt chloride, .1139; cobalt nitrate, .1600; cobalt sulphate, .2025; ferric chloride, .1560; ferric nitrate, .085; chromium chloride, .03396; chromium nitrate, .01067; uranyl chloride, .727. The concentration of the colorless salts was not kept strictly constant throughout, and will be taken up in the discussion of individual cases.

### MIXTURE OF COPPER CHLORIDE WITH OTHER CHLORIDES.

**With cerium chloride.** The concentration of the cerium chloride was .60. The curves are shown on plate 2-e. In all these curves the abscissa represents wave-length in milli-microns and in nearly all of them the ordinate represents absorption in terms of the extinction coefficient. The various sets of curves are displaced the one above the others at convenient distances so that while the origin of abscissas is the same, the origin of the ordinates is different for each set. Unless otherwise specified the dotted line represents the absorption of the colored salt alone, while the full-line curve represents that of the mixture. In this case no very great effect is shown, although there is increased absorption in the red.

**With zinc chloride,** plate 2-d. Concentration of the zinc chloride=1.50. Increased absorption in the red.

**With sodium chloride,** plate 2-c. Concentration of the sodium

chloride=2.8. Increased absorption in the violet, decrease from wave-length 530 to 615, and marked increase in the red. The equation of the curve has been determined as shown in the graph.

**With potassium chloride**, plate 2-b. Concentration of potassium chloride=2.2. Marked increase in absorption in the red. The curve is found to follow an exponential law, as shown in the graph.

**With ammonium chloride**, plate 2-a. Concentration of ammonium chloride = 3.1. The mixture shows very great absorption in the violet, although the copper chloride is transparent in that region of the spectrum. There is decrease in the green and yellow and increase in the red. The equation has been determined and found to be exponential.

**With ferric chloride**, plate 6-a. No very pronounced influence.

### COBALT CHLORIDE WITH OTHER CHLORIDES.

**With sodium chloride**, plate 3-e. Concentration of sodium chloride = 2.8. Very considerable increase in the green.

**With potassium chloride**, plate 3-d. Concentration of KCl = 2.2. Very greatly increased absorption in the green.

**With cerium chloride**, plate 3-c. Concentration of the cerium chloride = .60. Increased absorption throughout the spectrum.

**Cobalt chloride with zinc chloride**, plate 3-b. Concentration of zinc chloride = 1.5. Considerable increase in the green; increase throughout except in the yellow.

**With ammonium chloride**, plate 3-a. Concentration of ammonium chloride = 2.8. Very great increase in absorption in the green. It may be noticed that ammonium chloride, which does not form hydrates, produces a greater change in the absorption of cobalt chloride than either zinc chloride, sodium chloride, or lithium chloride, all of which form hydrates.

**With lithium chloride**, plate 16-b. Concentration of lithium chloride = 3.9. Considerable absorption except in the violet and blue.

**With ferric chloride**, plate 4-a. Marked increase in absorption in the blue and considerable increase in the region of the long wave lengths.

**With chromium chloride**, plate 4-b. Broadening of the principle absorption band in the blue and green, and increased absorption in the red.

With **nickel chloride**, plate 4-c. Increased absorption throughout, but especially at the red end of the spectrum.

With **copper chloride**, plate 4-d. Decrease in the yellow and increase in the red.

### NICKEL CHLORIDE WITH OTHER CHLORIDES.

With **sodium chloride**, plate 5-d. Concentration of sodium chloride = 2.75. Decrease in absorption throughout the visible spectrum.

With **potassium chloride**, plate 5-c. Concentration of potassium chloride = 2.00. Marked decrease in absorption for the middle of the spectrum.

With **cerium chloride**, plate 5-b. Concentration of cerium chloride = .60. Marked increase in transparency in the blue, green and orange.

With **lithium chloride**, plate 5-e. Concentration of LiCl = 4.0. There is a very great increase in absorption throughout the spectrum.

With **copper chloride**, plate 6-c. There is a rather large increase in absorption in the green.

With **ferric chloride**, plate 6-b. Enormous increase in the violet.

### AQUEOUS SOLUTIONS OF FERRIC CHLORIDE WITH OTHER CHLORIDES.

With **lithium chloride**, plate 7-c. Concentration of LiCl = 1.8. Greatly increased absorption in the region of the short wave lengths.

With **calcium chloride**, plate 7-b. Concentration of calcium chloride = 1.00. Great increase in absorption in the violet and blue.

With **aluminum chloride**, plate 7-a. Concentration of aluminum chloride = 0.340. This is the most striking example of color change produced by the addition of a colorless salt to a colored one that has been met with in this series of experiments. The change in color is from that of a clear amber to a brick red. Undoubtedly there is formation of ferric hydroxide.

With **ammonium chloride**, plate 8-a. Concentration of the ammonium chloride = 2.80. There is tremendous increase in absorption in the violet and blue, with considerable decrease in the green. At wave-length 480 the increase is more than 200%. This curve is found to be exponential, as shown in the graph.

With **zinc chloride**, plate 8-b. Concentration of zinc chloride = 1.30. Enormous increase in absorption in the violet, and decrease in the green. The curve is exponential in form.

With **sodium chloride**, plate 9-c. Concentration of NaCl = 2.60. There is enormous increase in absorption for the shorter wave lengths.

With **potassium chloride**, plate 9-b. Concentration of KCl = 2.00. Great increase in absorption in the violet and blue.

With **cerium chloride**, plate 9-a. Concentration of cerium chloride = 0.60. There is very great increase in absorption in the violet.

### MIXTURES OF CHROMIUM CHLORIDE WITH OTHER CHLORIDES.

With **sodium chloride**, plate 10-f. Concentration of NaCl = 3.00. There is increased absorption throughout the spectrum.

With **potassium chloride**, plate 10-e. Concentration of KCl = 2.50. There is increased absorption throughout the spectrum.

With **aluminium chloride**, plate 10-d. Concentration of the aluminium chloride = 0.30. There is increase in the absorption up to wave-length 590, beyond which there is decrease.

With **calcium chloride**, plate 10-c. Concentration of the calcium chloride = 1.50. There is scarcely any change in absorption. This fact seems to be widely at variance with the solvate theory, for calcium chloride, which has an enormous affinity for water, should produce a great change in the absorption.

With **zinc chloride**, plate 10-b. Concentration of zinc chloride = 1.60. No very decided change in absorption.

With **ammonium chloride**, plate 10-a. Concentration of ammonium chloride = 2.8. Decreased absorption throughout.

With **copper chloride**, plate 11-d. There is increase in absorption for the shorter wave-lengths.

With **nickel chloride**, plate 11-c. There is increase in absorption in the violet and decrease from wave-length 540 to 660.

With **ferric chloride**, plate 11-b. There is increase in absorption throughout.

With **cerium chloride**, plate 11-a. There is scarcely any change in absorption.

## URYANYL CHLORIDE WITH OTHER CHLORIDES.

With **cerium chloride**, plate 12-e. The curves show considerable increase in the violet.

With **potassium chloride**, plate 12-d. Concentration of  $KCl=2.30$ . There is very greatly increased absorption in the violet and blue.

With **aluminium chloride**, plate 12-c. Concentration of aluminium chloride = 0.30. There is great increase in absorption for the shorter wave lengths.

With **zinc chloride**, plate 12-b. Concentration of zinc chloride = 1.60. There is decrease in absorption throughout.

With **sodium chloride**, plate 12-a. Concentration of  $NaCl=3.00$ . The curve shows very great increase in absorption for the shorter wave lengths.

With **copper chloride**, plate 13-d. There is very little change except in the red where there is considerable increase in absorption.

With **nickel chloride**, plate 13-c. There is no very decided change in absorption.

With **cobalt chloride**, plate 13-b. There seems to be a slight increase in absorption for most of the visible spectrum.

With **calcium chloride**, plate 13-a. Concentration of calcium chloride = 1.50. There is a very large and general increase in absorption throughout the spectrum.

## MIXTURES OF THREE COLORED CHLORIDES.

**Copper chloride, cobalt chloride and chromium chloride**, plate 14-c. There is increase in absorption from 440 to 550, decrease from 550 to 670 and increase the rest of the way.

**Copper chloride, nickel chloride, and chromium chloride**, plate 14-b. Just as in the preceding case there is increased absorption from 440 to 550, decreased absorption from 550 to 650 and an increase from 650 to the end of the visible spectrum.

**Copper chloride, ferric chloride, and sodium chloride**, plate 14-a. There is an enormous increase in absorption at both ends of the spectrum with no change whatever in the center. An exponential curve was determined which fits the experimental curve almost perfectly.

**Copper chloride, cobalt chloride, and ferric chloride**, plate 15-a.

There is considerable increase in absorption at both ends of the spectrum, with a rather marked decrease from 560 to 640.

**Copper chloride, chromium chloride, and ferric chloride**, plate 15-b. There is very great increase in the violet, considerable increase in the blue, decrease in the yellow, and increase in the red.

**Cobalt chloride, nickel chloride and chromium chloride**, plate 15-c. There is considerable decrease in absorption between wave-lengths 540 and 640.

**Chromium chloride, cobalt chloride, and ferric chloride**, plate 16-a. There is rather marked increase in absorption for the shorter wave lengths.

### MIXTURES OF COPPER NITRATE WITH OTHER NITRATES.

**With aluminum nitrate**, plate 17-c. Concentration of aluminum nitrate was .44. The mixed solution is more transparent than that of copper nitrate for practically all of the visible spectrum.

**With calcium nitrate**, plate 17-b. The concentration of calcium nitrate was 0.70. The mixed solution is more transparent than the solution of copper nitrate from wave-length 540 to 640, while for longer wave-lengths it is more opaque.

**With sodium nitrate**, plate 17-a. The influence of the sodium nitrate manifests itself as an increase in transparency between wave-length 540 and 640.

**With lithium nitrate**, plate 17-d. Concentration of lithium nitrate = 2.40. The change consists in an increase in absorption from wave-length 560 to the red end of the visible spectrum.

**With ammonium nitrate**, plate 17-e. Concentration of the ammonium nitrate = 1.85. There is increased absorption in the region of the longer wave-lengths.

### COBALT NITRATE WITH OTHER NITRATES.

**With ammonium nitrate**, plate 18-a. Concentration of ammonium nitrate = 1.85. The influence of the ammonium nitrate manifests itself as an increase in transparency throughout the visible spectrum, the greatest change being at about wave-length 600.

**With sodium nitrate**, plate 18-b. Concentration of sodium nitrate = 1.90. There is decrease in absorption from wave-length 480 to the red end of the spectrum.

With **calcium nitrate**, plate 18-c. Concentration of calcium nitrate = 1.50. It will be seen that there is a general increase in transparency throughout the spectrum.

With **aluminum nitrate**, plate 18-d. Concentration of aluminum nitrate = .440. There is a slight decrease in absorption throughout the spectrum.

With **lithium nitrate**, plate 19-a. Concentration of lithium nitrate = 2.400. There is some increase in absorption in the violet, blue, green, and red.

With **copper nitrate**, plate 21-a. There is greatly increased transparency from wave-length 570 to the red end of the spectrum.

### MIXTURES OF NICKEL NITRATE WITH OTHER NITRATES.

With **ammonium nitrate**, plate 20-a. Concentration of ammonium nitrate = 1.850. It will be observed that there is a remarkable increase in transparency throughout the spectrum. The mixed solution is transparent as water to wave-length 580.

With **calcium nitrate**, plate 20-b. Concentration of calcium nitrate = .700. There is a general decrease in absorption except for a small region in the green.

With **aluminum nitrate**, plate 20-c. Concentration of aluminum nitrate = .440. There is a considerable increase in absorption in the green and decrease in the red.

With **lithium nitrate**, plate 20-d. Concentration of lithium nitrate = 2.40. The only striking change is an increase in transparency from wave-length 550 to 640.

With **sodium nitrate**, plate 20-e. Concentration of sodium nitrate = 1.90. Increased transparency in the yellow and red.

With **cobalt nitrate**, plate 21-b. There is an enormous increase in transparency for almost the entire length of the spectrum.

With **copper nitrate**, plate 21-c. The curves show decrease in absorption in the blue, increase in the green, decrease in the yellow and enormous decrease in the red.

### MIXTURES OF FERRIC NITRATE WITH OTHER NITRATES.

With **calcium nitrate**, plate 22-a. Concentration of calcium nitrate = .700. There is marked increase in absorption in the region of the shorter wave-lengths.



With **lithium nitrate**, plate 22-b. Concentration of lithium nitrate = 2.40. There is very little change in absorption except from wave-length 520 to 610, where there is increased transparency.

With **sodium nitrate**, plate 22-c. Concentration of sodium nitrate = 1.90. There is considerable increase in transparency in the middle of the spectrum and a general but smaller increase for the longer wave-lengths.

With **aluminium nitrate**, plate 22-d. Concentration of aluminum nitrate = .440. Slightly increased transparency throughout.

With **ammonium nitrate**, plate 22-e. Concentration of ammonium nitrate = 1.850. Very great increase in transparency throughout the visible spectrum.

With **cobalt nitrate**, plate 23-a. There is enormous increase in transparency especially in the middle of the spectrum.

With **nickel nitrate**, plate 23-b. There is a very great increase in transparency at about wave-length 600, and a smaller general increase throughout.

With **copper nitrate**, plate 23-c. There is very great increase in transparency from wave-length 540 to 660, and a smaller increase in the region of the shorter wave-lengths.

### MIXTURES OF CHROMIUM NITRATE WITH OTHER NITRATES.

With **aluminium nitrate**, plate 24-a. Concentration of aluminum nitrate = 0.440. There is very great decrease in absorption in the violet, the decrease growing gradually smaller as the wave-length increases.

With **calcium nitrate**, plate 24-b. Concentration of calcium nitrate = 0.500. There is considerable increase in transparency in the region of the shorter wave-lengths.

With **lithium nitrate**, plate 24-c. Concentration of lithium nitrate = 2.400. There is great decrease in absorption in the violet, blue, and green.

With **sodium nitrate**, plate 24-d. Concentration of sodium nitrate = 2.300. The curves show decrease in absorption in the region of the shorter wave-lengths.

With **cobalt nitrate**, plate 25-a. There is a general and very great decrease in absorption, the greatest effect being found in the region of the shorter wave-lengths.

With **nickel nitrate**, plate 25-b. The decrease in absorption is very pronounced throughout the visible spectrum.

With **copper nitrate**, plate 25-c. Very great increase in transparency is shown throughout the spectrum.

### DIDYMIUM NITRATE WITH ALUMINIUM NITRATE.

Two and 728-1000 grams of didymium nitrate were dissolved in sufficient distilled water to make 7.5 c. c. of solution. The concentration of the aluminium nitrate was 0.400. The absorption was measured and the curve plotted as shown in plate 36-b. The aluminium nitrate seems to produce no appreciable effect on the absorption of the didymium nitrate. The curve of the mixture practically coincides with that of the simple salt. It will be noticed that there are many sharp bands, the most prominent having their maxima at about wave-lengths 445, 423, 578.5, and 744. The extinction coefficient was not plotted. The ordinates are plotted in terms of the readings of the instrument.

### MIXTURES OF THREE COLORED NITRATES.

**Copper nitrate, nickel nitrate, and ferric nitrate**, plate 26-a. There is a small decrease in absorption in the violet, blue, and green, and a very pronounced decrease for the remainder of the spectrum.

**Copper nitrate, cobalt nitrate, and ferric nitrate**, plate 26-b. There is greatly increased transparency throughout, the greatest change coming in the middle of the spectrum.

**Nickel nitrate, cobalt nitrate, and ferric nitrate**, plate 26-c. Again there is a very great decrease in absorption throughout the spectrum, with the greatest decrease coming at about wave-length 580.

### MIXTURES OF COPPER SULPHATE WITH OTHER SULPHATES.

With **aluminium sulphate**, plate 27-a. The absorption curve shows very little deviation from that of the copper sulphate alone. Concentration of aluminium sulphate = 0.270.

With **nickel sulphate**, plate 27-b. There is considerable decrease in absorption for the longer wave-lengths.

With **cobalt sulphate**, plate 27-c. There is increase in absorption in the violet and blue, and decrease beyond wave-length 560.

With **potassium sulphate**, plate 27-d. Concentration of potas-

sium sulphate = 0.510. There is no noticeable change in absorption whatever.

**With ammonium sulphate**, plate 27-e. Concentration of ammonium sulphate = 1.500. There is no very pronounced change in absorption.

### MIXTURES OF COBALT SULPHATE WITH OTHER SULPHATES.

**With aluminium sulphate**, plate 28-a. Concentration of aluminium sulphate = 0.270. The curves show some increase in absorption in the violet and blue and some decrease in the red.

**With ammonium sulphate**, plate 28-b. Concentration of ammonium sulphate = 1.250. There is slight increase in the violet and blue.

**With nickel sulphate**, plate 28-c. There is a slight increase for the shorter wave-lengths and decrease for the longer.

**With potassium sulphate**, plate 28-d. Concentration of potassium sulphate = 0.510. There is a general increase in absorption throughout the spectrum.

### THE EFFECT OF TEMPERATURE UPON ABSORPTION.

For the investigation of the effect of temperature upon absorption, an electric furnace of inside dimensions 1.9 x 8.6 x 5.7 cms. was constructed. It was made of brass and covered with two or three layers of asbestos paper over which was wound about 20 feet of manganin wire having a total resistance of about 60 ohms. This in turn was covered with a paste made of magnesium oxide and sodium silicate, so that the total thickness of covering was about one centimeter. In order to allow the light to pass through, two holes of 1.8 cm. diameter were bored through each side. A wooden lid, boiled in beeswax and containing a hole for the insertion of a mercury thermometer was made for the furnace.

About this time the glass cells used as containers for the solutions went to pieces. Some of the solutions attacked the cement of the cells, thus setting up strains which caused the glass to break. A great number of cements were tried and found useless. A brass cell was then constructed and gold-plated on the inside with glass plates fastened on the sides by mechanical means. The hot solutions attacked the brass through the gold, probably for the reason that the

gold plating was not thick enough or not uniformly distributed. Finally the inside of the cell was coated with de Khotinsky wax. This resisted the action of the aqueous solution perfectly and also proved to be a good cement for fastening the parts of the cell together. Some of the readings are shown in tables III and IV. These values are copied from the book just as they were recorded at the time of taking the observations. In the curves the absorption at the higher temperature is always represented by the full line curve, while that at room temperature is shown by the dotted curve.

### MEASUREMENT OF TEMPERATURE EFFECT UPON VARIOUS SOLUTIONS

**Copper chloride**, plate 34-d. Readings were taken at 23.5° C, 46.7°, and 66.0° C. The increase in absorption extends from wave-length 500 to the red end of the spectrum.

**Copper chloride with ammonium chloride**, plate 29-a. The higher temperature was 67.0° C. There is tremendous increase in absorption in the violet and blue, although neither the copper chloride nor the ammonium chloride shows any temperature effect in that region. There is also very great increase in the red.

The equations of these curves have been determined as shown in the graph. For the full line curve, between wave-lengths 460 and 530 the  $b$  of the formula has the value  $-.05128$  and the  $k$  of the formula  $5.956$ . Between 530 and 610,  $b = .0296$  and  $k = .1479$ . Between 610 and the red end of the spectrum,  $b = .02257$  and  $k = 1.706$ . For the dotted line, from wave-length 440 to 500,  $b = -.04582$  and  $k = 5.83$ . From 560 to the red end of the spectrum,  $b = .01946$  and  $k = .4678$ .

**Copper chloride with sodium chloride**, plate 29-b. The higher temperature was at 58.5° C. The mixed solution shows tremendous increase in absorption in the violet, although neither of the simple solutions of which the mixture is composed shows any temperature effect in that region. There is increased absorption throughout the spectrum. The equations of these curves have been determined as shown in the graph. For the full line curve between the wave-lengths 440 and 520 the  $b$  of the formula  $= -.04552$  and  $k = 7.13$ . From wave-length 520 to the red end of the spectrum,  $b = .02256$  and  $k = .2144$ .

**Copper chloride with potassium chloride**, plate 29-c. The

higher temperature was  $69.6^{\circ}\text{C}$ . There is a remarkable increase in the violet and a smaller increase throughout the spectrum. The equation of the curves have been determined as shown in the graphs.

**Cobalt chloride**, plate 30-a. The higher temperature was  $68.5^{\circ}\text{C}$ . There is great increase in absorption throughout the spectrum.

**Ferric chloride**, plate 32-c. Temperatures were  $23.5^{\circ}$  and  $51.0^{\circ}\text{C}$ . There is very great increase in absorption for the shorter wave-lengths.

**Ferric chloride with ammonium chloride**, plate 33-a. Temperatures were  $23.5^{\circ}$  and  $49.0^{\circ}\text{C}$ . There is very great increase in absorption for nearly the entire length of the spectrum.

**Ferric chloride with potassium chloride**, plate 33-b. Temperatures were  $23.5^{\circ}$  and  $52.0^{\circ}\text{C}$ . The curves show tremendous increase in absorption for the entire spectrum.

**Ferric chloride with sodium chloride**, plate 33-c. Temperatures were  $23.5^{\circ}$  and  $48.0^{\circ}\text{C}$ . Tremendous increase in absorption for the shorter wave-lengths.

**Nickel chloride**. The temperatures were  $23.5^{\circ}$  and  $69.7^{\circ}\text{C}$ . There was no change in the absorption whatever and the curve was not plotted.

**Nickel chloride with sodium chloride**, plate 34-a. The temperatures were  $23.5^{\circ}$  and  $68.0^{\circ}\text{C}$ . In the violet and blue the increase in absorption is 400 to 600%. There is great increase throughout the spectrum.

**Chromium chloride**. The temperatures were  $23.5^{\circ}$  and  $67.1^{\circ}\text{C}$ . No change in absorption could be detected and the curve was not plotted.

**Chromium chloride with potassium chloride**, plate 35-c. Temperatures were  $23.5^{\circ}$  and  $73.0^{\circ}\text{C}$ . There is a rather large and general increase in absorption throughout the spectrum, although the chromium chloride alone shows no increase and potassium chloride is transparent.

**Neodymium chloride**, plate 36-a. Temperatures were  $23.5^{\circ}$  and  $73.0^{\circ}\text{C}$ . It will be seen that there is very great increase in absorption in the violet and blue, and again in the yellow and red. For the middle of the spectrum there is no apparent change.

**Ferric nitrate**, plate 31-a. Temperatures were  $23.5^{\circ}$  and  $58.2^{\circ}\text{C}$ . There is very great increase in absorption in the region of the shorter wave-lengths.

**Ferric nitrate with sodium nitrate**, plate 31-b. Temperatures were  $24.0^{\circ}$  and  $61.6^{\circ}$  C. The increase in absorption is very great, being about 90% at wave-length 460.

**Ferric nitrate with ammonium nitrate**, plate 31-c. The temperatures were  $23.2^{\circ}$  and  $57.3^{\circ}$  C. The increase in absorption is very great.

**Ferric nitrate with calcium nitrate**, plate 32-a. Temperatures were  $27.3^{\circ}$  and  $59.3^{\circ}$  C. There is very great increase in absorption in the region of the shorter wave-lengths.

**Ferric nitrate with aluminium nitrate**, plate 32-b. Temperatures were  $23.5^{\circ}$  and  $57.7^{\circ}$  C. The curves show greatly increased absorption for the shorter wave-lengths, the increase at 440 being 60%.

**Copper nitrate**. The temperatures were  $23.5^{\circ}$  and  $70.0^{\circ}$  C. No change in absorption could be detected.

**Copper nitrate with aluminium nitrate**. Up to  $70^{\circ}$  C no change in absorption could be detected.

**Copper nitrate with ammonium nitrate**, plate 34-b. Temperatures were  $23.5^{\circ}$  and  $69.0^{\circ}$  C. There is very little if any change in absorption.

**Copper nitrate with sodium nitrate**, plate 34-c. Temperatures were  $23.5^{\circ}$  and  $66.3^{\circ}$  C. There is considerable increase in absorption for the region of the longer wave-lengths.

**Cobalt nitrate**. Up to  $71.0^{\circ}$  C the absorption seemed to be the same as at room temperature.

**Cobalt nitrate with sodium nitrate**, plate 30-b. The temperatures were  $23.5^{\circ}$  and  $74.4^{\circ}$  C. There is very great increase in absorption throughout the visible spectrum, although neither cobalt nitrate nor sodium nitrate show any temperature effect.

