THERMAL ANALYSIS
OF THE SYSTEM
SODIUM HYDROXIDE-ROCHELLE SALT

by

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Being a thesis
submitted to the Committee
on Post-Graduate Studies of
the University of Manitoba in
candidacy for the Degree of
Master of Science.

April, 1938.

To Dr. A. N. Campbell
who directed this work and gave
invaluable assistance and advice
the writer wishes to express
his indebtedness and to
offer his sincere thanks.

PREFATORY NOTE.

It was originally intended to work on the Adsorption of Nitrogen by Manganese which would have been a continuation and extension of the work done by Mr. J. Royal in this laboratory last year. However, Mr. T. Martin, working in this laboratory, later disproved Mr. Royal's work and on the advice of Dr. A. N. Campbell the investigation of this problem was discontinued.

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- THEORETICAL. -

I. Historical Survey.

In the early days of organic chemistry many of the ideas and doctrines of inorganic chemistry were tacitly assumed to be true also for organic chemistry. Every inorganic substance had, or was assumed to have, its own distinctive composition, and the principle was applied to organic compounds.

1. Early Work of Faraday & Dalton.

That two substances might have the same composition and yet possess different properties was first clearly recognized by Faraday. It appears that in 1820 Dalton obtained by the distillation of certain fatty oils a hydrocarbon which combined with chlorine like olefiant gas, and he drew the conclusion that "most probably the atom of the new gas consists of two of olefiant gas". This suggestion was afterwards confirmed by Faraday, who in 1825 undertook an investigation into the nature of the oil gas, which was being manufactured, compressed into metal vessels and distributed among consumers. This compressed gas contained a considerable quantity of a liquid of low boiling point, from which Faraday isolated a hydrocarbon which had the same composition as olefiant gas but twice its density. Of this Faraday wrote: "In reference to the existence of bodies composed of the same elements and in the same proportion, but differing in their qualities, it may be observed that now we are taught to look for them they will probably multiply."

2. Work of Wöhler & Berzelius.

In 1828 Wöhler obtained urea which possessed the same composition as ammonium cyanate but different properties. The existence of substances of this character aroused a lively interest; for Berzelius, in his Jahresbericht for 1829, after describing the artificial preparation of urea, proceeds: "This fact opens the door to clearer views and indicates that the number of simple atoms may be distributed in the compound in various ways, and thereby give rise to compounds with different properties, as we have already begun to discover in other cases."

Two years later Berzelius, in studying an acid which had been found in the mother liquors from the manufacture of tartaric acid showed that it possessed the same composition as tartaric acid, but different properties, and named it racemic acid. In reference to his discovery of racemic acid in the Jahresbericht for 1831, Berzelius writes: "The absolute identity in composition of two compounds possessing different properties had now been positively established by the analysis of racemic acid, an acid of organic origin. This acid has the same composition, contains the same elements in the same atomic proportion, and possesses the same saturation capacity as tartaric acid." He proceeds to explain it by a different arrangement of the atoms, and points out that Mitscherlich's discovery of isomorphism must undergo a further extension, for as isomorphous bodies consist of different atoms similarly arranged in the crystalline state so the same atoms may be grouped in such a way as to produce different crystalline substances, which is the case with tartaric and racemic acid.

Thus the principles of isomerism became an established fact in organic chemistry, and, as Faraday had foretold, examples soon began to multiply.

As examples of isomerism became more and more numerous various theories were put forward to account for this behaviour.

II. Optical Activity and Asymmetry.

1. Optical Activity & Molecular Structure.

The theory of van't Hoff and Le Bel connects optical activity with molecular structure. Substances which are optically active in the fused state or in solution contain within the molecule at least one multivalent atom united to different elements or groups forming an unsymmetrical space arrangement. As four is the minimum number of material points demanded by any space arrangement in three dimensions the multivalent atom which unites the elements or groups must be at least tervalent. In the majority of carbon compounds the multivalent atom is carbon: but optically active compounds are known in which the central element of the system is nitrogen, sulphur, silicon, phosphorus or many others.