**Cobalt sulphate**, plate 30-c. The temperatures were  $23.5^{\circ}$ ,  $47.0^{\circ}$ , and  $70.5^{\circ}$  C. As the temperature rises there is a steady increase in absorption throughout the spectrum.

**Copper sulphate**, plate 35-a. Temperatures were  $23.5^{\circ}$  and  $69.0^{\circ}$  C. There is very great increase in absorption in the red.

**Copper sulphate with potassium sulphate**, plate 35-b. The temperatures were  $23.5^{\circ}$  and  $71.0^{\circ}$  C. There is increased transparency at about wave-length 580 and increased absorption in the red. While taking observations on this solution it was discovered that the addition of sulphuric acid completely destroyed the temperature effect.

## ABSORPTION OF LIGHT BY ALCOHOLIC SOLUTIONS OF ORGANIC COMPOUNDS

The absorption of three compounds: azobenzene, benzene azo ortho cresol acetate, and benzene azo phenol benzoate was measured.\* These compounds are insoluble in water, but soluble in most organic solvents. Absolute alcohol was used as solvent. This introduced a new difficulty, for the alcohol attacked the wax with which the cells were lined. Fortunately a glass cell was found that answered the purpose very well. It was thought, however, that this cell would not stand a very high temperature, so no attempt was made to measure the temperature effect.

**Azobenzene**, plate 37-a. The concentration was .01841. At this concentration the solution is a deep red. The solution is practically opaque between wave-lengths 440 and 480. From 570 to the red end of the spectrum it is quite transparent. The equation of this curve was determined as shown in the graph. Unlike all the other curves whose equations have been determined it is not exponential but a power curve.

**Benzene azo ortho cresol acetate**, plate 37-b. The concentration was .005961. At this concentration the solution is a beautiful red. From the curve it will be noticed that there is very great absorption in the violet and blue. From wave-length 560 to the red end of the spectrum it is quite transparent.

**Benzene azo phenol benzoate**, plate 37-c. The concentration was .009536. The color of the solution is that of a beautiful red. The absorption curve is almost exactly the type of curve found for the preceding compound, but the extinction coefficient is not so great. There is, as before, very great absorption in the violet. From wave-length 540 to 720 it is almost entirely transparent.

### RATIO OF ABSORPTION OF MIXTURE TO SUM OF ABSORPTIONS OF COMPONENT PARTS.

A critical study of the various cases discussed on the preceding pages and shown graphically on the sheets that follow, brings to light a very curious fact. The ratio of the absorption of the mixture to the sum of the absorptions of the component parts has a minimum

—\*Kindly furnished by Doctor Board, of the Chemistry Department.

somewhere between wave-lengths 510 and 610 milli-microns, the average position of this minimum being about 580. Or, expressed another way, if the ordinate of the full line curve is divided by the ordinate of the dotted curve, and if the ratio thus determined is plotted as a function of the wave-length, the resulting curve shows a minimum near the middle of the visible spectrum. Some of the most striking examples are shown on plate 38. This tendency is more or less apparent in about 60 out of a total of 103 sets of curves taken at room temperature, so it cannot be attributed to coincidence. Furthermore, it is believed that this tendency would manifest itself in a greater number of cases were it not for the fact that a great many solutions are so nearly transparent for one or the other half of the spectrum that no accurate measurements are possible over that region.

On first thought it seems rather remarkable that the result of any kind of mixing of salts should be to increase the absorption at the ends of the spectrum at the expense of the middle. After a little reflection, however, a possible explanation suggests itself. All of the colored salts studied in these series of experiments, with the exception of the cobalt and chromium salts, have their main absorption bands (in so far as the visible spectrum is concerned) at one or the other end of the spectrum. Moreover, the cobalt salts have their maximum absorption to the left of this minimum region under discussion, and chromium nitrate has its principle absorption in the violet and blue. Besides, chromium chloride shows but little change in absorption due to the addition of colorless salts, as compared with similar changes in most of the other colored salts under investigation. Eliminating chromium chloride, then, from the present discussion, we see that most of the absorption comes near the ends of the spectrum. Now if we may assume that the main absorption bands are due to the molecules and not to the ions, and if the mixing of salts tends to drive the ions back into the molecular state, we should expect to increase the absorption in the region of the main absorption bands and decrease it elsewhere. And this is just what happens in the large majority of cases. The most striking examples are shown on plate 8.

### EQUATIONS OF CURVES.

The equations of a number of curves were determined, and with one exception, found to be simple exponential equations. For some of these curves the points computed from the equation fall directly on



top of the experimental curve. In all cases the greatest deviations occur in those regions where the absorption is slight and the consequent experimental error very large. This remarkably close agreement between mathematical and experimental curves is quite surprising for two reasons: first, that the photometric readings had actually been taken with sufficient accuracy to give such regular curves; and, second, that the absorption should obey a simple exponential law so closely. The interpretation of this fact is not at present clear to the writer, but he hopes to be able to make some report on the subject later.

### ANOMALOUS TEMPERATURE EFFECTS.

Neither cobalt nitrate nor sodium nitrate shows any appreciable change in absorption with increase of temperature, yet the mixed solution shows an exceedingly large temperature effect. The same thing is true of nickel chloride and sodium chloride, of chromium chloride and potassium chloride, and of cobalt sulphate and potassium sulphate. These examples suggest that the colorless salt plays the part of a catalytic agent in accelerating secondary chemical reactions, or in accelerating or retarding the dissociation of the colored salt. It was also found that the addition of sulphuric acid to the mixture of copper sulphate and potassium sulphate completely destroyed the temperature effect. It would seem that this could be easily explained on the assumption that the excess of the hydrogen ions from the dissociated sulphuric acid prevented the OH radicals from the dissociated water from uniting with the other salts with the formation of colored hydroxides.

### CONCLUSIONS.

(1) These experiments show that the change in absorption produced by the mixing of sulphates with other sulphates seem to be small in comparison with corresponding changes in nitrates, and still smaller in comparison with the changes obtained in the mixtures of chlorides.

(2) The influence of temperature on the absorption of solutions of mixed salts seem to be greatest in chlorides. From this fact, together with the preceding, it seems that Ostwald's idea that the colored ion is alone effective in the absorption of light if not well founded,

as Jones has already pointed out. For evidently the radical has considerable influence.

(3) When the ratio of the absorption of the mixture to the sum of the absorptions of the component parts is plotted as a function of the wave-length, the resulting curve generally shows a minimum near the middle of the spectrum. An attempt has been made to explain this on the two following assumptions: first, that the principal absorption bands are due to the molecules of the salt and not the ions; and second, that the effect of mixing different salts which contain a common radical is to drive some of the ions back into the molecular state, thus increasing the concentration of the molecules of the salt in the solution. This would naturally increase the intensity of the principal bands and decrease the absorption elsewhere.

(4) Where the increase in absorption is excessively large and is general throughout the spectrum, it is believed that part of this increase is due to secondary chemical reactions. The colorless salt in that case probably plays the part of a catalytic agent in accelerating these secondary reactions.

(5) Equations have been determined for a good many of the curves and found to be exponential in form.

(6) It is believed that the application of Jones's "Solvate Theory" to the effects recorded in this paper is undesirable and unnecessary. The absorption of light by any colored electrolyte is undoubtedly a function of its dissociation, and there seems to be little reason to doubt that the degree of dissociation is changed upon the addition of another salt containing one radical common to that of the salt in solution.

(7) No attempt has been made to differentiate experimentally between scattering, reflection, and true absorption. In the changes recorded on the previous pages and shown graphically by the curves that follow, all three of these phenomena undoubtedly play their part.

In conclusion I wish to express my thanks to Profesor Alpheus W. Smith, at whose suggestion the above problem was undertaken, and whose helpful suggestion and kindly council has been a constant inspiration throughout the investigation.

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Ohio State University.

TABLE I.

COPPER CHLORIDE.

$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.
440	00	480	00	520	00	560	.17	600	.344	640	.685	680	1.33
	00		00		00		.11		.326		.650		1.33
	00		00		00		.04		.347		.690		1.33
							.13		.348		.670		1.34
						.11		.341		.674		1.33	
450	00	490	00	530	00	570	.190	610	.407	650	.810	690	1.53
	00		00		00		.177		.405		.800		1.57
	00		00		00		.212		.427		.795		1.55
							.191		.400		.790		1.56
						.192		.410		.825		1.55	
										.790			
										.802			
460	00	500	00	540	.02	580	.230	620	.492	660	.935	700	1.77
	00		00		00		.00		.475		.965		1.77
	00		00		00		.00		.478		.975		1.82
							.01		.484		.940		1.72
						.234		.482		.954		1.77	
470	00	510	00	550	.04	590	.303	630	.595	670	1.11	710	2.02
	00		00		00		.09		.290		.545		2.02
	00		00		00		.02		.286		.575		1.90
							.04		.293		.580		1.96
						.05		.293		.574		1.98	

TABLE II.

COPPER CHLORIDE WITH SODIUM CHLORIDE.

$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.		
440	.33	480	00	520	00	560	00	600	.25	640	.79	680	1.92
	.34		00		00		00		.28		.79		1.93
	.30		00		00		00		.26		.78		1.94
	.32							.26		.79		1.93	
460	.07	500	00	540	00	580	.15	620	.47	660	1.23		
	.05		00		00		00		.07		1.26		
	.03		00		00		00		.09		1.24		
	.05		00		00		00		.10		1.24		

as Jones has already pointed out. For evidently the radical has considerable influence.

When the ratio of the  $\alpha$ -component of the mixture to the sum of the absorptions of the component parts is plotted as a function of the

Wavelength	100%	90%	80%	70%	60%	50%	40%	30%	20%	10%	0%
2000	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1800	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1600	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1400	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1200	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1000	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
800	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
600	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
400	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55

the effects recorded in this paper is considered self-explanatory. The absorption of light  $\alpha$  is undoubtedly a function of its absorption coefficient.

Wavelength	100%	90%	80%	70%	60%	50%	40%	30%	20%	10%	0%
2000	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1800	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1600	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1400	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1200	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
1000	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
800	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
600	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55
400	1.00	0.98	0.95	0.90	0.85	0.80	0.75	0.70	0.65	0.60	0.55

in connection with the above are thanks to Professor R. W. Smith, at whose invitation the above problem was undertaken, and whose helpful suggestions and kind counsel has been a constant inspiration throughout the investigation.

Thames Research Laboratory,  
The State University.

T A B L E III

COPPER CHLORIDE WITH AMMONIUM CHLORIDE AT 23.5° C

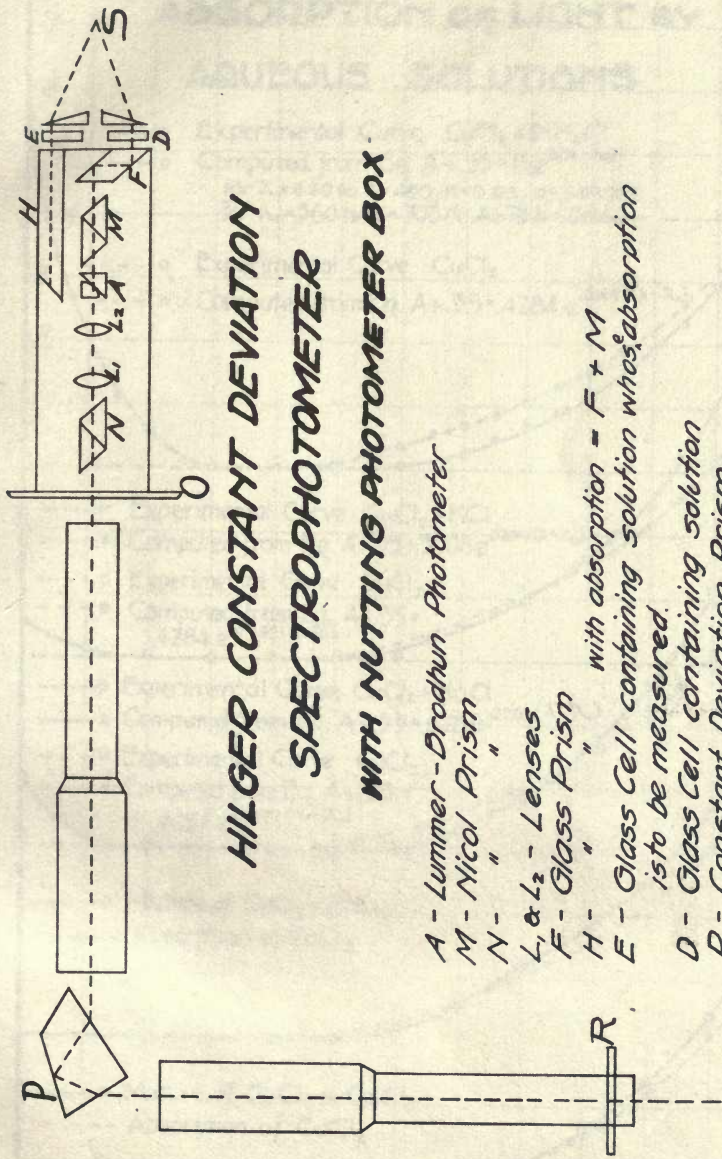
$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.		
450	.86	480	.13	520	00	560	.01	600	.20	640	.53	680	1.23
	.86		.16		00		.01		.21		.55		1.23
	.87		.15		00		.01		.21		.52		1.23
	.92		.15				.01		.20		.53		1.25
	.96		.15						.20		.53		1.23
	.86								.20				
.89													
460	.58	500	00	540	00	580	.05	620	.32	660	.80	690	1.49
	.58		00		00		.05		.33		.82		1.54
	.56		00		00		.06		.31		.82		1.52
	.57						.08		.32		.80		1.51
	.57						.06		.32		.81		1.515
							.06						

T A B L E IV.

COPPER CHLORIDE WITH AMMONIUM CHLORIDE AT 70.0° C

$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.	$\lambda$	Read- ing.		
460	1.55	500	.24	540	.05	580	.18	620	.55	660	1.42
	1.70		.24		.05		.18		.56		1.48
	1.64		.24		.05		.19		.59		1.46
	1.60		.20		.05		.19		.59		1.46
	1.67		.20				.185		.57		1.455
	1.65		.244								
1.635											
480	.57	520	.11	560	.09	600	.32	640	.89	670	1.79
	.58		.07		.11		.32		.91		1.76
	.59		.06		.11		.33		.91		1.79
	.60		.05		.09		.33		.92		1.79
	.585		.05		.10		.325		.91		1.78
			.06								
	.07										





# HILGER CONSTANT DEVIATION SPECTROPHOTOMETER

WITH NUTTING PHOTOMETER BOX

- A - Lummer-Brodhun Photometer
- M - Nicol Prism
- N - " "
- L<sub>1</sub> & L<sub>2</sub> - Lenses
- F - Glass Prism
- H - " " with absorption =  $F + M$  is to be measured.
- E - Glass Cell containing solution
- O - Glass Cell containing solution
- P - Constant Deviation Prism
- R - Graduated Disk for rotating prism - N
- R - Slit of variable width





# ABSORPTION OF LIGHT BY AQUEOUS SOLUTIONS

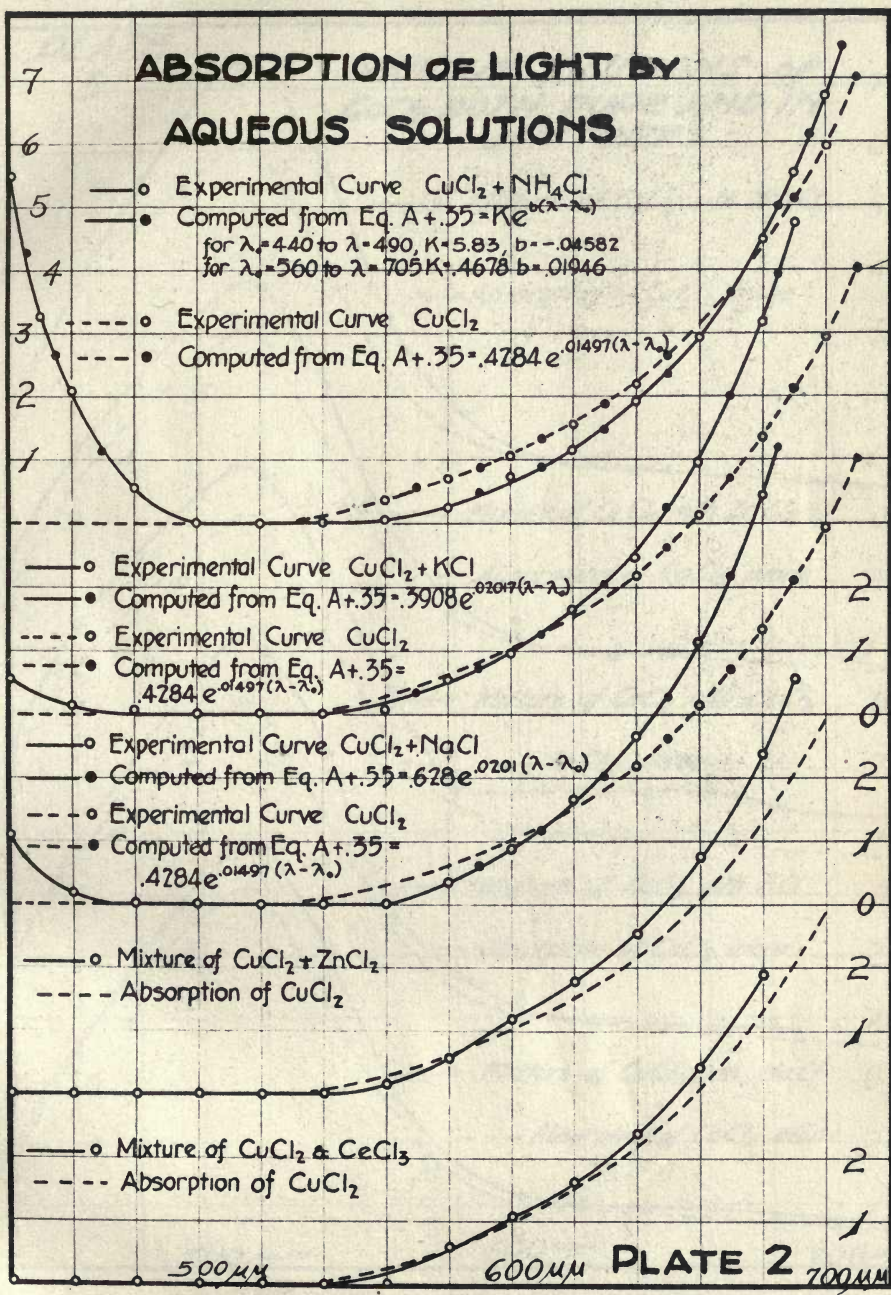
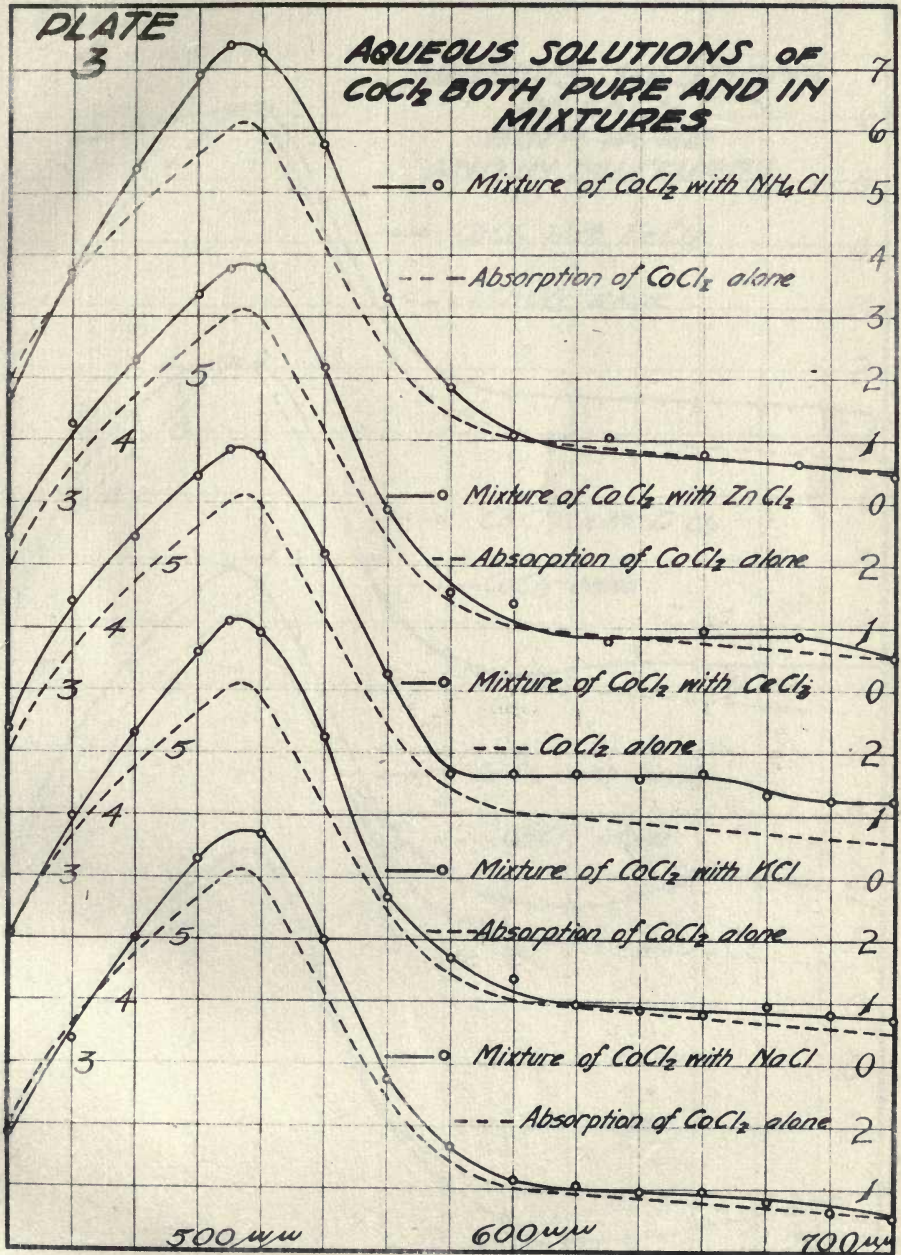




PLATE  
3

7  
6  
5  
4  
3  
2  
1  
0  
2  
1  
0  
2  
1  
0  
2  
1

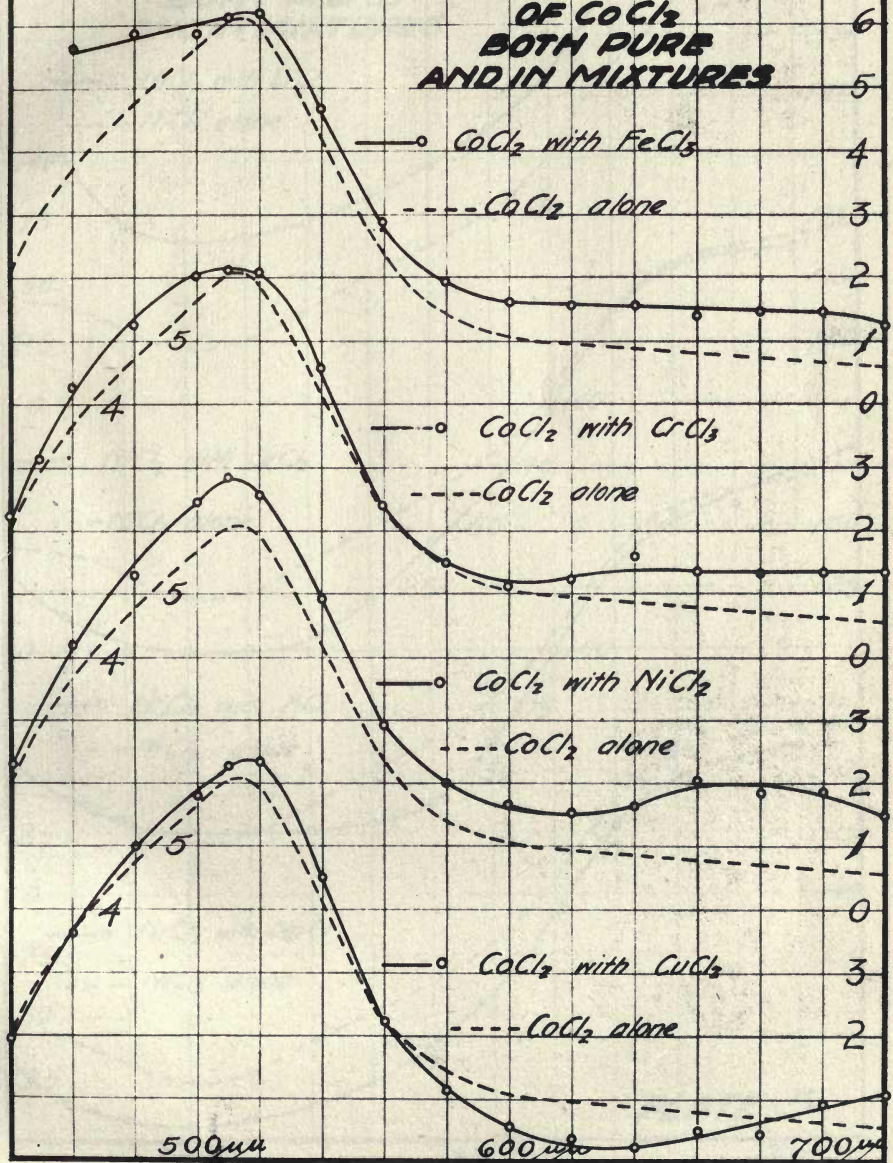
AQUEOUS SOLUTIONS OF  
 $\text{CoCl}_2$  BOTH PURE AND IN  
MIXTURES





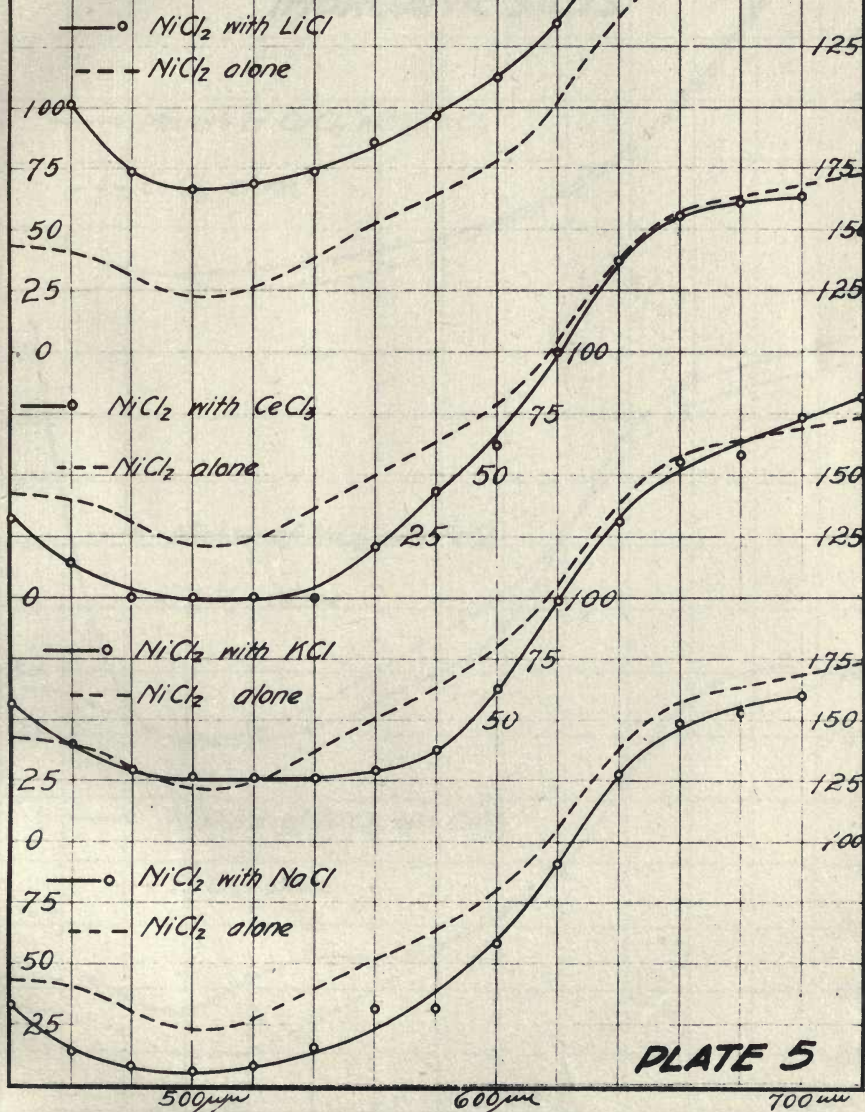
**PLATE  
4**

**AQUEOUS SOLUTIONS  
OF  $\text{CoCl}_2$   
BOTH PURE  
AND IN MIXTURES**





**AQUEOUS SOLUTIONS  
OF  $NiCl_2$   
BOTH ALONE  
AND IN MIXTURES**







# PLATE 6

## AQUEOUS SOLUTIONS OF INORGANIC SALTS

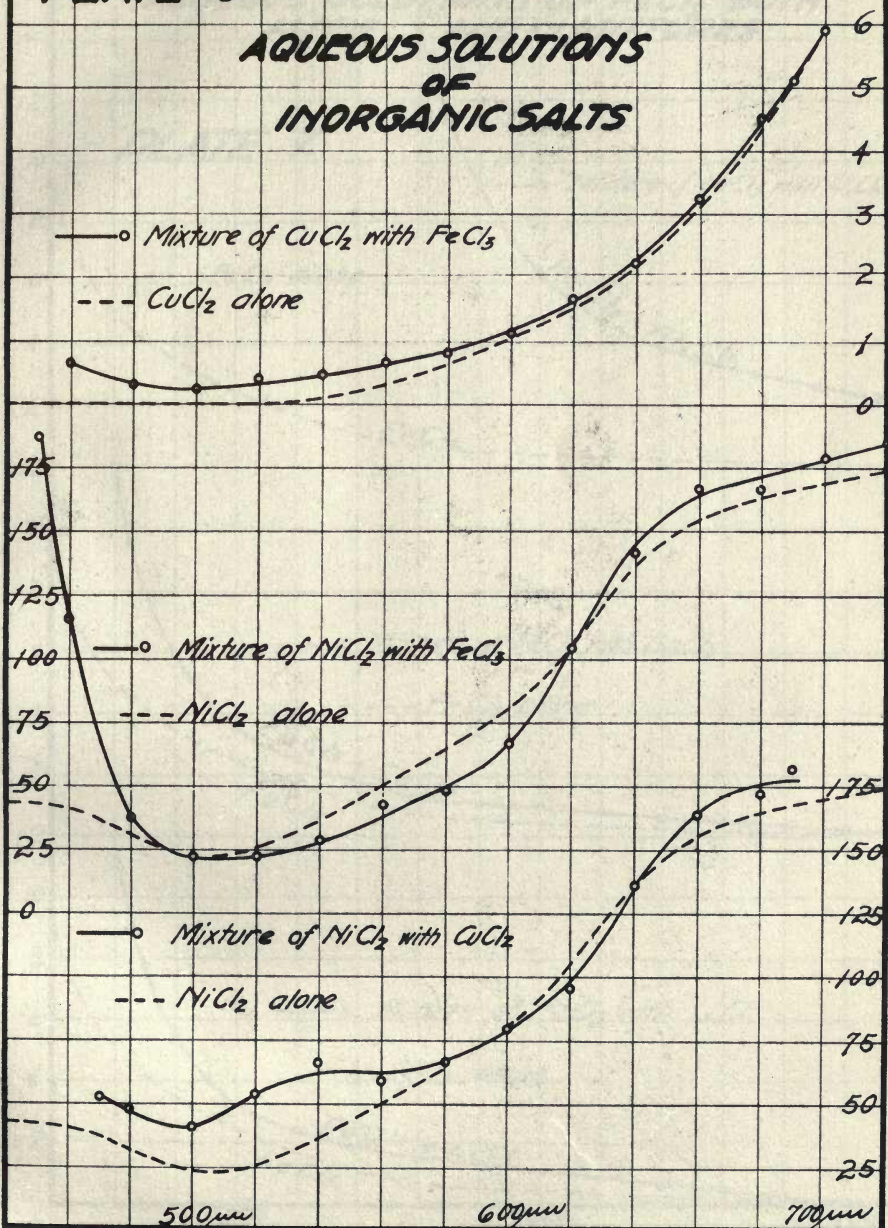
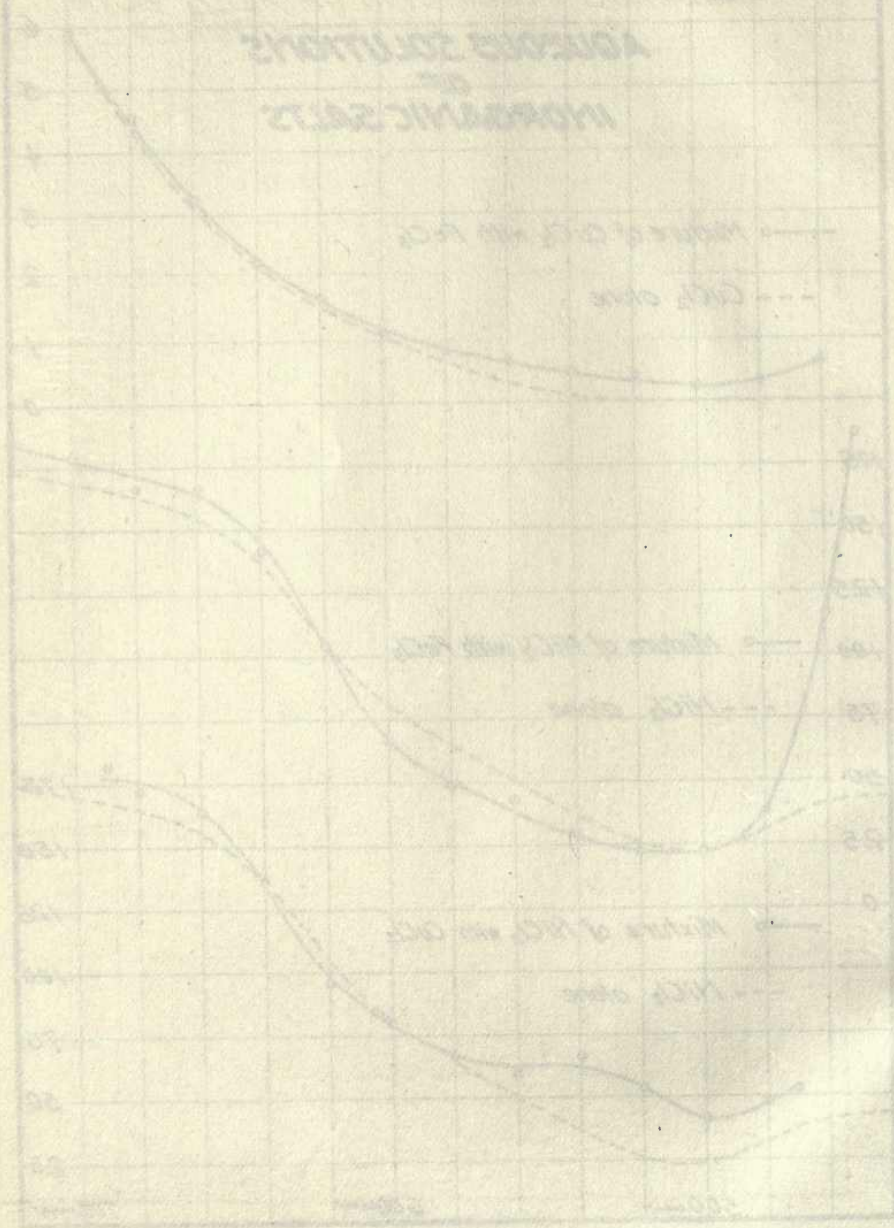


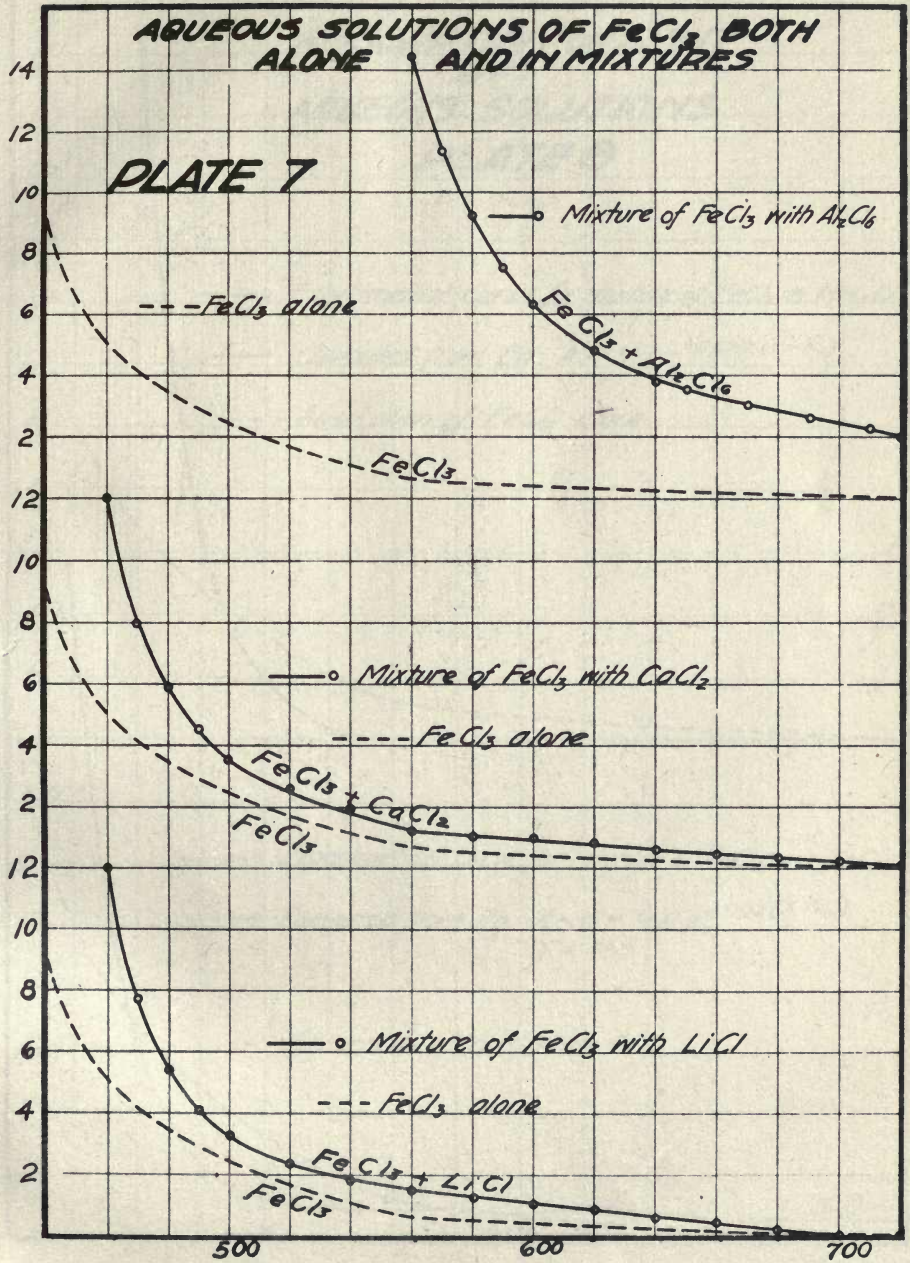
PLATE 8

AQUEOUS SOLUTIONS  
OF  
INORGANIC SALTS



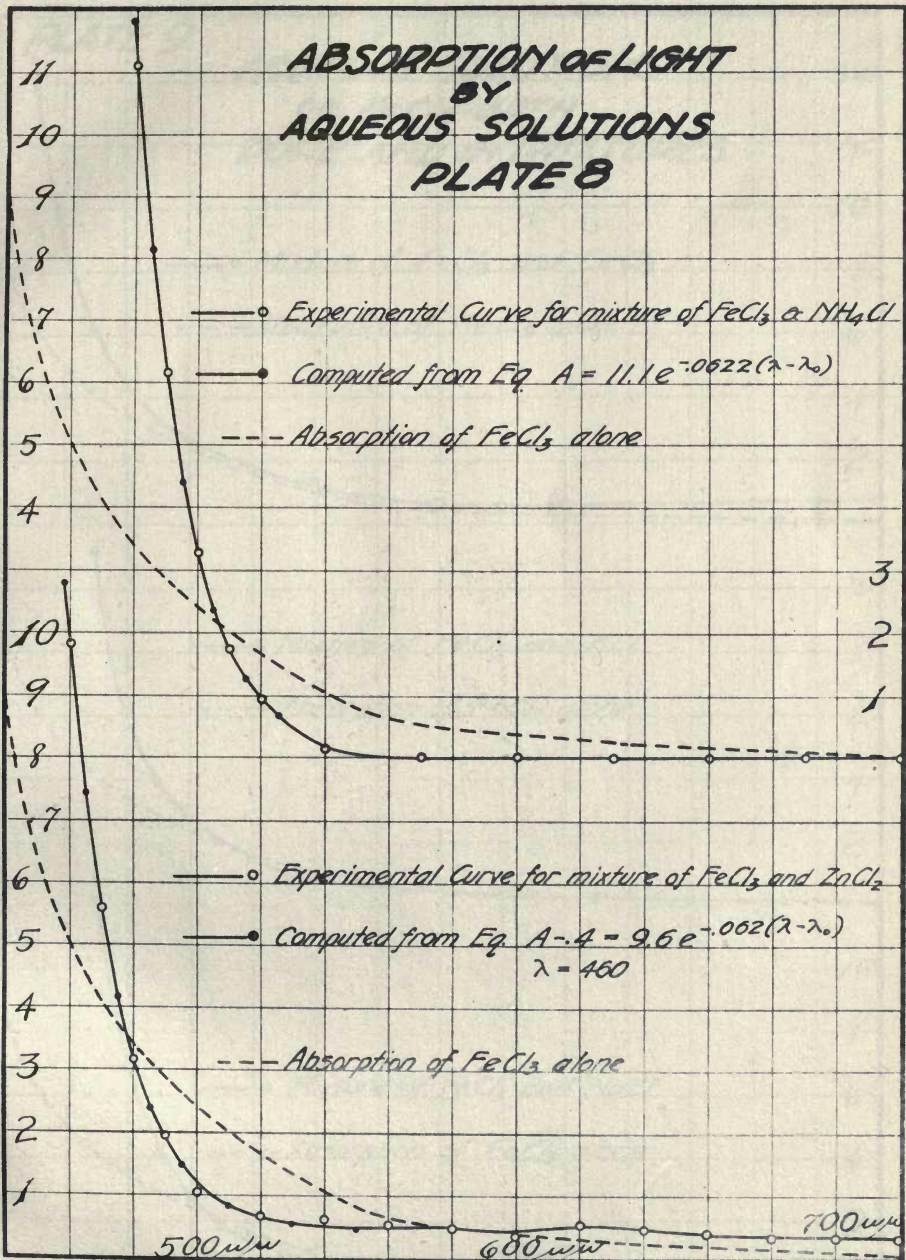
aqueous solutions of  $FeCl_3$  both alone and in mixtures