2. Optical Isomerism. Object and Mirror Image.

Every asymmetrical object, such as a glove, has its fellow but they are non-superposable. In the same way a substance containing a carbon atom, round which four different groups are distributed in three-dimensional space, is capable of existing in two forms which correspond to a left and right hand, or to an object and its mirror image.

The chief point of difference between two substances, having a space arrangement or configuration of their atoms corresponding to object and mirror image, lies in their action on polarized light, the one turning it to the right, and the other turning it to the left, when in the dissolved state. In the two cases the angle through which the light is turned is the same but is different in direction. In all other physical and chemical properties the two substances are identical. The two complementary active forms are variously termed active components, antipodes or enantiomorphs.

3. Van't Hoff's Theory.

Van't Hoff regards the carbon atom as possessing four valencies directed towards the summits of a tdtrahedron, of which it occupies the centre. If the groups represented by a, b, c, d, attached to these four bonds are different, then the substance will exhibit optical activity. Represented by space formulae the grouping is asymmetrical in the sense that it forms a figure which cannot be divided into exactly similar halves.

The central carbon atom of the group is termed the asymmetric carbon atom.

Such an asymmetrical group has a complementary form or mirror image possessing the reverse rotation. According to the theory all optically active compounds contain an asymmetric carbon atom.*

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* Excluding for the present compounds such as $Co[(OH)_2Co(NH_3)_4]_3Br_6$ prepared by Werner and shown to possess optical activity.

A great many compounds known to be optically active have been studied and in every case they contain one or more asymmetric carbon atoms. It appears to be the exception rather than the rule that the substance will be active in both the solid and the liquid states. There is, however, no necessary connection between the activity of the two states, and it may be noted that stereo-isomerism is concerned with the activity of the liquid or dissolved substance, and not with that of the solid.

4. Loss of Optical Activity.

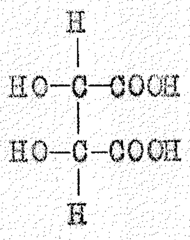
If a compound containing an asymmetric carbon atom is so treated that the carbon is no longer asymmetric, then the compound is no longer active. Further it should be pointed out that where one group replaces another so that asymmetry is preserved, the product is not always active. This fact is accounted for by the compound undergoing during the process, what is known as racemisation.

5. Some types of Optical Inactivity.

However, the presence of an asymmetric carbon atom does not necessarily mean that the compound will be optically active. The compound may consist of equal quantites of the two optically active varieties, in which case the activities will be neutralized and the substance will appear to be inactive.

In certain cases the two active varieties crystallize together, forming a product which has physical properties distinct from those of either constituent. Such a compound is called racemic. Such differences disappear in solution, and the substance then behaves like a mixture.

There is another type of optical inactivity which is entirely different in origin. It depends upon the presence in the molecule of an even number of similar asymmetric carbon atoms, that is, carbon atoms to each pair of which a similar set of groups is attached. As an example take the structural formula of tartaric acid, as shown, there are two asymmetric carbon atoms present in the molecule. Each asymmetric carbon atom is attached to similar groups. Suppose that each asymmetric carbon atom with its associated groups brings about a certain rotation in a given direction. The following combinations of the two asymmetric groups may be imagined. Both produce dextro-rotation or both produce laevo-rotation. The mixture of the two will produce inactive racemic acid. Then racemic acid is said to be inactive by external compensation. If instead the two asymmetric groups produce rotation in opposite directions then the compound is said to be inactive by internal compensation. In this way two types of compounds may be produced. Those which are inactive by internal compensation and those which are inactive by external compensation.



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{HO-C-COOH} \\ | \\ \mathrm{HO-C-COOH} \\ | \\ \mathrm{H} \end{array}$$

The inactive compounds mentioned above may, with the exception of those compounds which are inactive by internal compensation, be resolved into their active components. Various methods may be used for this but they need not be gone into for the purpose of this paper.

6. Racemisation.

The reverse process, whereby an active substance is rendered inactive, is frequently met with. The partial or complete conversion of optically active substances into inactive mixtures of the same constitution is known as racemisation. That the change is not due to the formation of some structurally different and inactive compound has been shown many times by the resolution of the product of racemisation into its originally active components.