PLATE 7





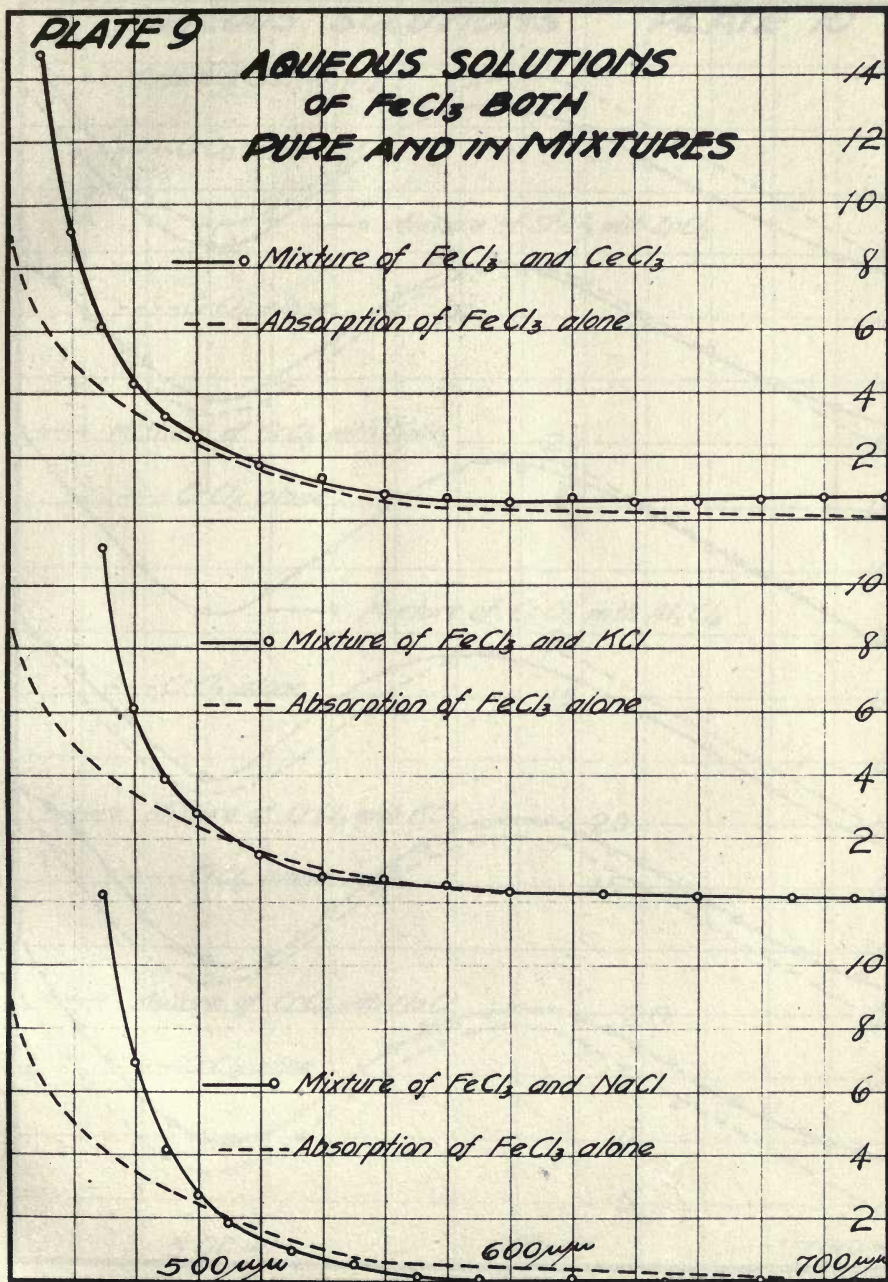
# ABSORPTION OF LIGHT BY AQUEOUS SOLUTIONS PLATE 8





**PLATE 9**

**aqueous solutions  
of  $FeCl_3$  both  
pure and in mixtures**

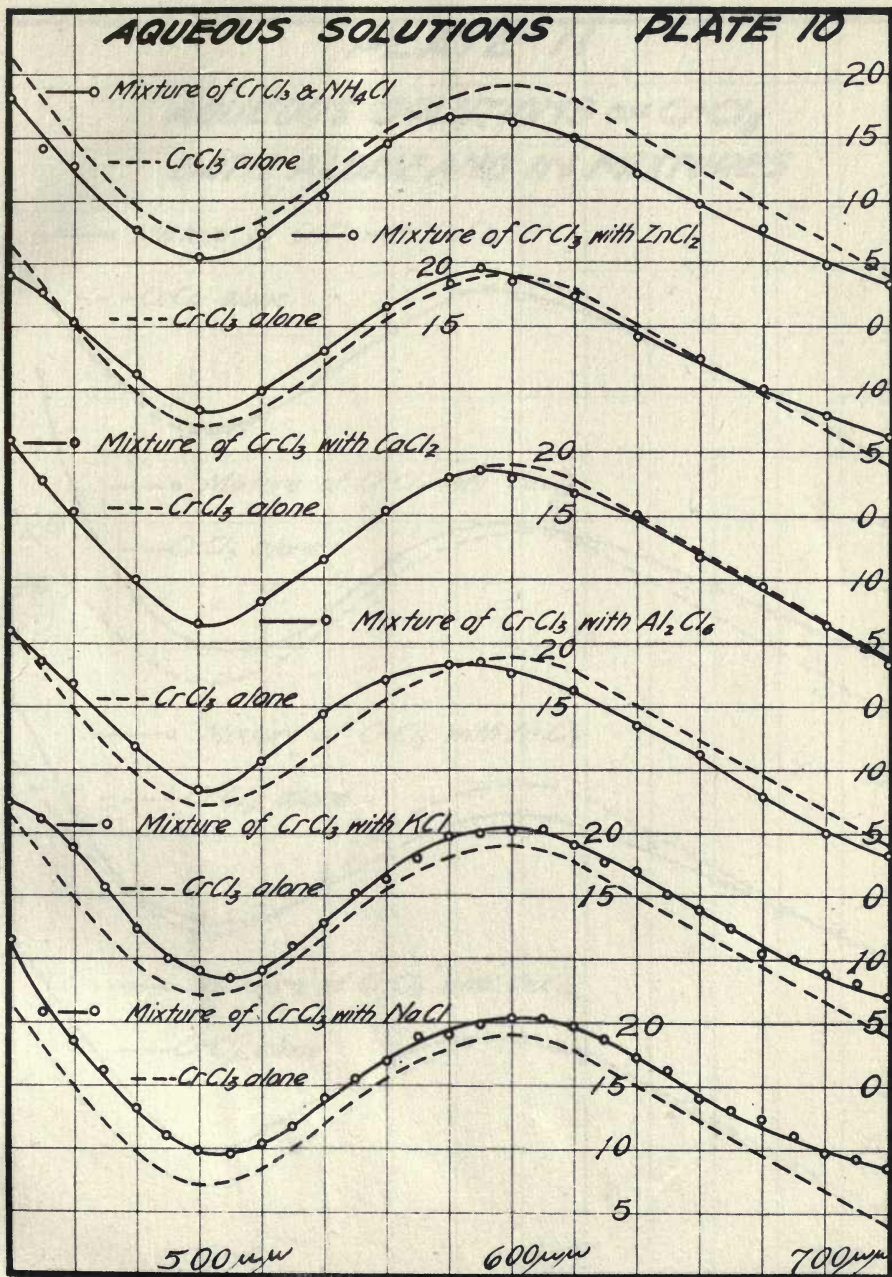






# AQUEOUS SOLUTIONS

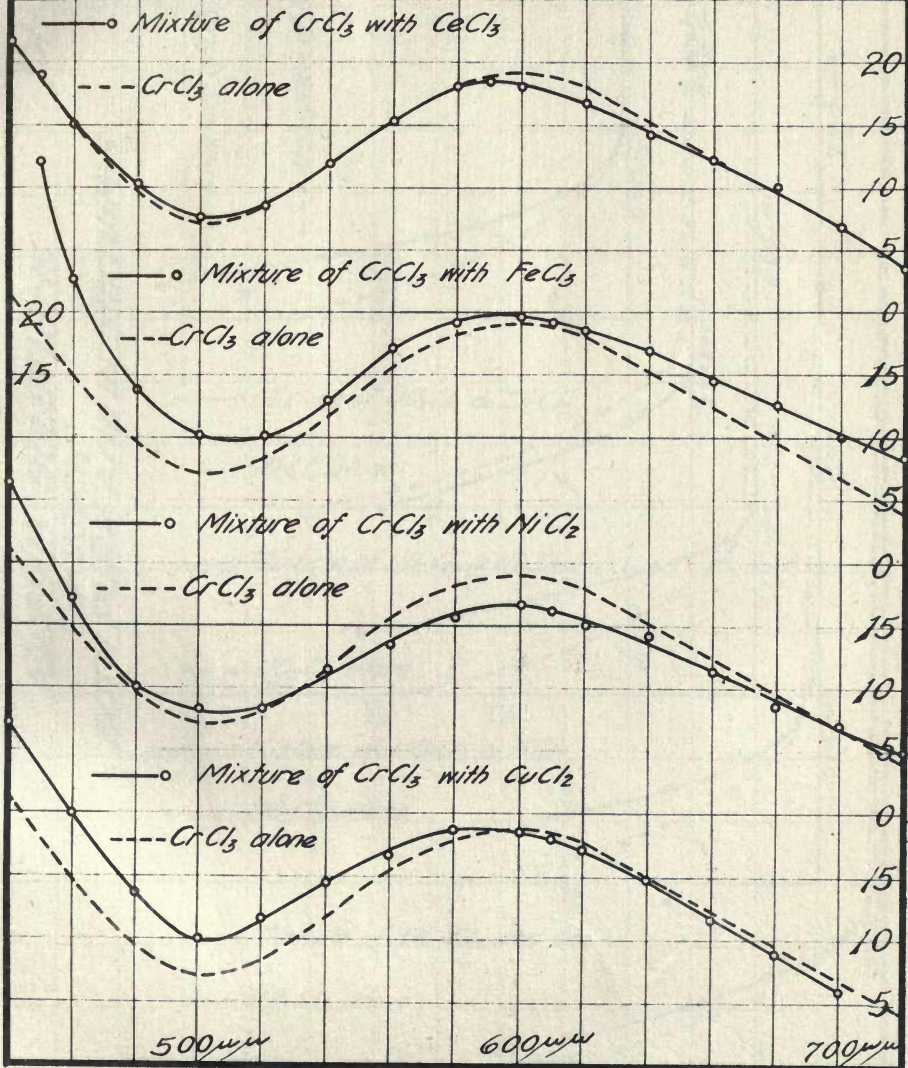
# PLATE 10





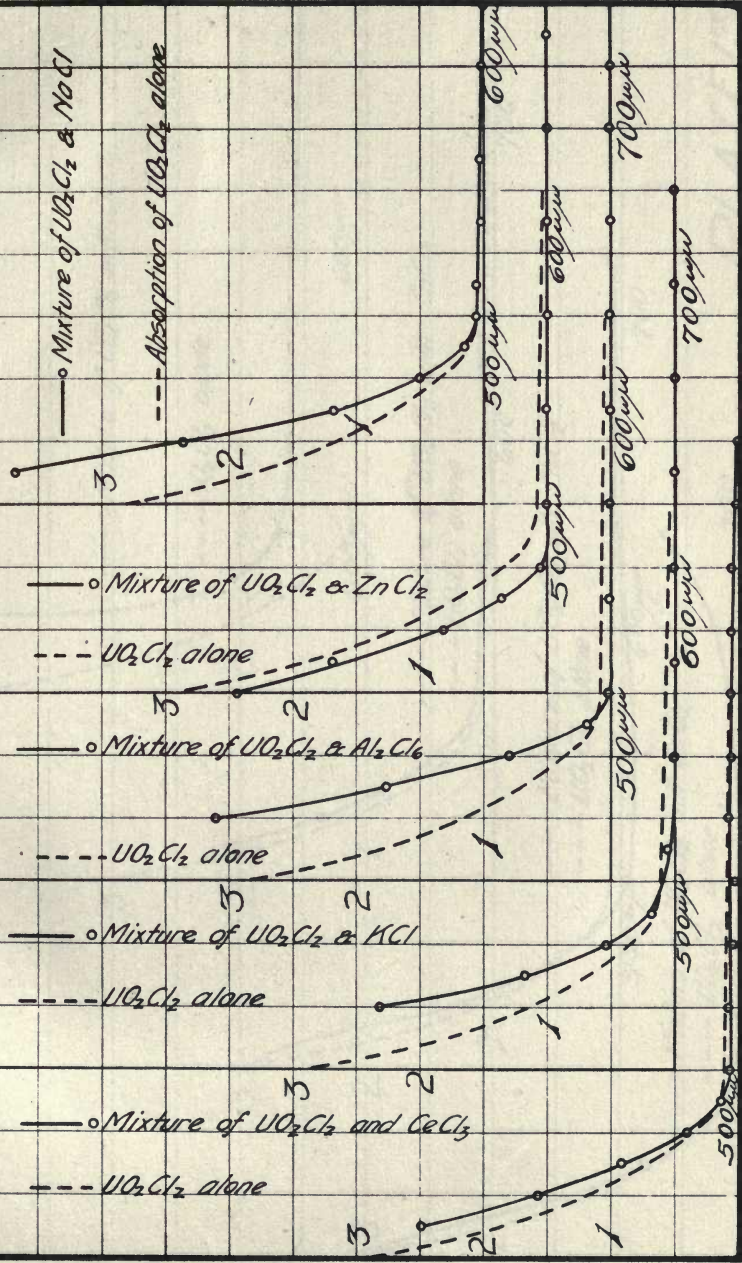
# PLATE II

## AQUEOUS SOLUTIONS OF $\text{CrCl}_3$ BOTH ALONE AND IN MIXTURES



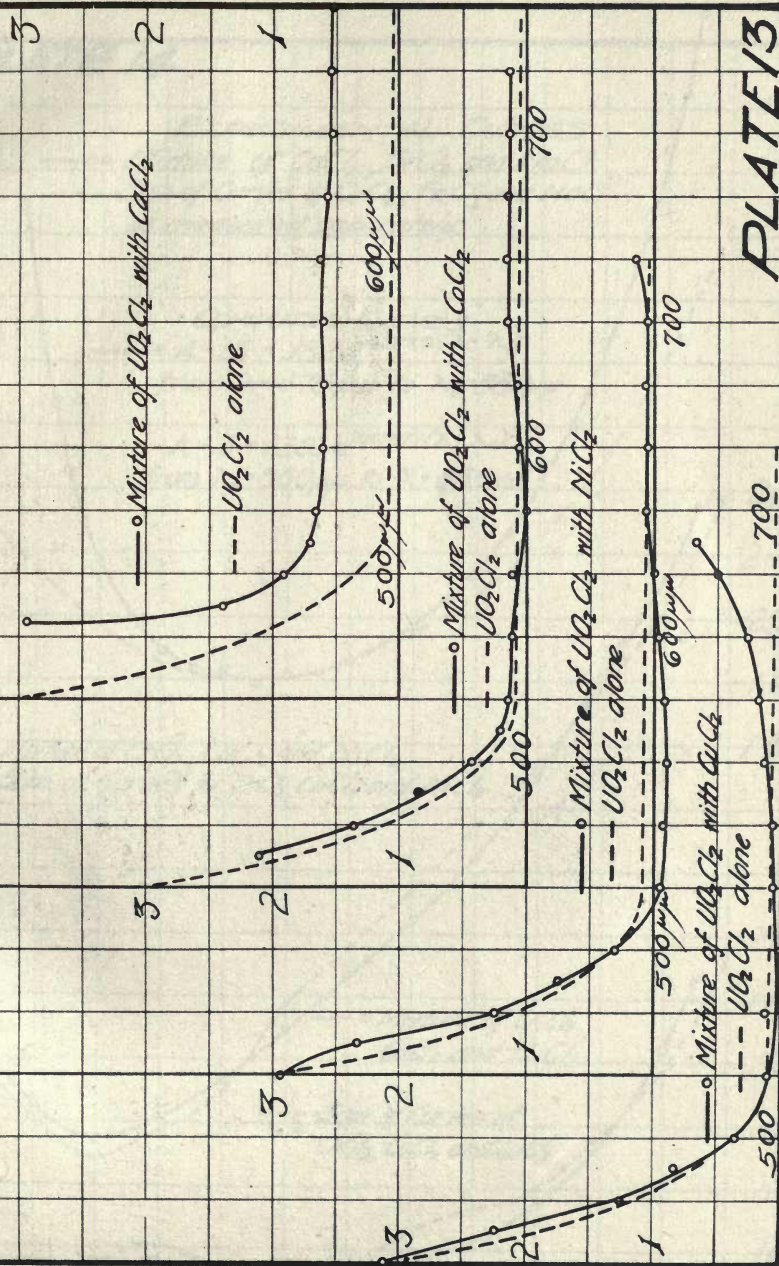


aqueous solutions  
of  $UO_2Cl_2$   
BOTH PURE AND IN MIXTURES





# AQUEOUS SOLUTIONS OF $UO_2Cl_2$ BOTH PURE AND IN MIXTURES







# PLATE 14

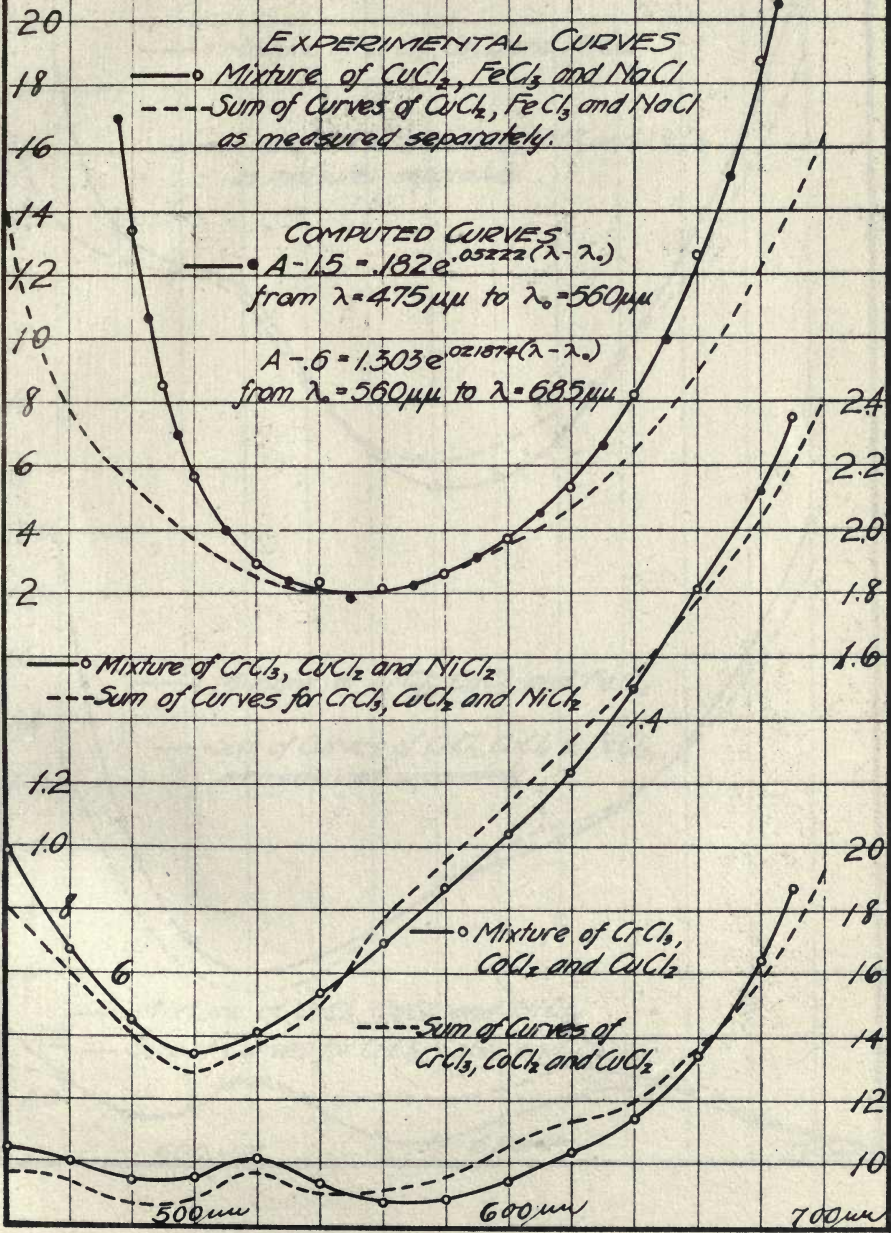


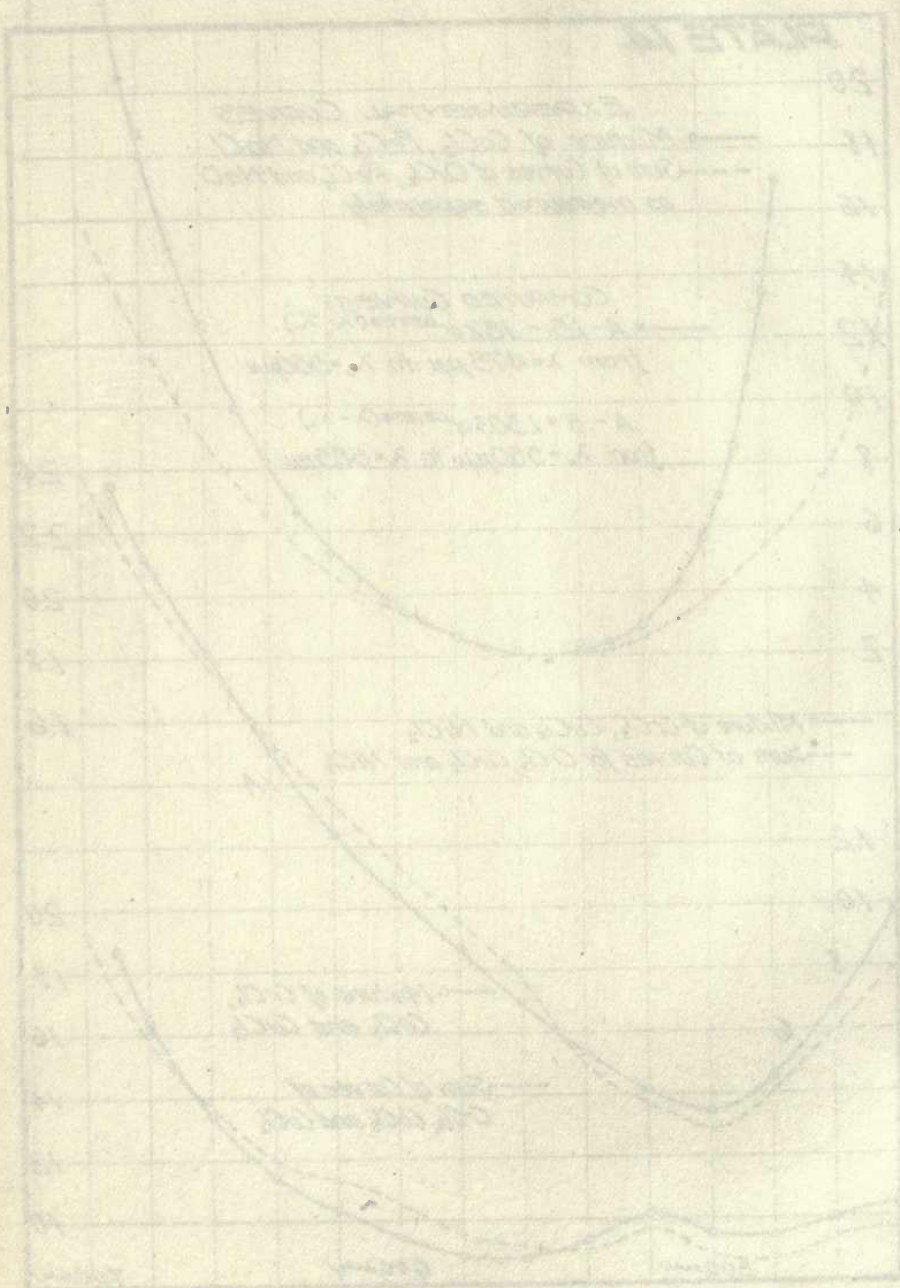
PLATE III

Experimental Curves  
of the rate of  
diffusion of  
a substance  
through a  
membrane

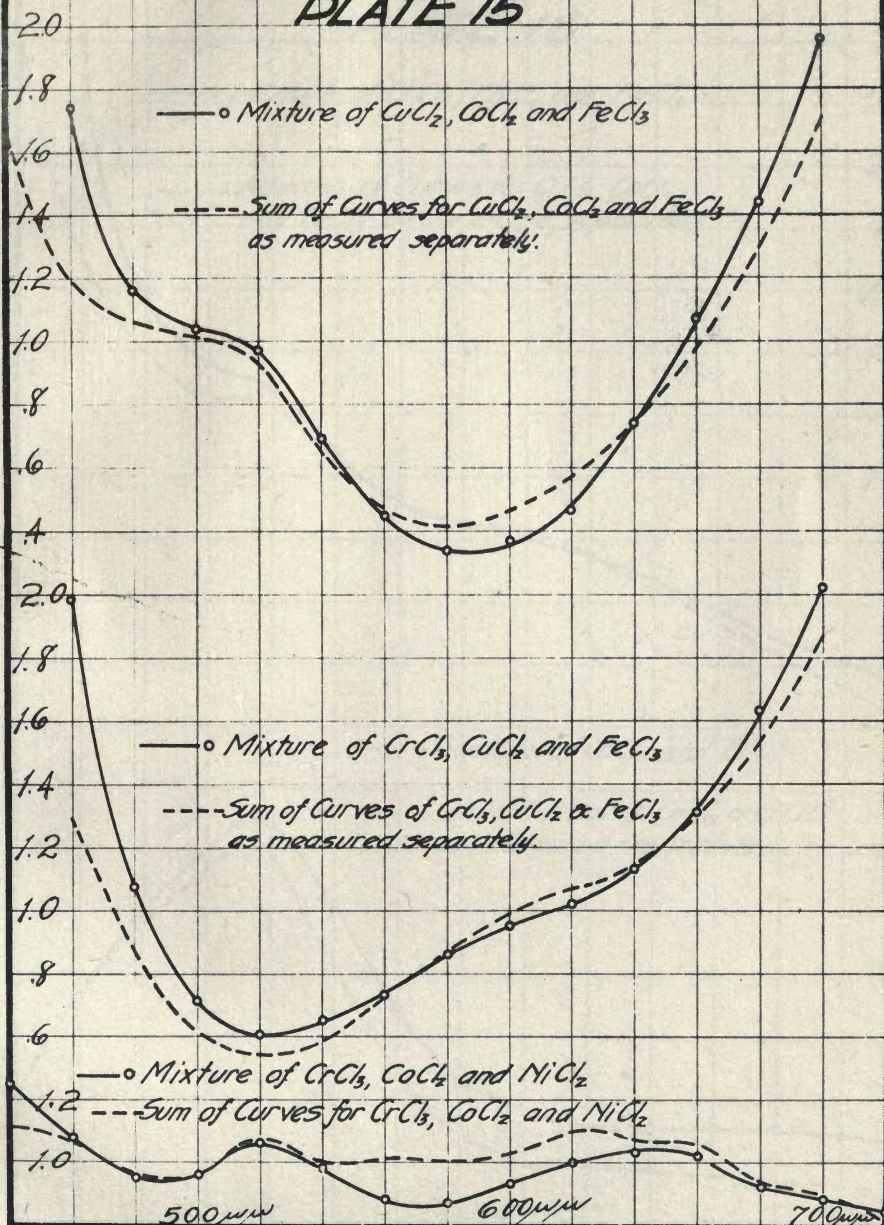
Curve A - 10% solution  
Curve B - 20% solution  
Curve C - 30% solution  
Curve D - 40% solution

Time in hours  
0 1 2 3 4 5 6 7 8 9 10 11 12

Curve E - 50% solution  
Curve F - 60% solution  
Curve G - 70% solution  
Curve H - 80% solution

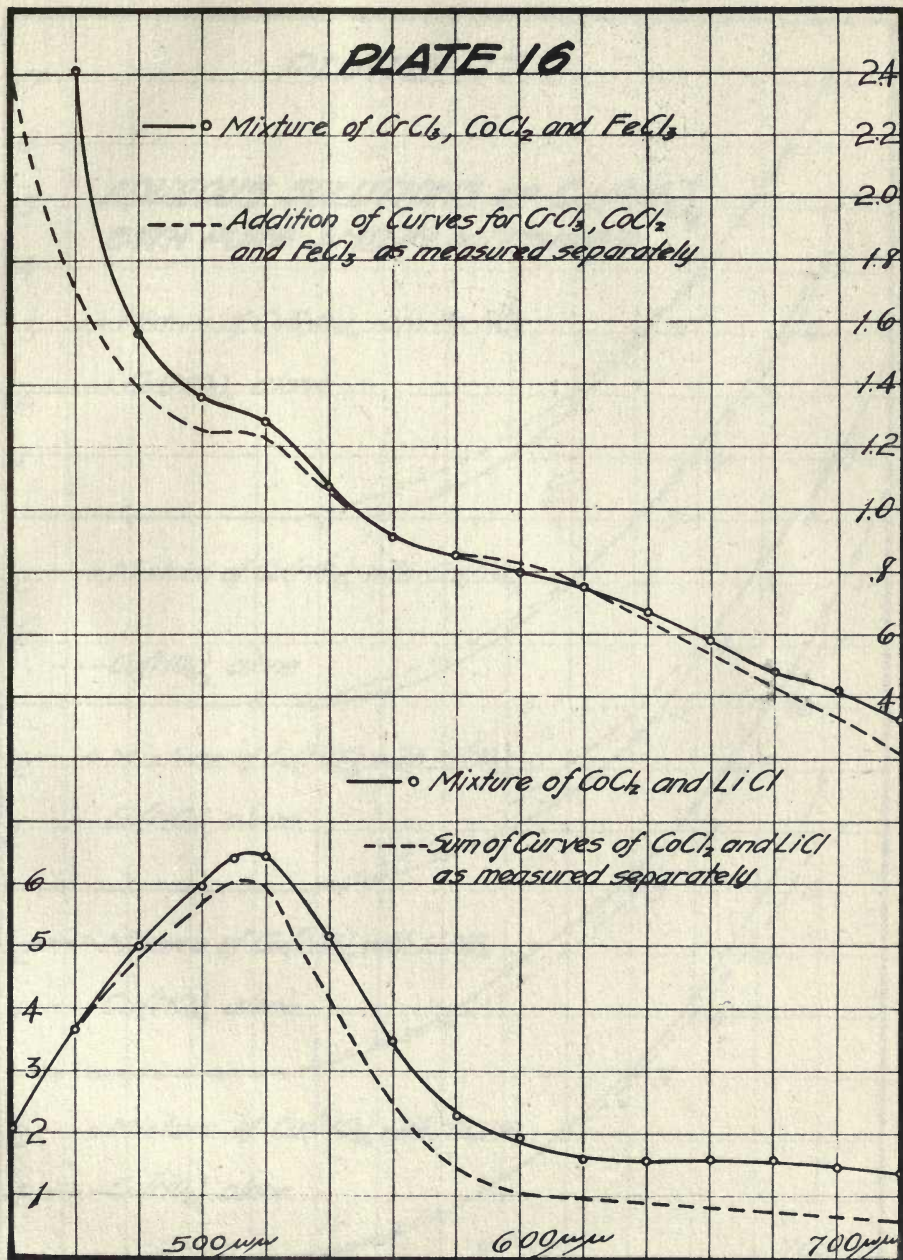


# PLATE 15





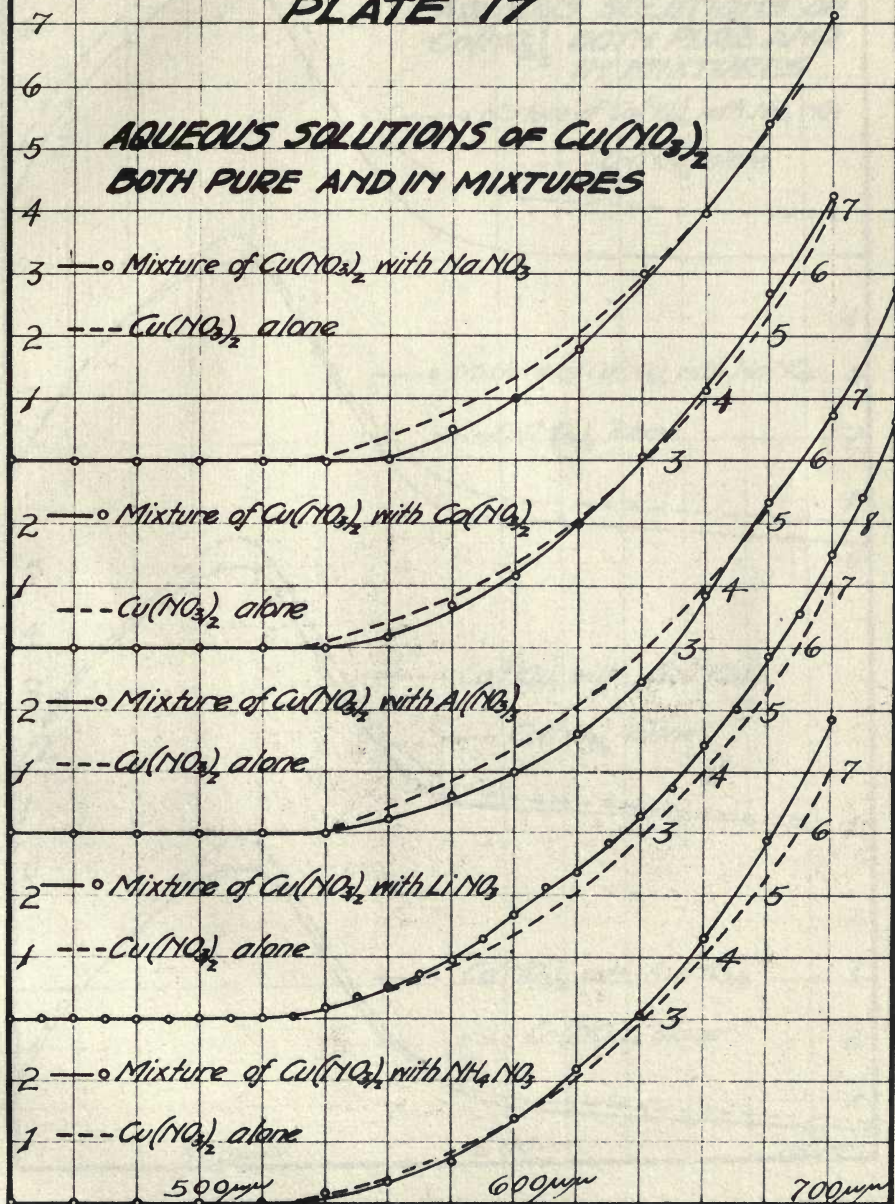
# PLATE 16





# PLATE 17

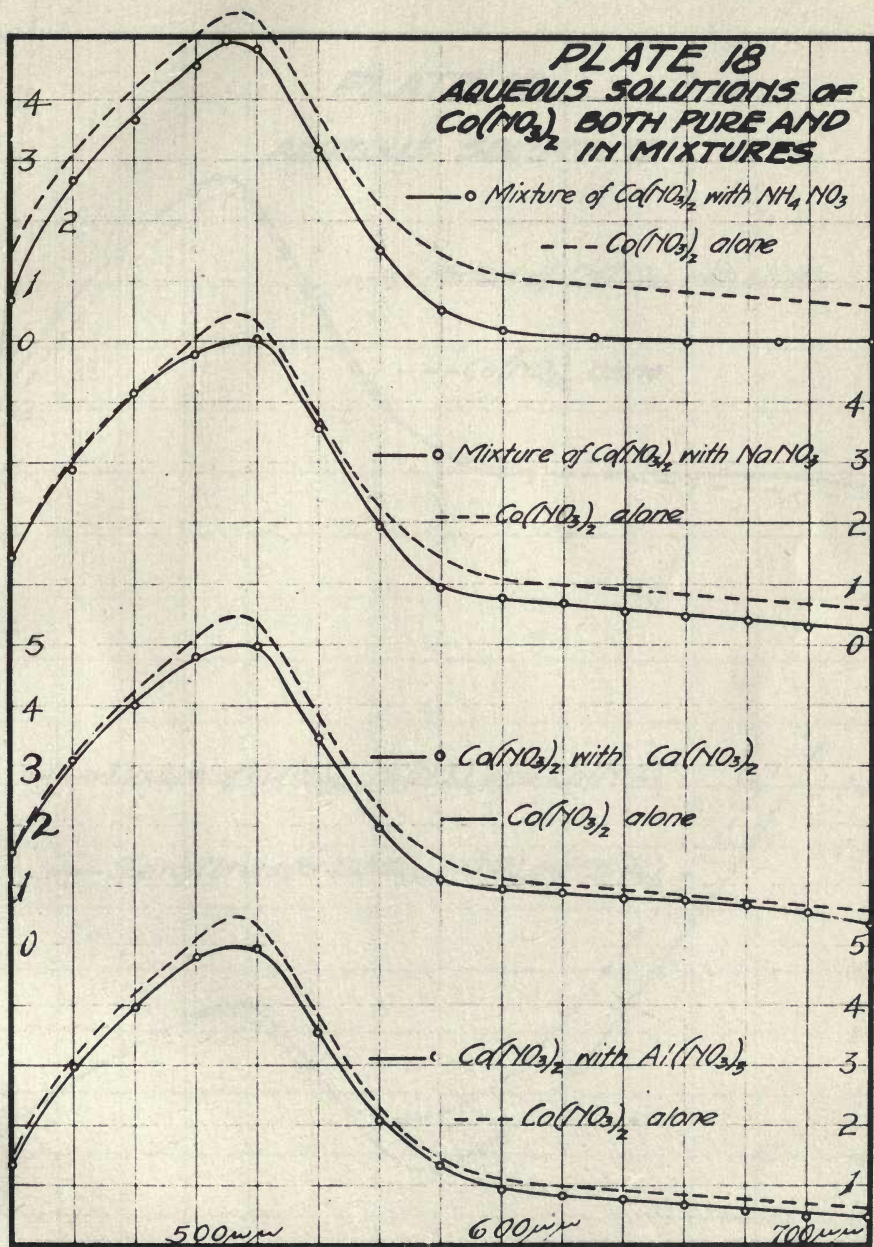
## AQUEOUS SOLUTIONS OF $\text{Cu}(\text{NO}_3)_2$ BOTH PURE AND IN MIXTURES







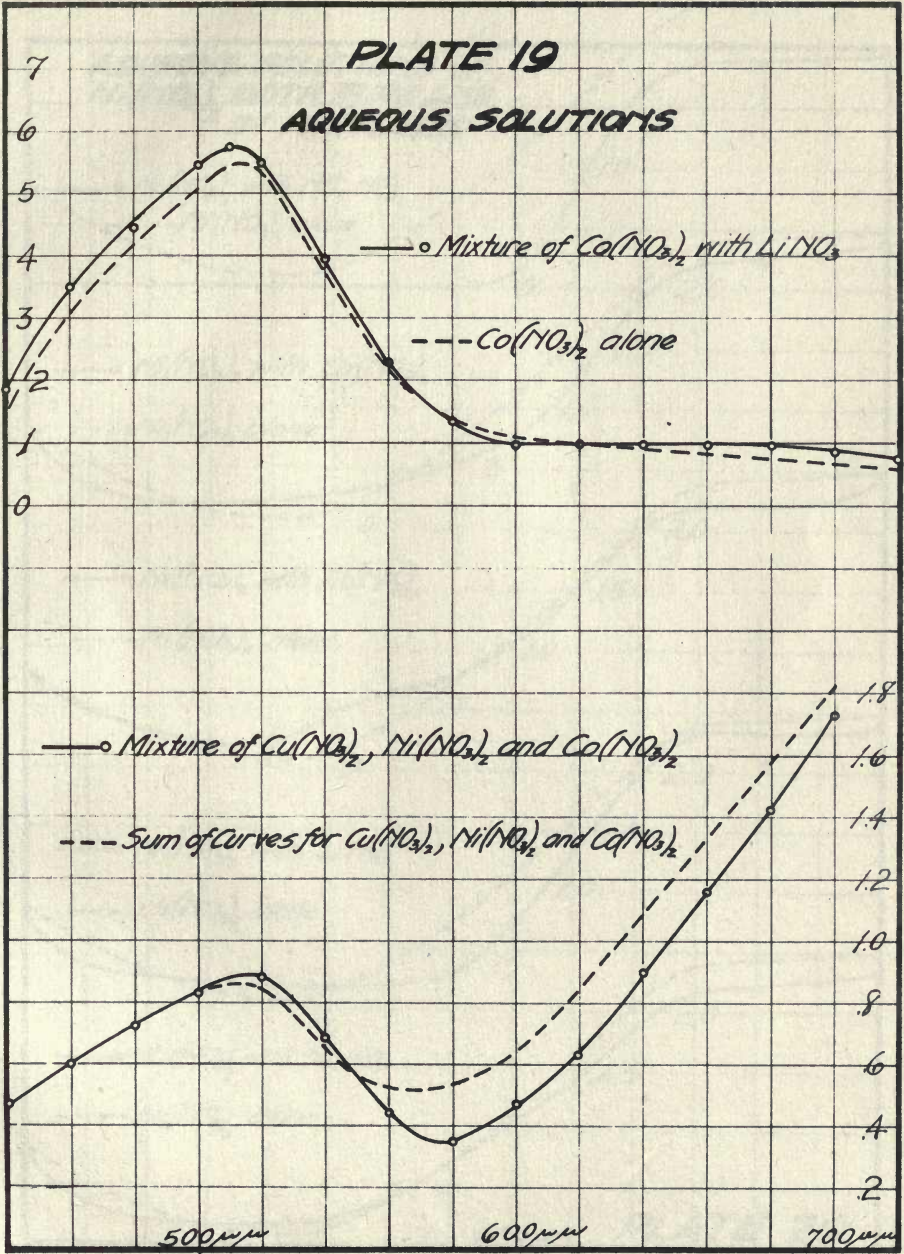
**PLATE 18**  
**AQUEOUS SOLUTIONS OF**  
 **$\text{Co}(\text{NO}_3)_2$  BOTH PURE AND**  
**IN MIXTURES**





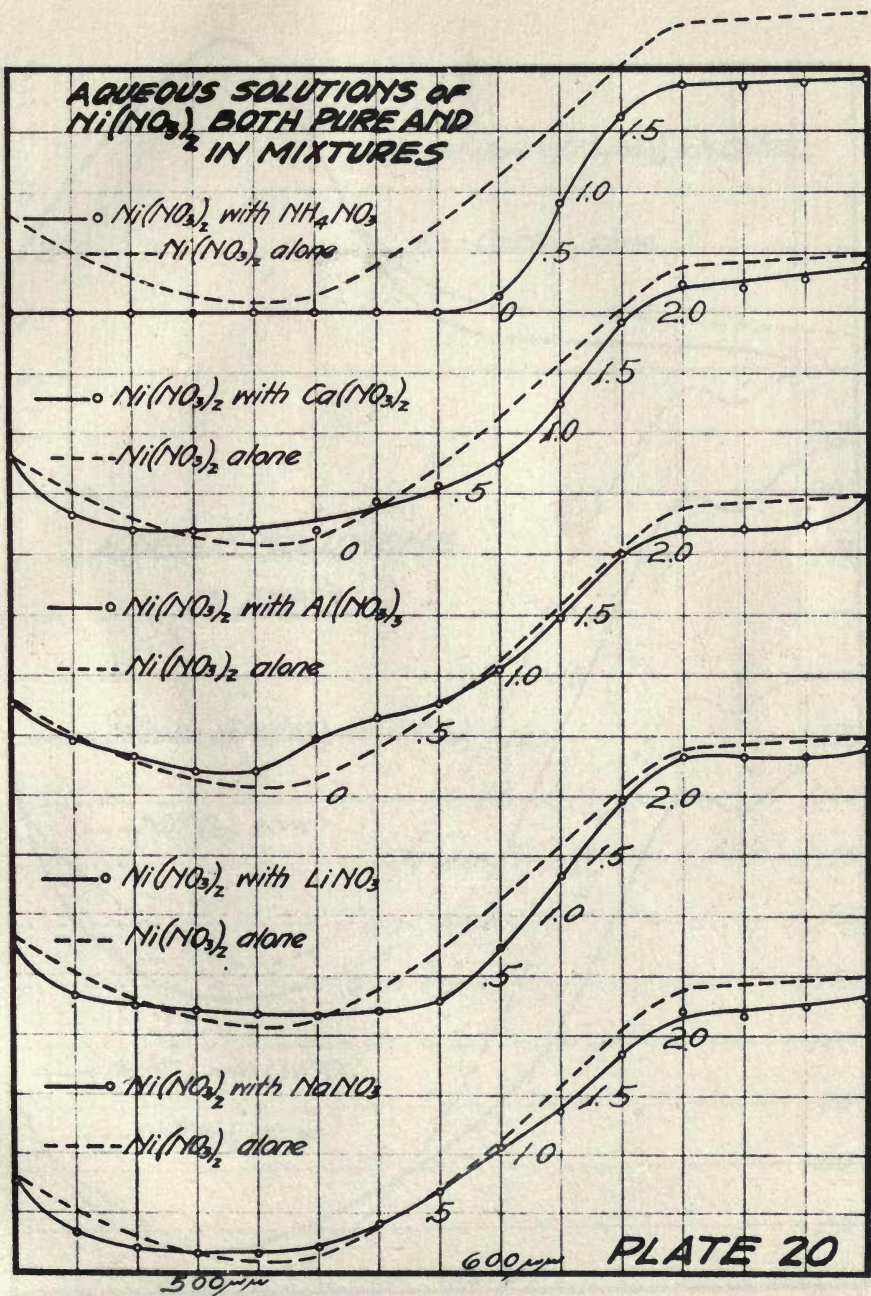
# PLATE 19

## AQUEOUS SOLUTIONS

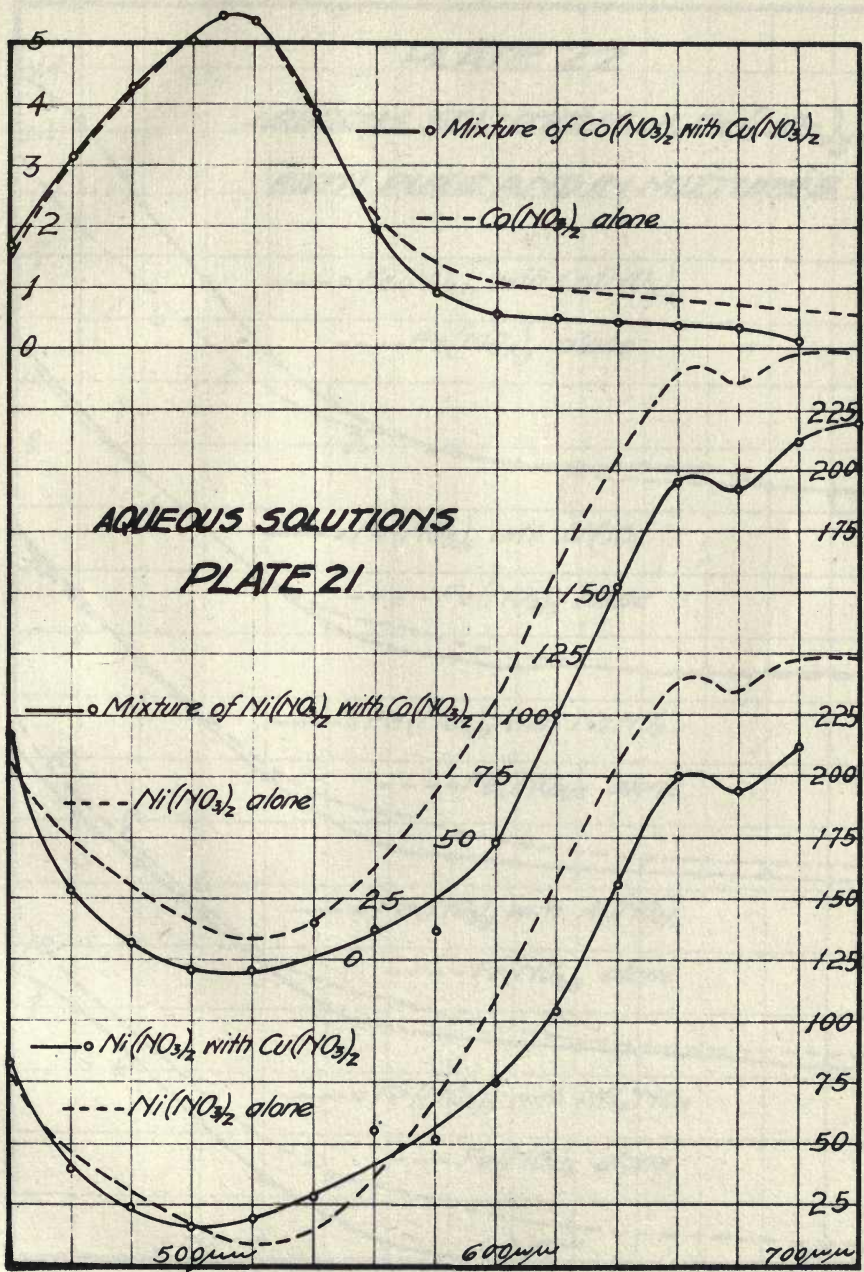




**AQUEOUS SOLUTIONS OF  
 $Ni(NO_3)_2$  BOTH PURE AND  
 IN MIXTURES**





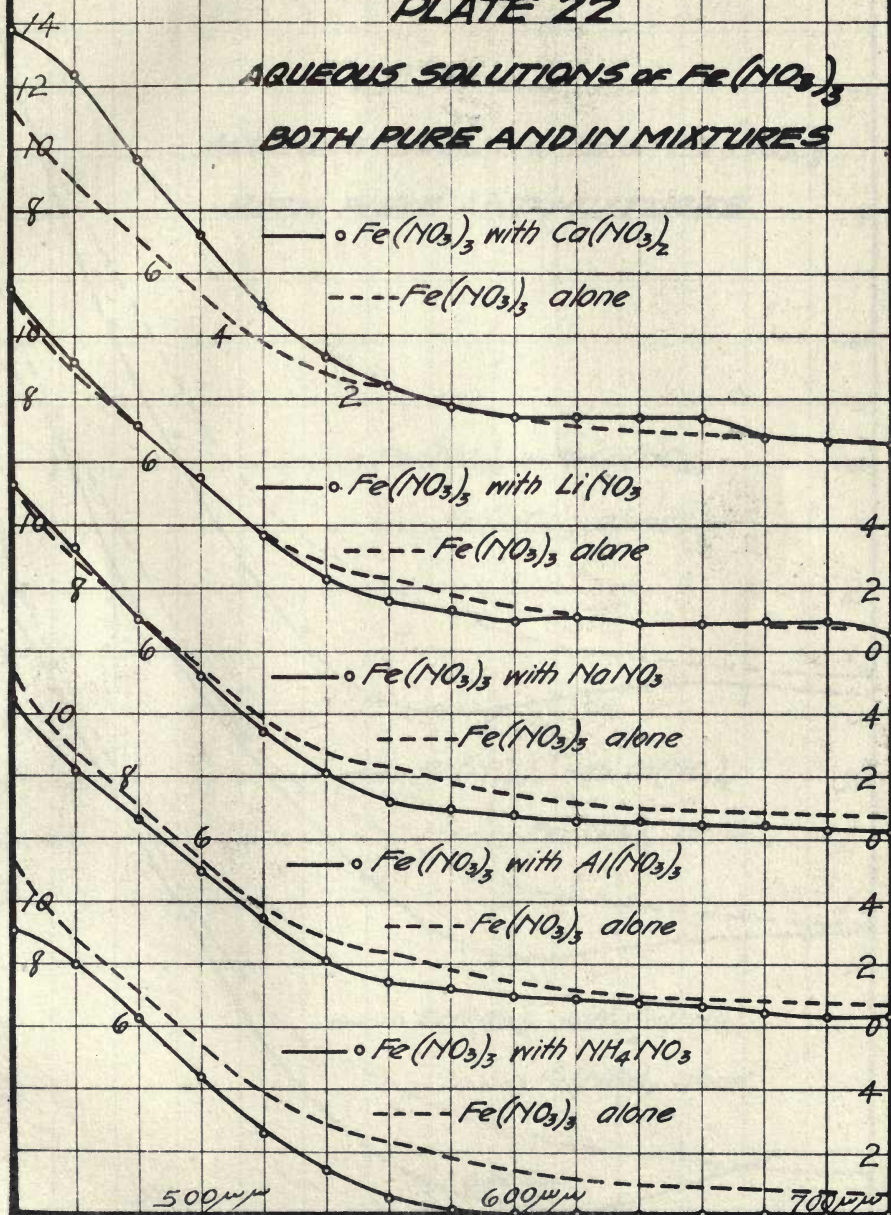






# PLATE 22

## AQUEOUS SOLUTIONS OF $\text{Fe}(\text{NO}_3)_3$ BOTH PURE AND IN MIXTURES

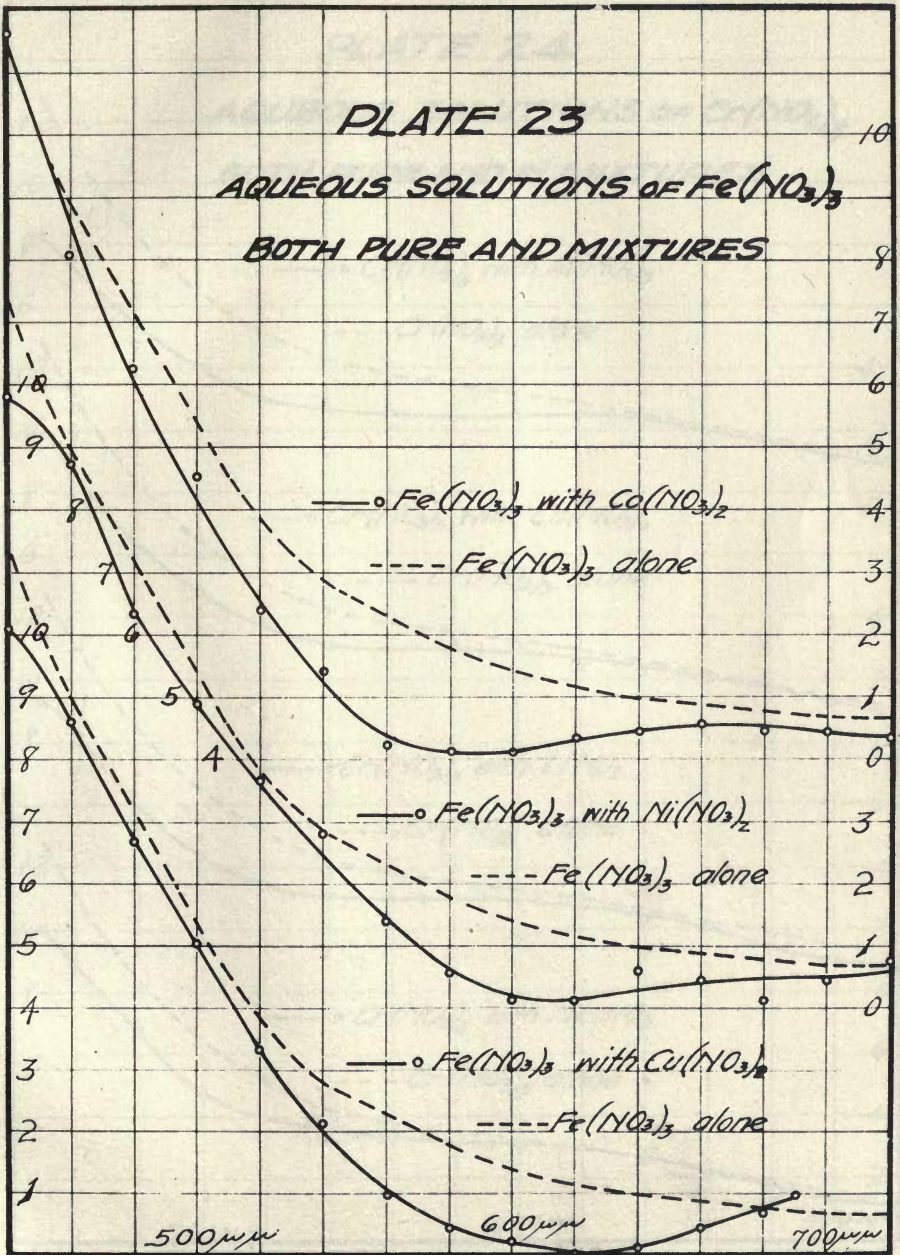




# PLATE 23

AQUEOUS SOLUTIONS OF  $Fe(NO_3)_3$

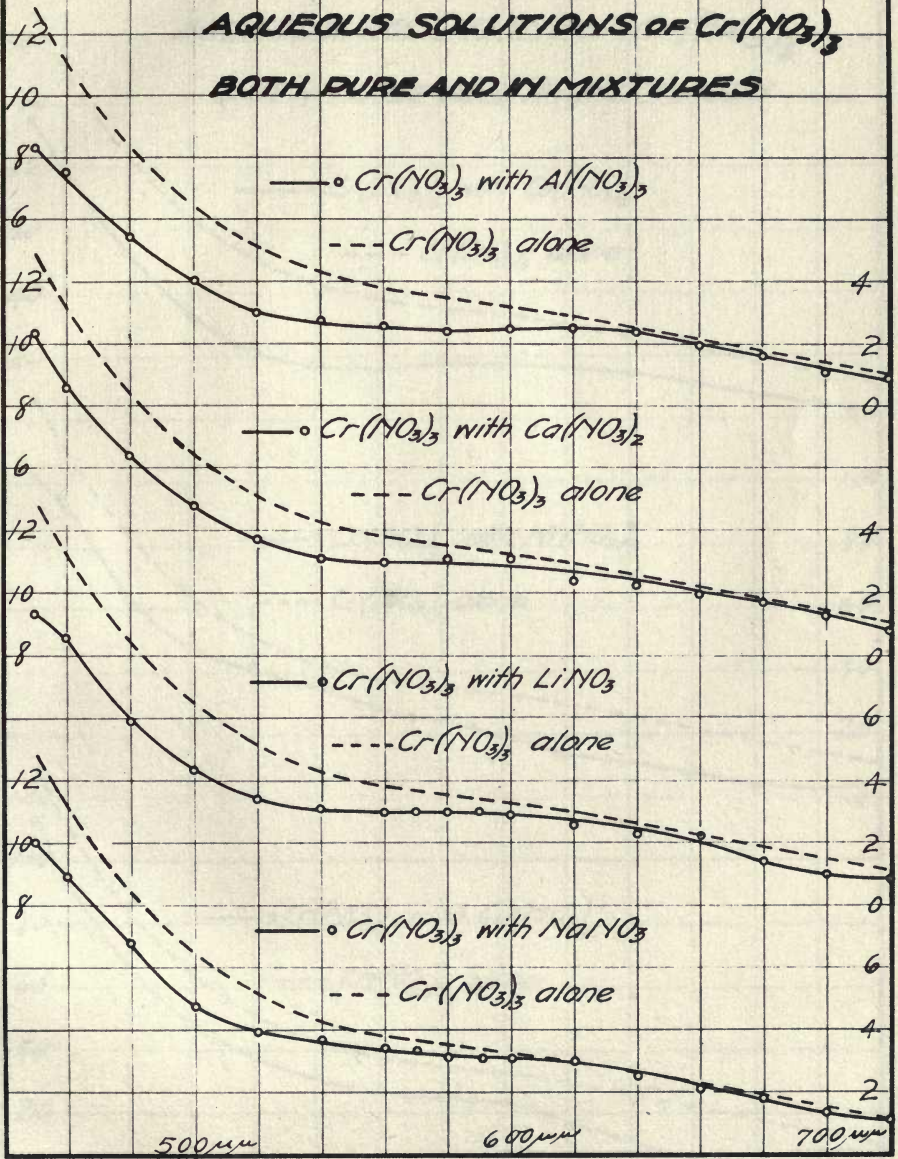
BOTH PURE AND MIXTURES





# PLATE 24

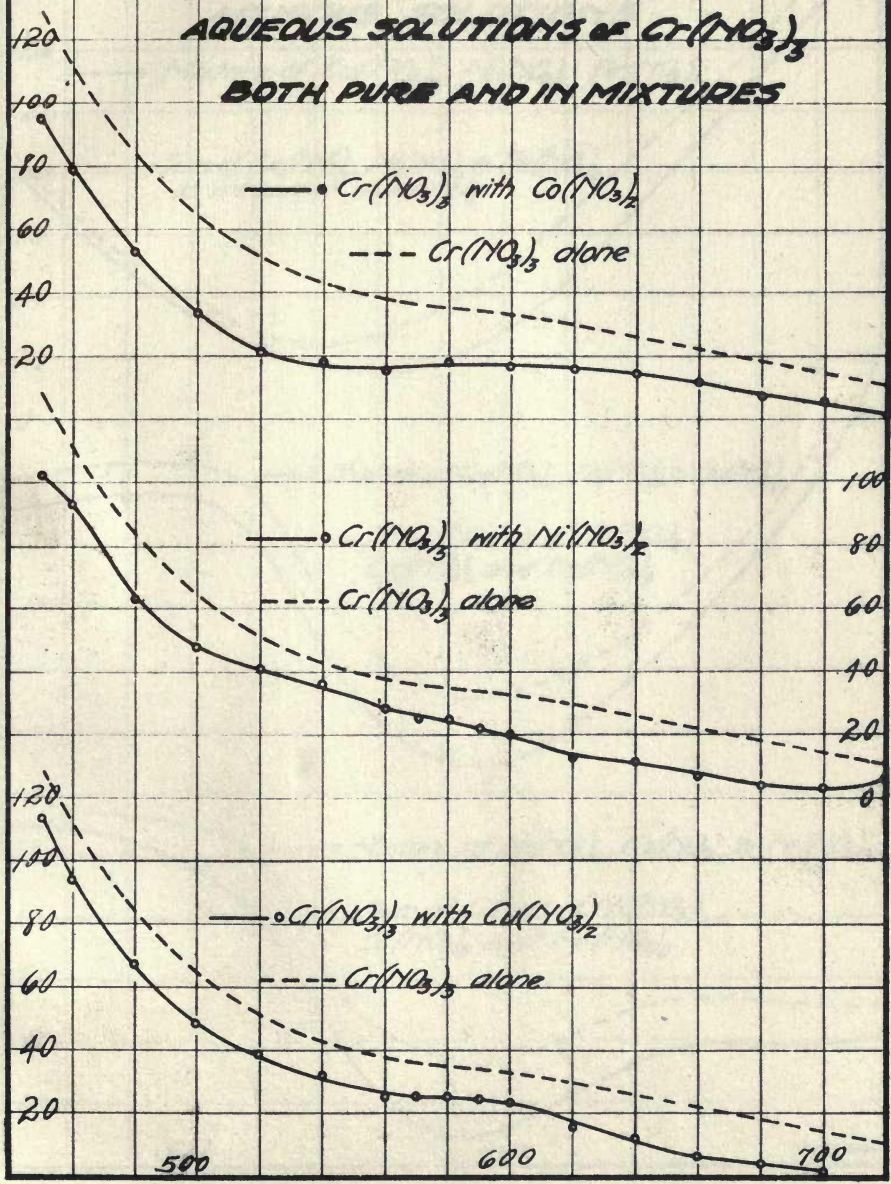
## AQUEOUS SOLUTIONS OF $\text{Cr}(\text{NO}_3)_3$ BOTH PURE AND IN MIXTURES





# PLATE 25

## AQUEOUS SOLUTIONS OF $\text{Cr}(\text{NO}_3)_3$ BOTH PURE AND IN MIXTURES







# PLATE 26 AQUEOUS SOLUTIONS

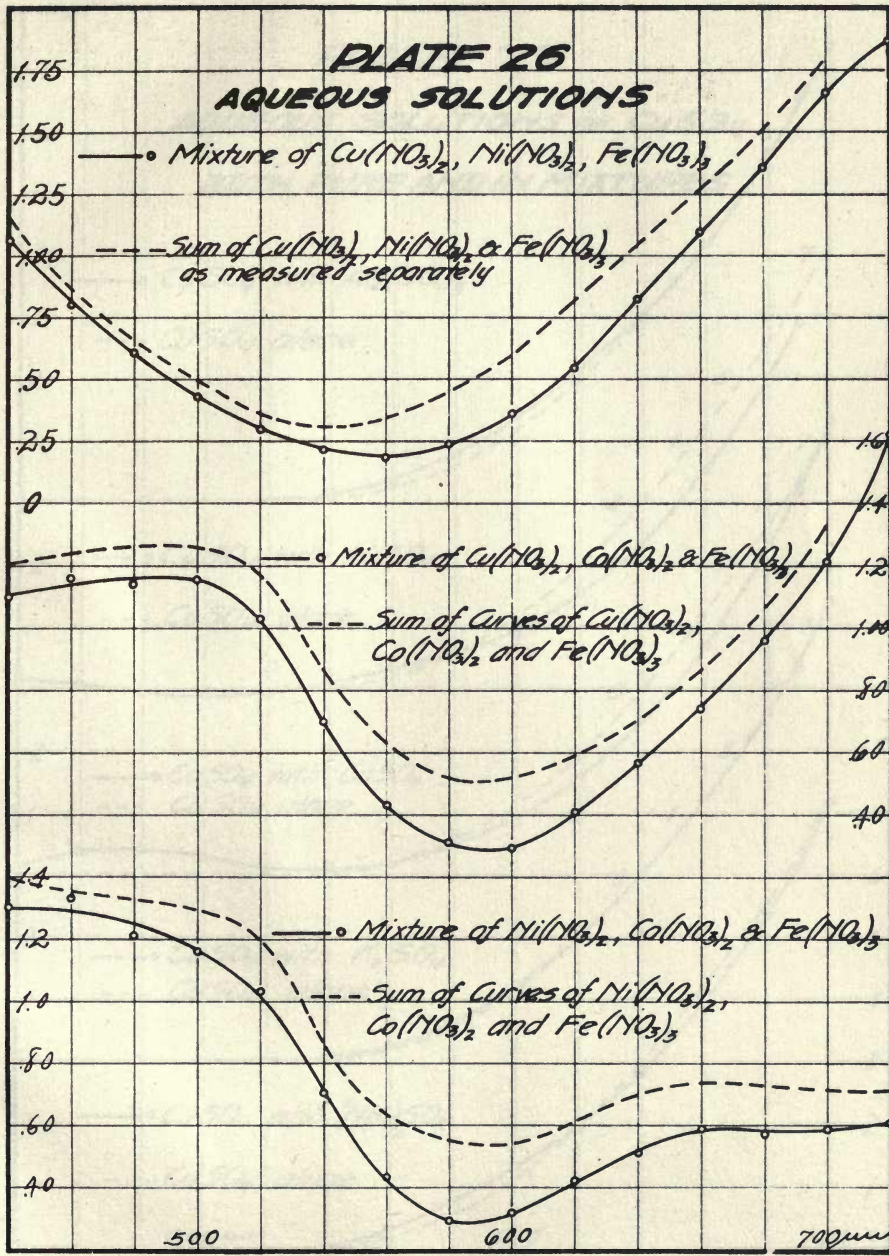
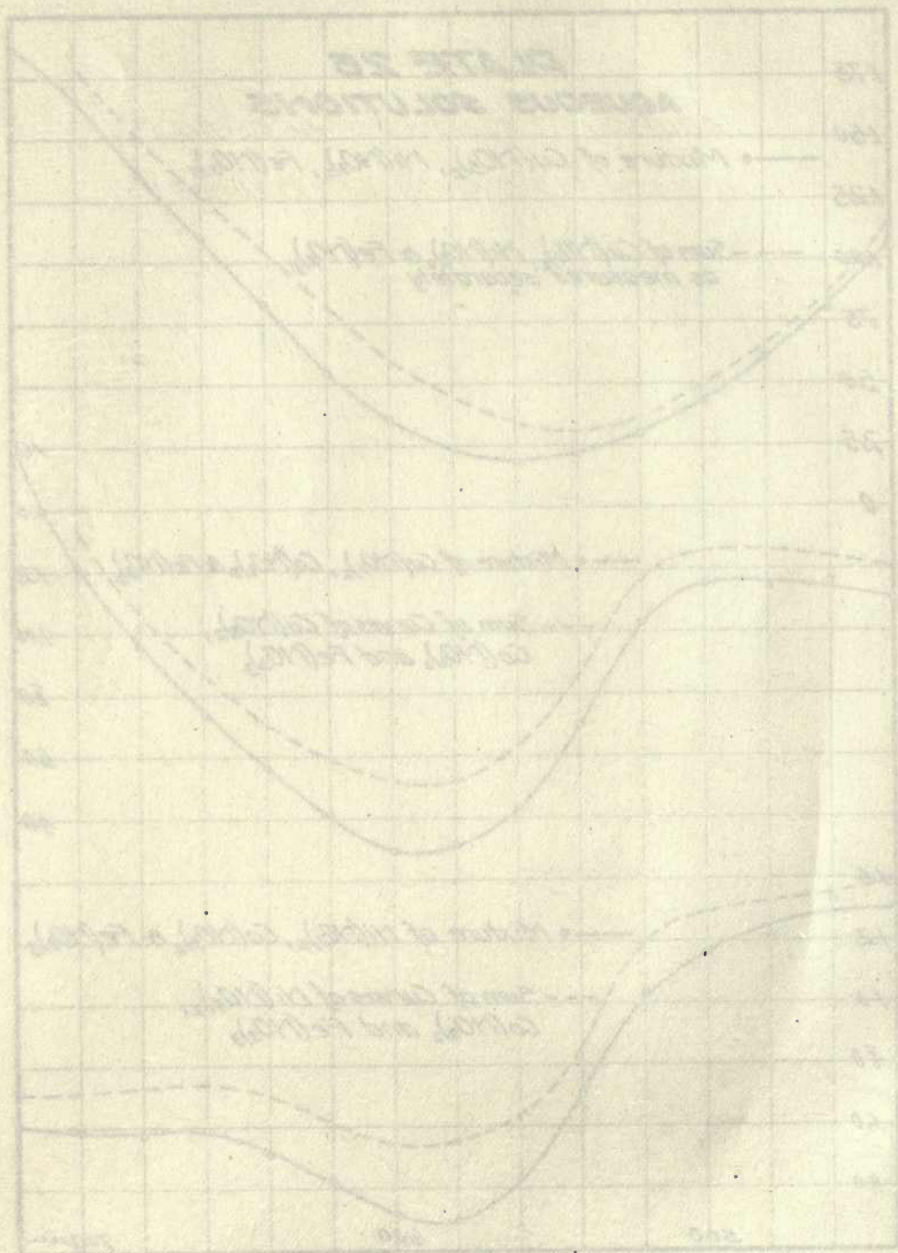


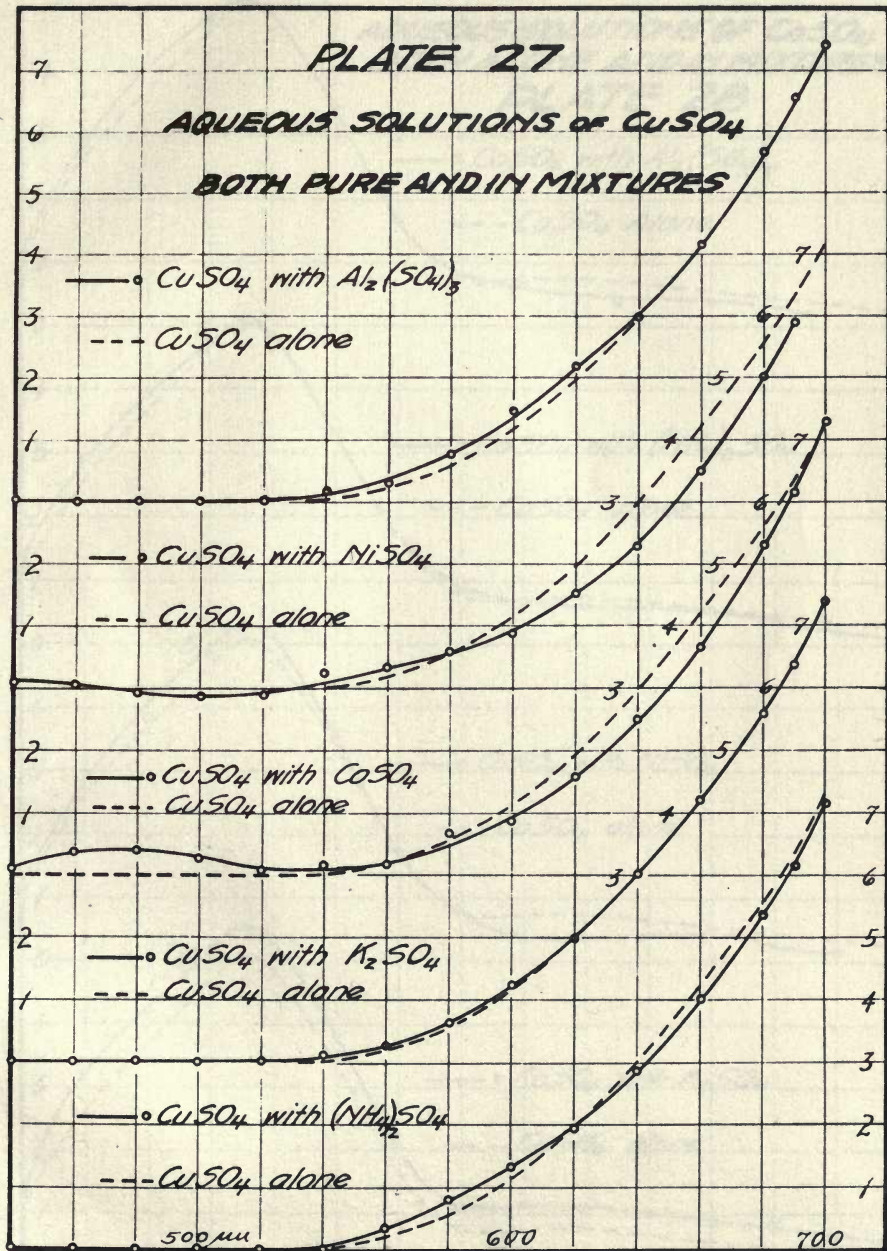
PLATE 22

AQUEOUS SOLUTIONS



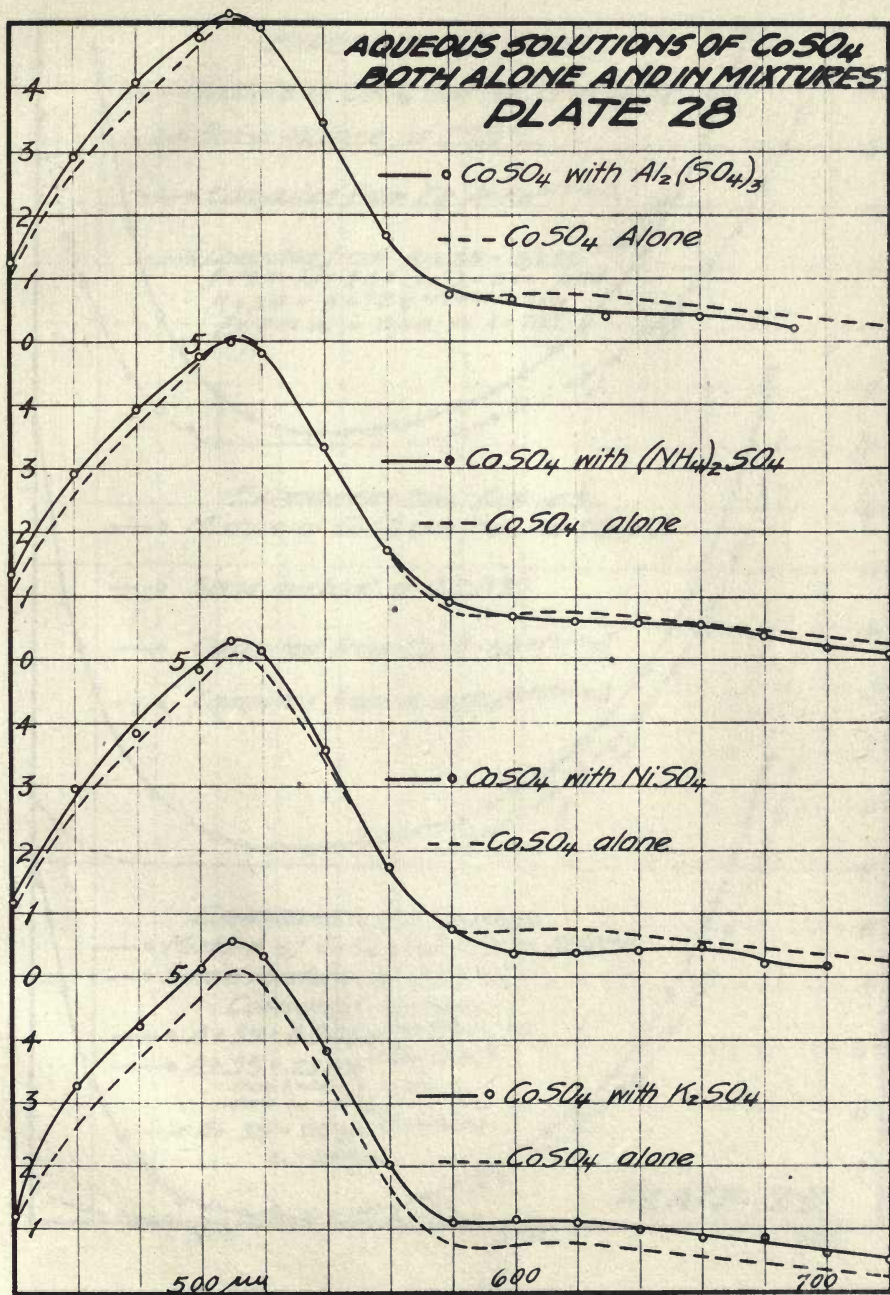
# PLATE 27

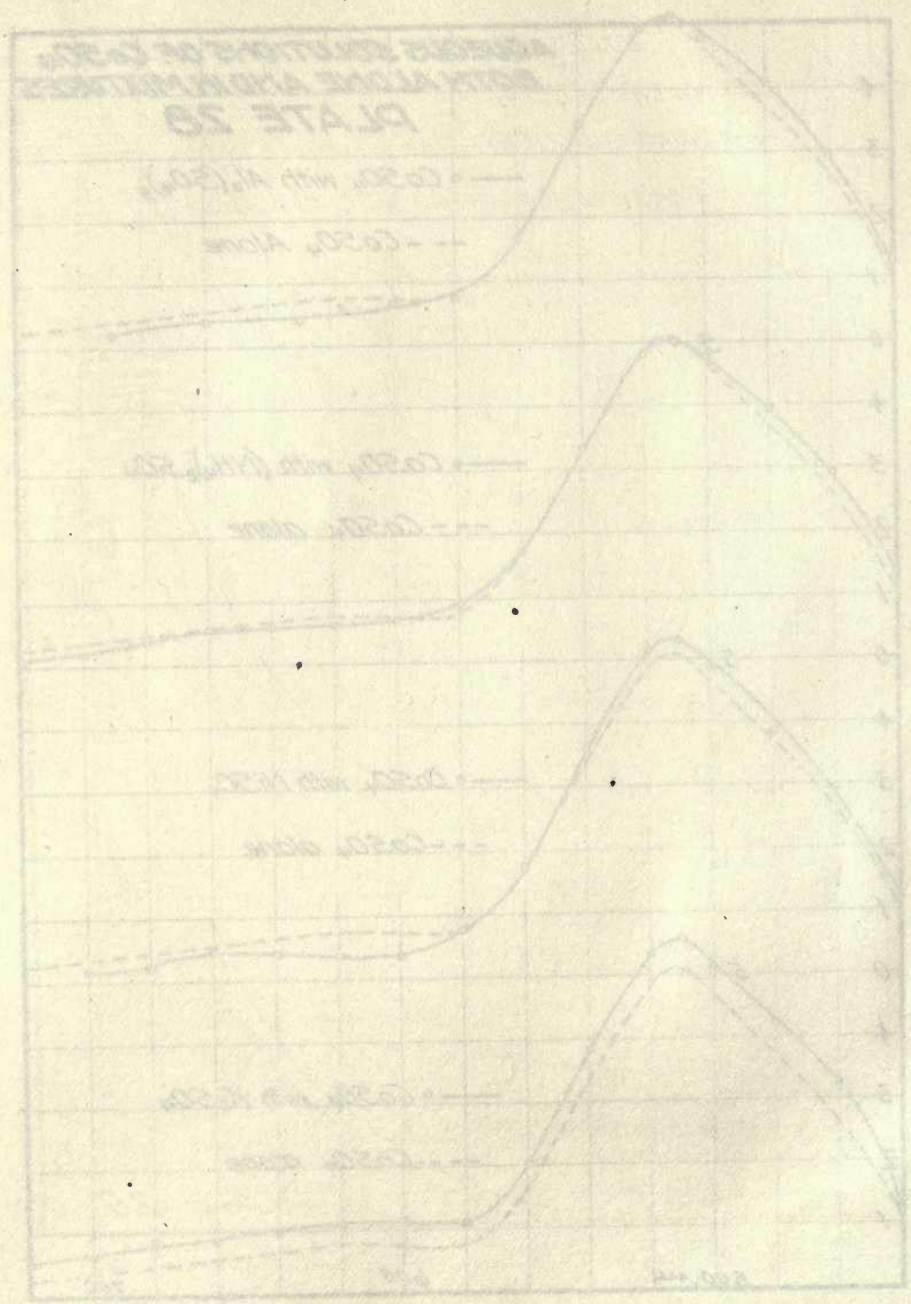
## AQUEOUS SOLUTIONS OF $\text{CuSO}_4$ BOTH PURE AND IN MIXTURES

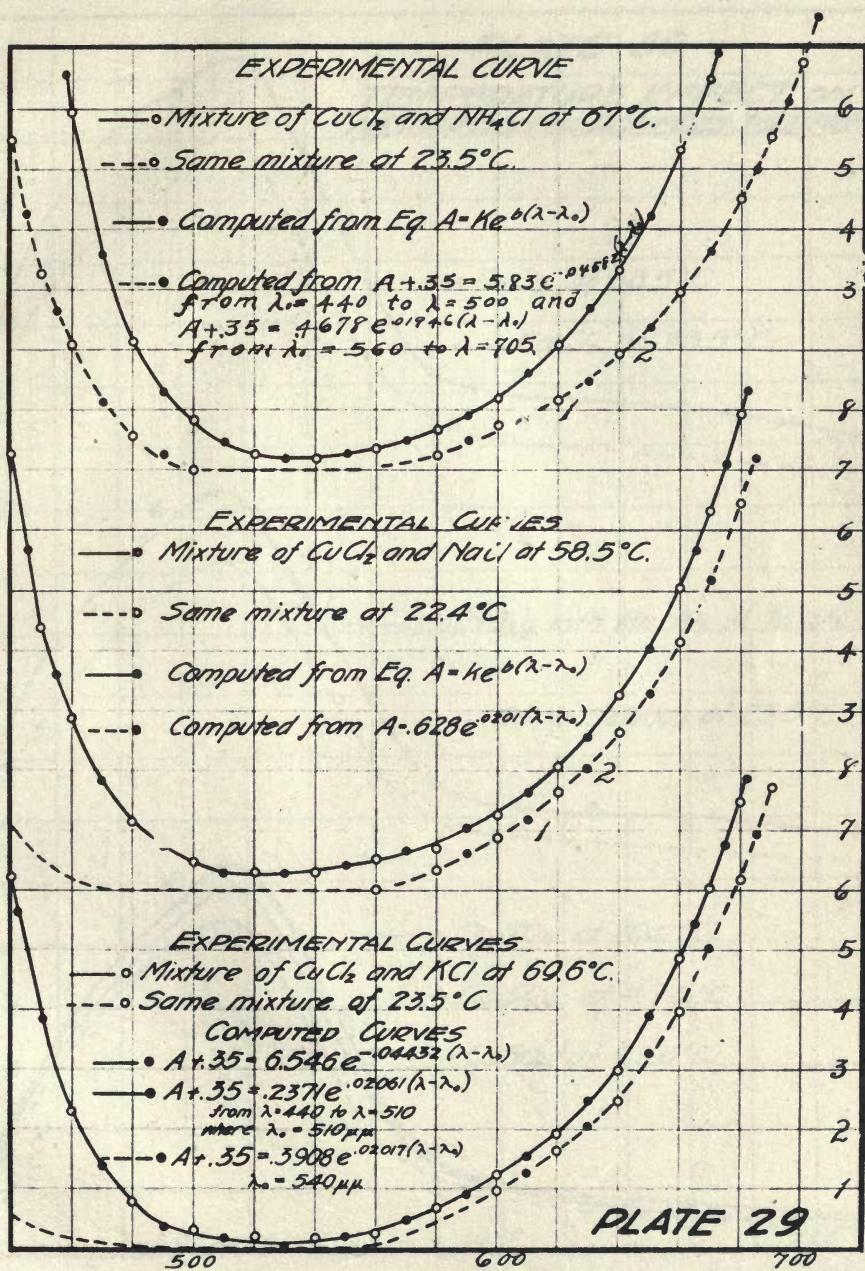




**AQUEOUS SOLUTIONS OF  $\text{CoSO}_4$   
BOTH ALONE AND IN MIXTURES  
PLATE 28**





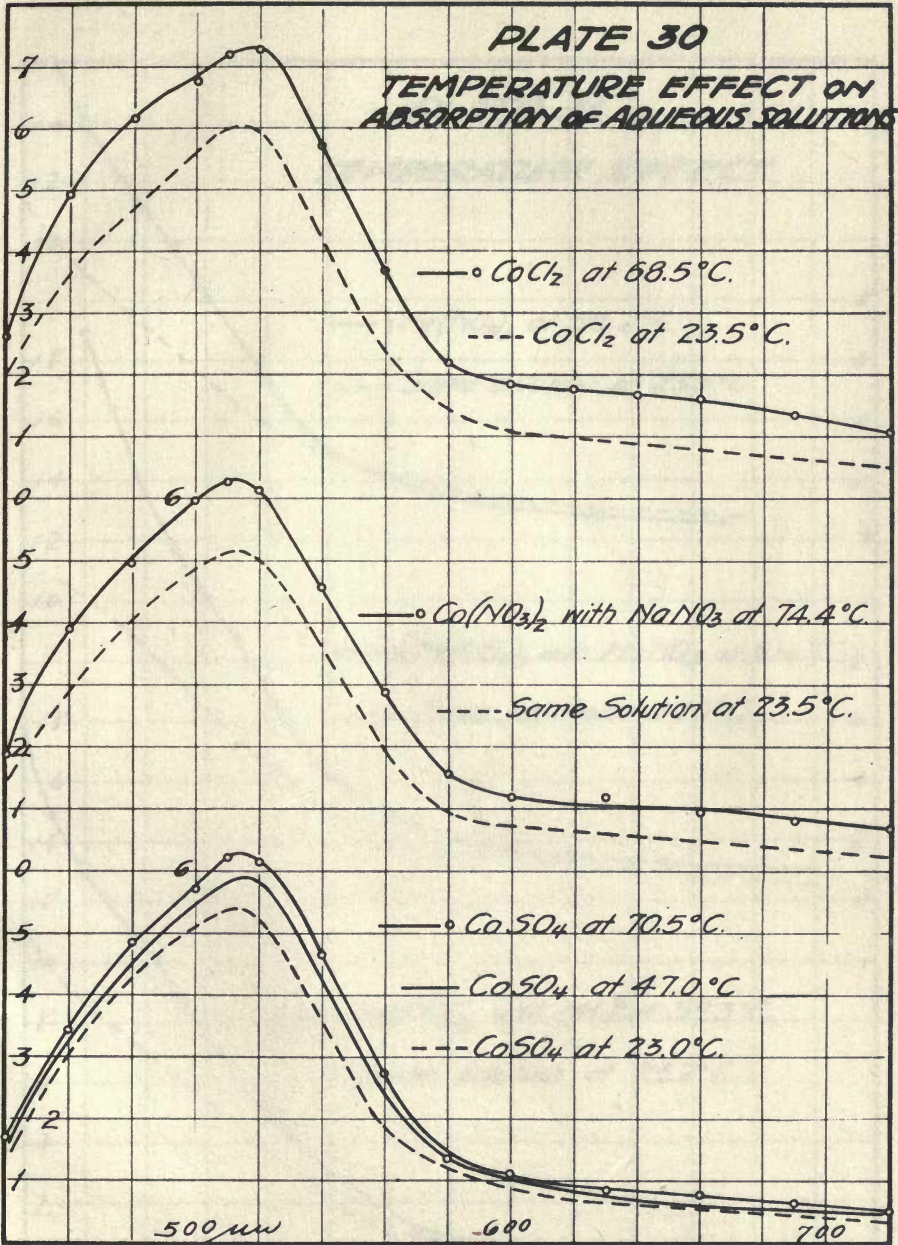






# PLATE 30

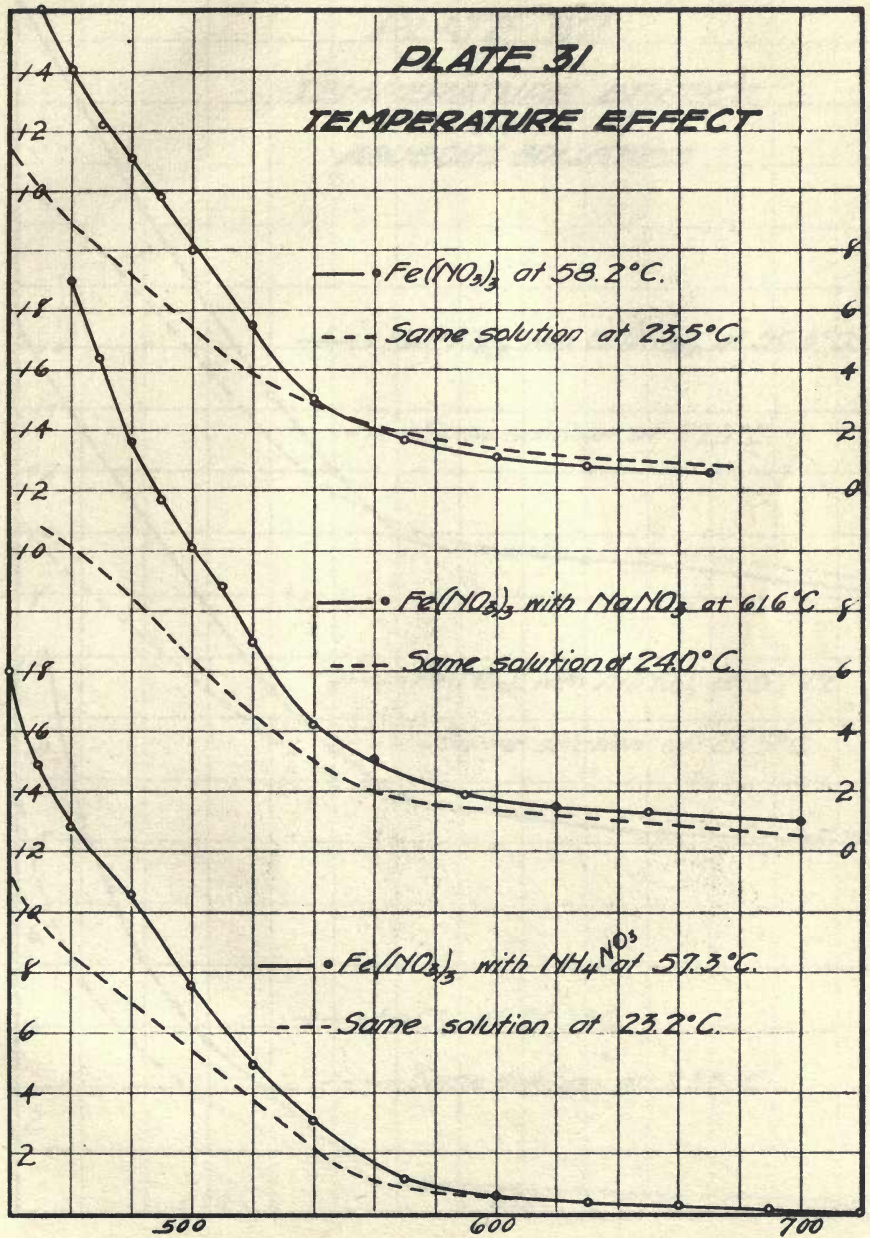
## TEMPERATURE EFFECT ON ABSORPTION OF AQUEOUS SOLUTIONS





# PLATE 31

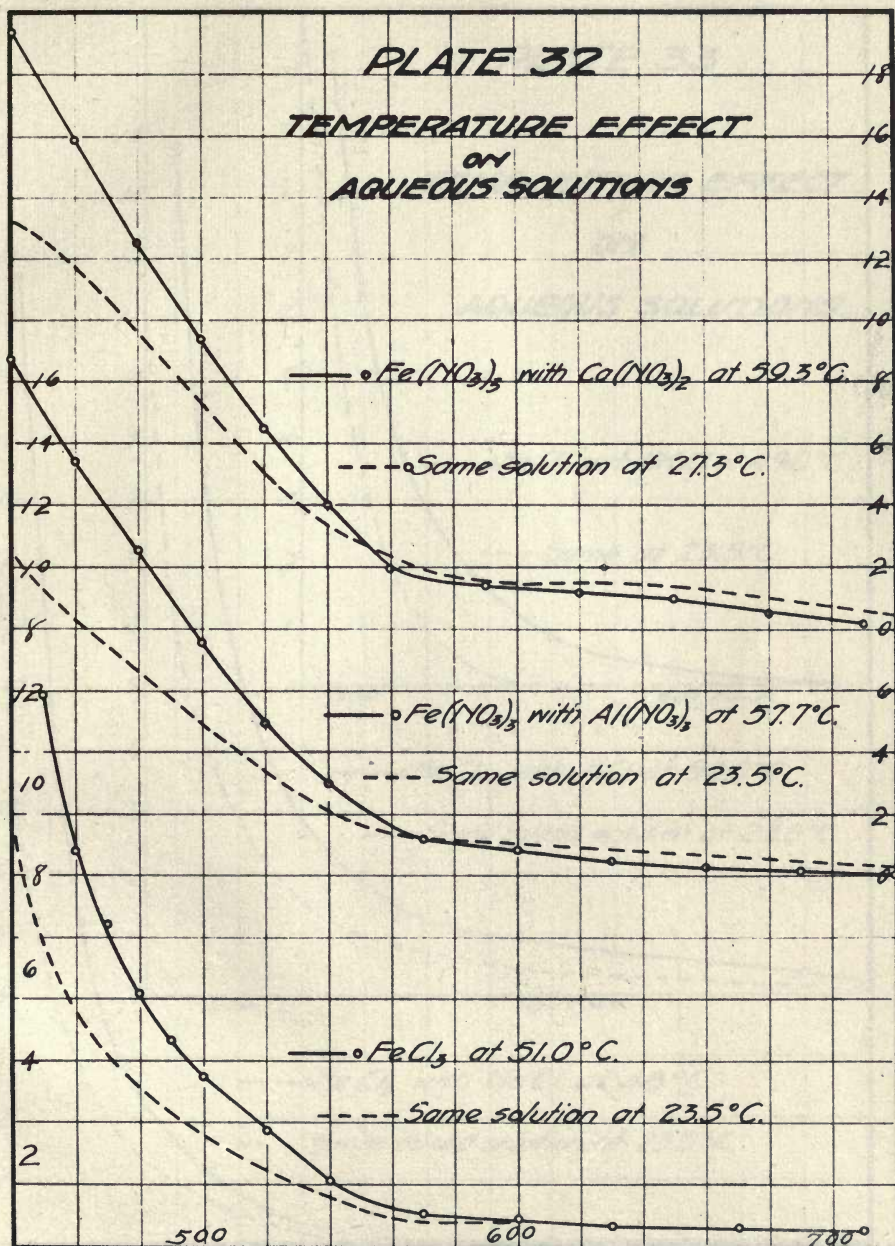
## TEMPERATURE EFFECT





# PLATE 32

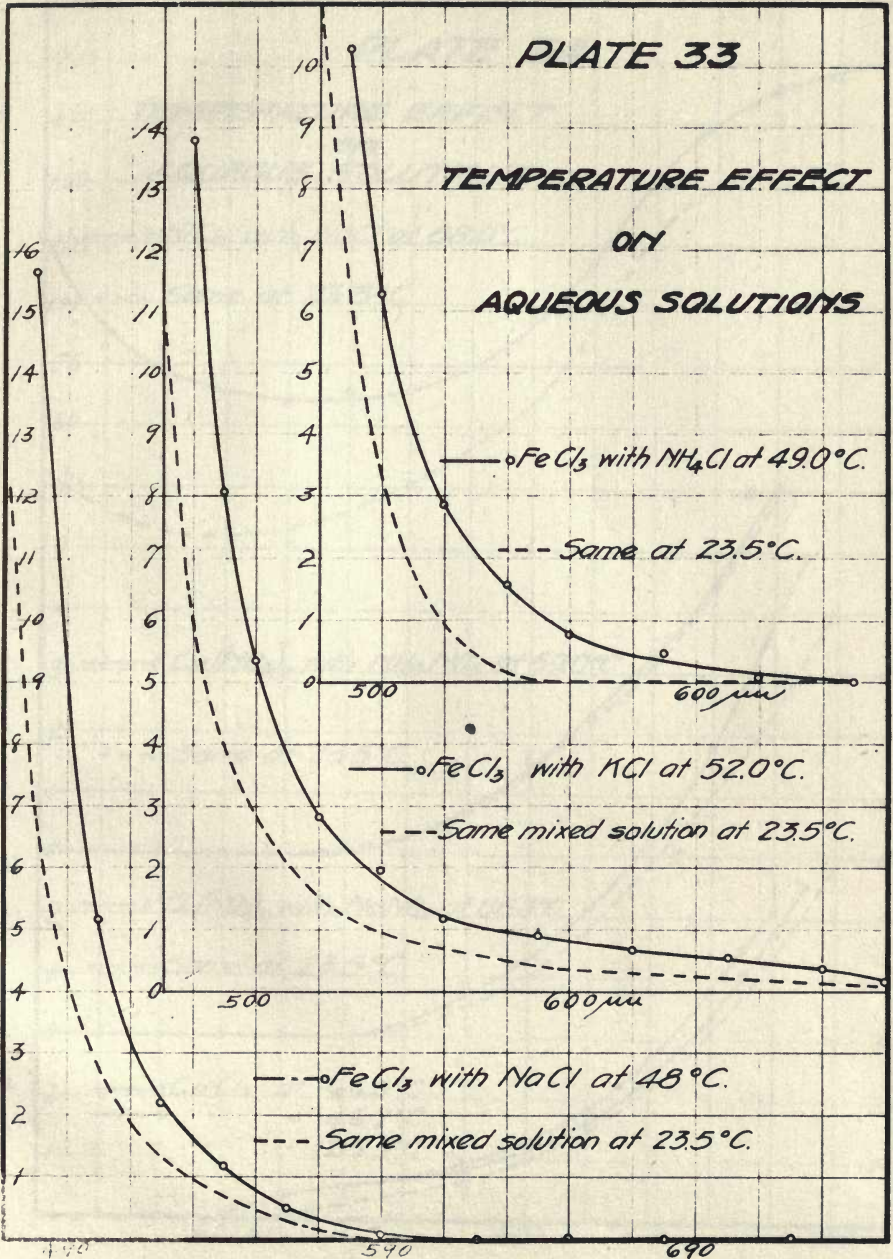
## TEMPERATURE EFFECT ON AQUEOUS SOLUTIONS





# PLATE 33

## TEMPERATURE EFFECT ON AQUEOUS SOLUTIONS



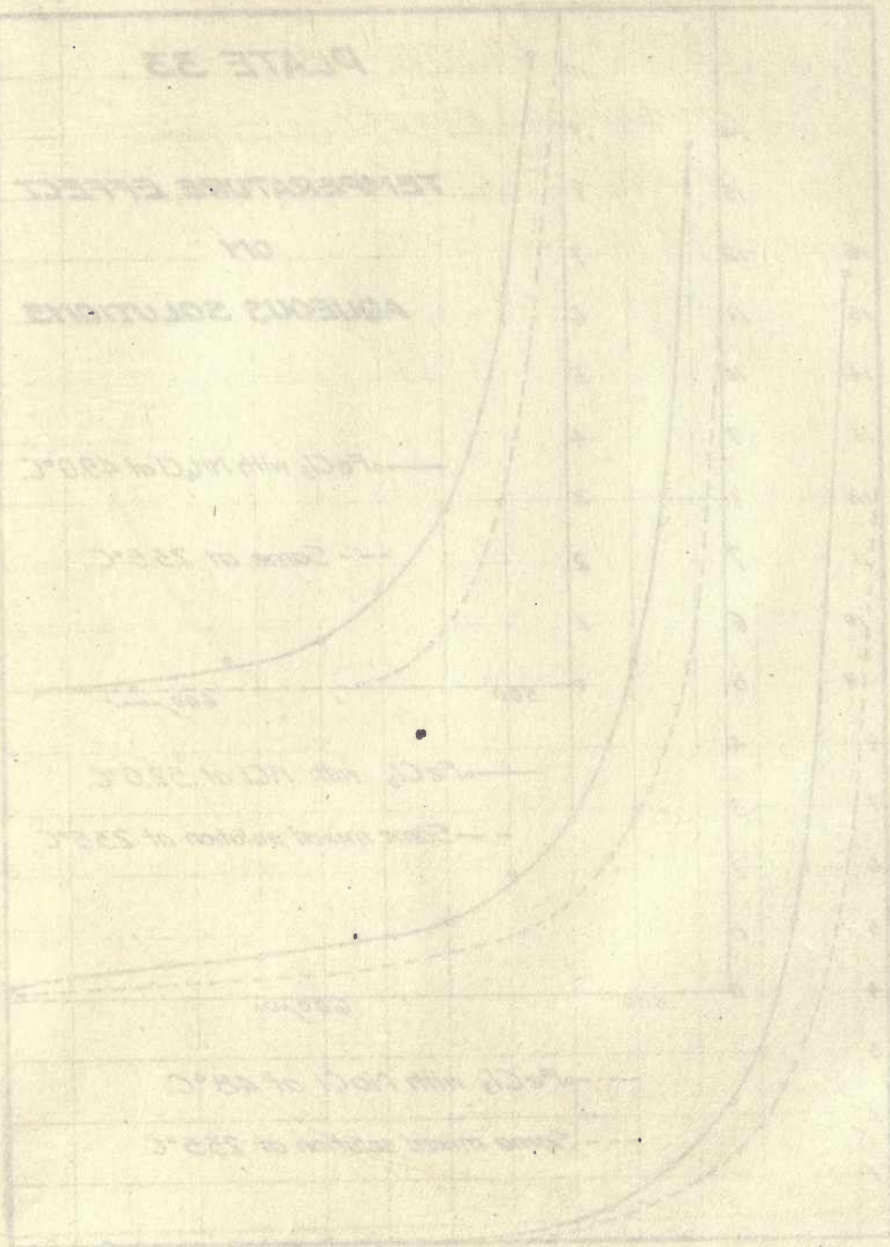
490

540

690

PLATE 33

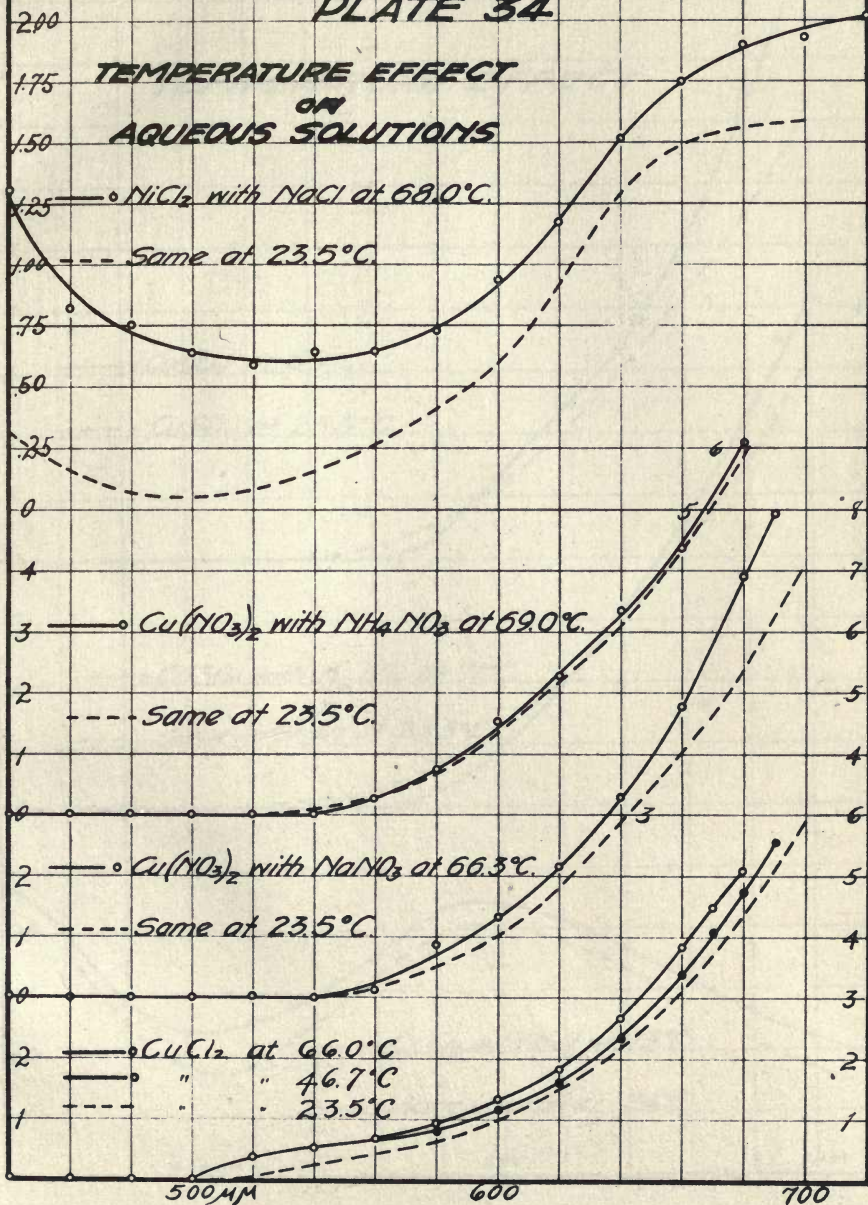
TEMPERATURE EFFECT  
ON  
AQUEOUS SOLUTIONS





# PLATE 34

## TEMPERATURE EFFECT ON AQUEOUS SOLUTIONS





# PLATE 35

## TEMPERATURE EFFECT

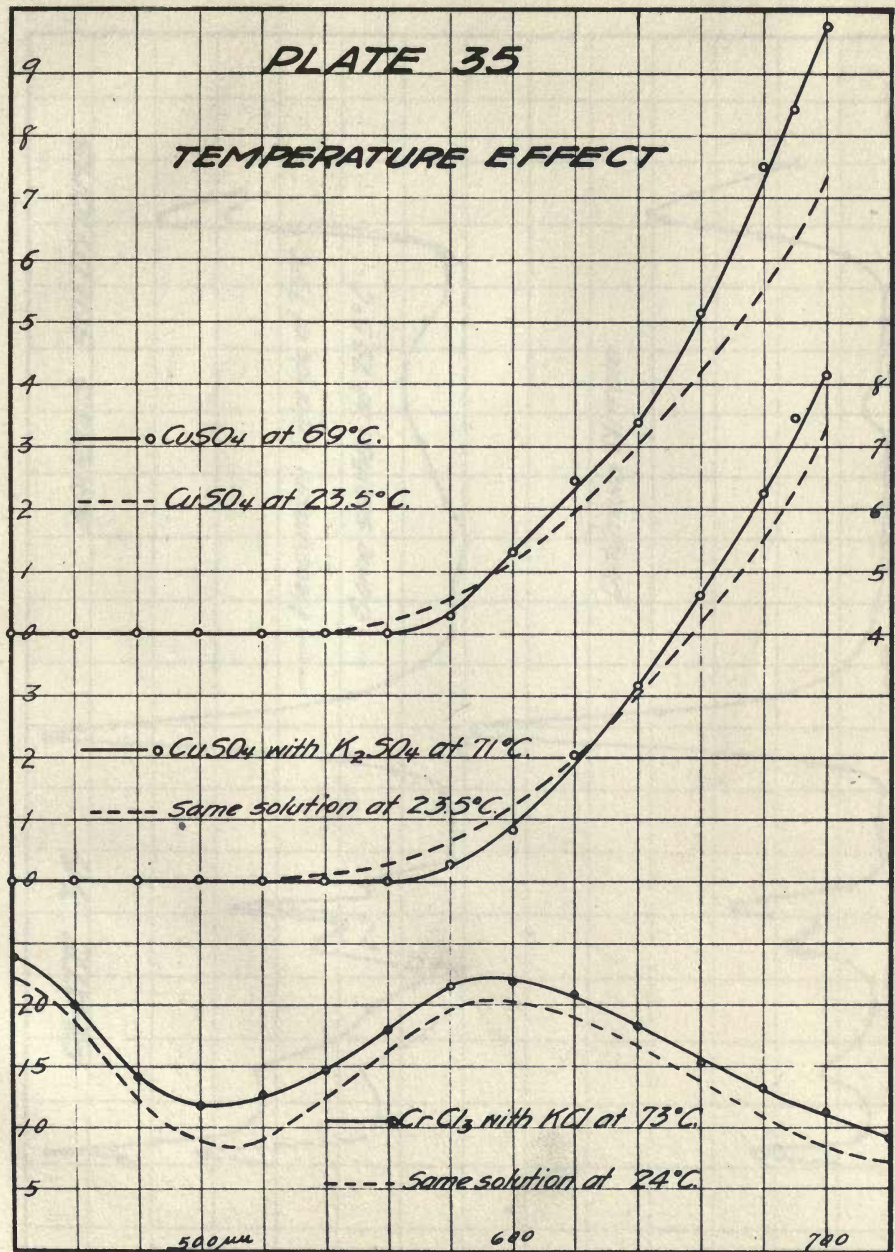
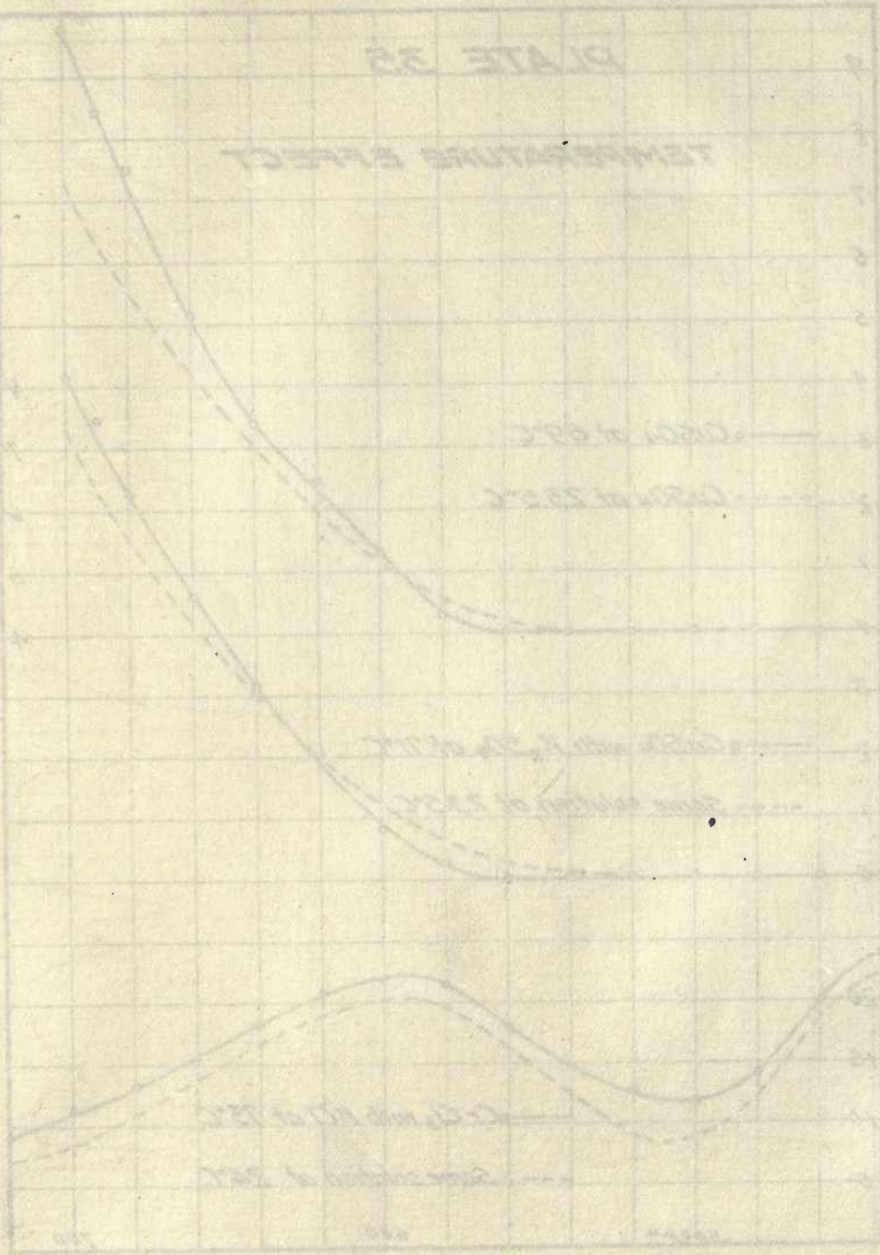


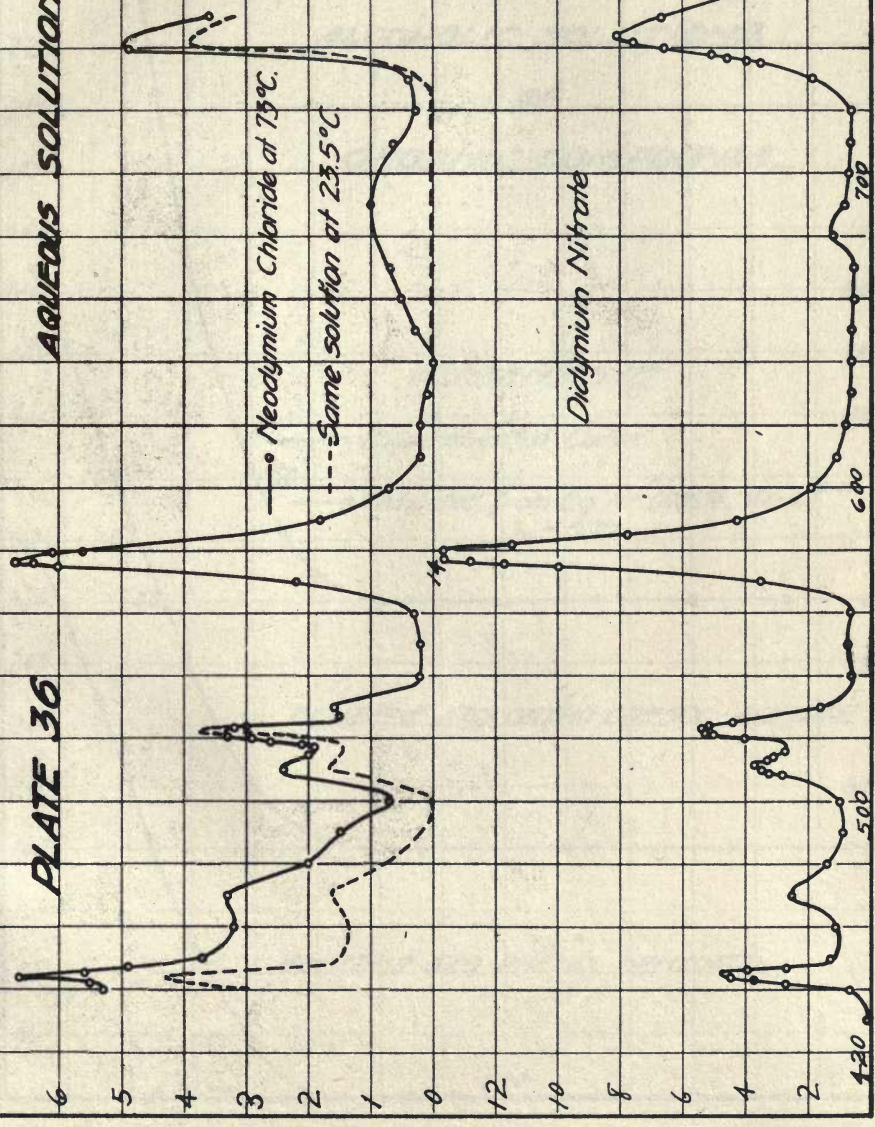
PLATE 32

TEMPERATURE EFFECT



**AQUEOUS SOLUTIONS**

**PLATE 36**





# PLATE 37

## ALCOHOLIC SOLUTIONS OF ORGANIC COMPOUNDS

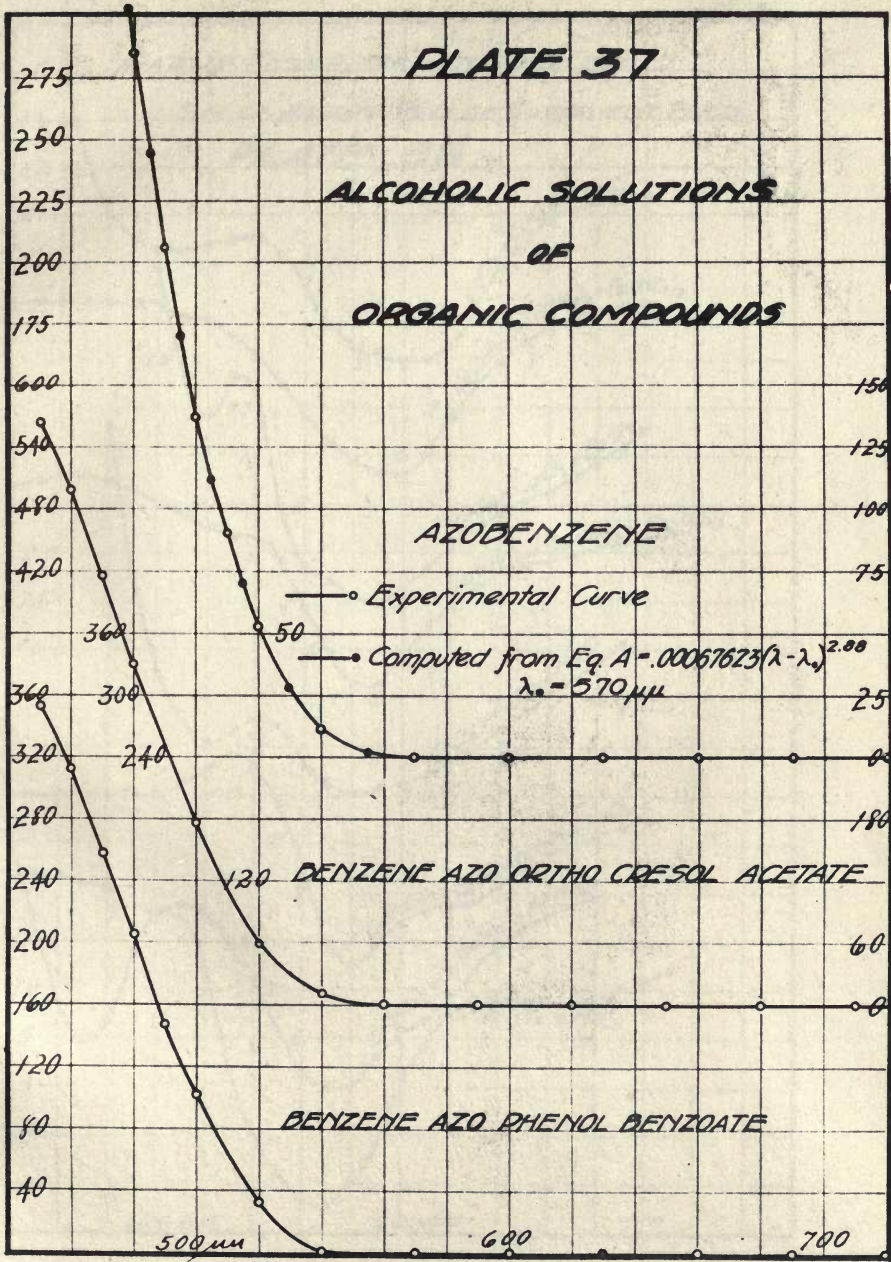
### AZOBENZENE

—○— Experimental Curve

—●— Computed from Eq.  $A = .00067623(\lambda - \lambda_0)^{2.00}$   
 $\lambda_0 = 570 \mu\mu$

120 BENZENE AZO ORTHO CRESOL ACETATE

80 BENZENE AZO PHENOL BENZOATE

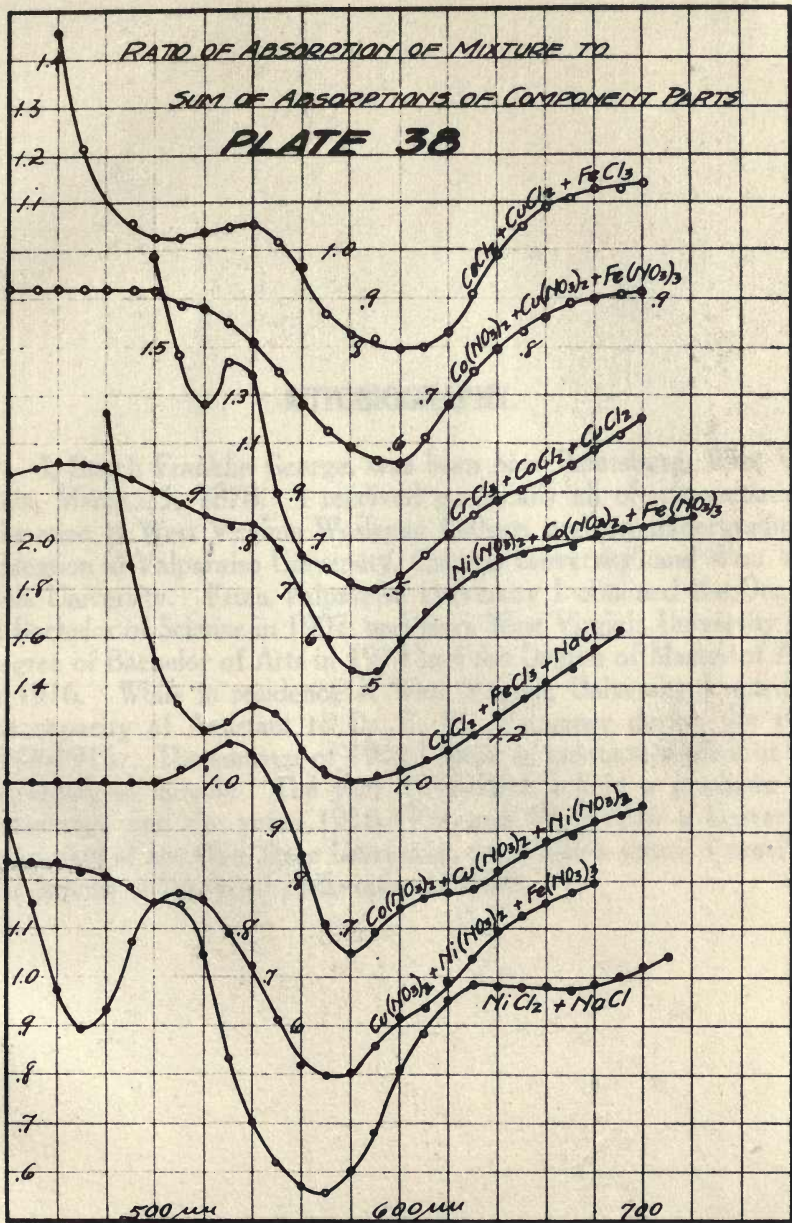






RATIO OF ABSORPTION OF MIXTURE TO  
SUM OF ABSORPTIONS OF COMPONENT PARTS

PLATE 38





## **AUTOBIOGRAPHY.**

I, Enoch Franklin George, was born near Petersburg, West Virginia, March 25, 1878. I received practically all of my secondary education at West Virginia Wesleyan College, and my undergraduate education at Valparaiso University, Chicago University, and West Virginia University. From Valparaiso University I obtained the Degree of Bachelor of Science in 1907, and from West Virginia University the Degree of Bachelor of Arts in 1914 and the Degree of Master of Arts in 1916. While in residence at West Virginia University I acted in the capacity of Assistant to Dr. C. W. Waggoner during the year 1914-1915. The summer of 1914 I spent as graduate student at the University of Illinois. The year 1915-1916 I held a graduate assistantship, and the years 1916-1917 and 1919-1920 a University fellowship at the Ohio State University, from which school I received the Degree of Doctor of Philosophy in 1920.





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