Racemisation may be effected with varying degrees of ease under the influence of heat, acids, alkalis or other reagents. Racemisation seems to occur more readily when substances are in the act of formation than when they are already formed. In a few cases the change proceeds of itself in the apparently pure compound, the optical activity being completely lost in the course of time; the phenomenon being then known as auto-racemisation.

The mechanism of racemisation is capable of various interpretations. Van't Hoff points out that in the conversion of one stereoisomer into the other, where the stability is slight, equilibrium will be attained when the inactive mixture is formed; for it follows from the complete mechanical symmetry of the two isomers that the tendency to conversion is equal in both, and consequently the one present in large quantity will always be converted in larger quantity until equal quantities of each are present.

III. The Phase Rule and the Temperature-Composition Diagram.

1. Introduction.

It was known in the last quarter of the eighteenth century that chemical reactions do not take place completely in one direction, but go so far and then stop. However it was not until the last quarter of the nineteenth century that a theorem which was not weakened by any assumptions as to the constitution of matter was put forward by Willard Gibbs. By means of this rule we can state under what conditions a system will be in equilibrium and it also serves as a guide to the similarities and differences existing in different systems.

Before this time Guldberg and Waage, by means of the Mass Action Law, were enabled to summarise the conditions of equilibrium in many cases of both homogeneous and, with the help of certain assumptions, of heterogeneous equilibrium. However, since this theorem was based on certain assumptions as to the nature and condition of the substances taking part in the reaction, it was not satisfactory when applied to those systems in which neither of the above requirements was known.

Ten years after the Law of Mass Action was propounded by Guldberg and Waage, Willard Gibbs brought forward the Phase Rule. In this theory of equilibrium there are no assumptions as to the molecular condition of the participating substances. In deducing the law of equilibrium, Gibbs regarded a system as possessing only three independently variable factors--temperature, pressure and the concentration of the components of the system--and he enunciated the general theorem now known as the Phase Rule, by which he defined the conditions of equilibrium as a relationship between the number of phases and the components of the system.

2. Statement of the Phase Rule.

The Phase Rule may be stated as follows: A system consisting of n components can exist in $n + 2$ phases, only when the temperature, pressure, and concentration have fixed and definite values: if there are n components in $n + 1$ phases, equilibrium can exist while one of the factors varies, and if there are only n phases, two of the varying factors may be arbitrarily fixed. This may be more concisely put in the form of an equation:

$$F = n - r + 2$$

where F denotes the variability of the system, n is the number of components and r is the number of phases. From the equation it can be seen that with increase in the number of the phases, the condition of the system becomes more and more defined.

3. Discussion of the Cooling Curves.

(a) General.

In the system under investigation, NaOH and Rochelle Salt, there are two components and they are both solid at the ordinary temperature. When such a state of things exists the best way of determining the equilibrium curve or the freezing point curve is to determine the freezing points of homogeneous liquid mixtures of different initial compositions or the temperatures at which the solid phase begins to crystallize out from the liquid mixture.

When a pure substance in the fused state is allowed to cool slowly and the temperature noted at short intervals of time the curve obtained showing the relation between time and temperature will be a smooth continuous curve. When the freezing point is reached, solid will begin to separate out and the temperature will remain constant until complete solidification has taken place, that is, supposing that there is no super-cooling. From this point on the fall of temperature will again be uniform.

If a solution is allowed to cool slowly and the temperature determined as above a smooth curve is again obtained as long as the solution is completely liquid. When a solid phase begins to be formed, heat is evolved and this will cause the rate of cooling to alter. On the cooling curve then, there will be a break or a change in direction at the freezing point of the solution. As more and more of the solid phase separates out the composition of the residual solution will alter, therefore the temperature will not remain constant but will gradually fall until the eutectic point is reached. At this point a second solid phase is formed and the system becomes invariant; supposing that there is no super-cooling; and the temperature will therefore remain constant until complete solidification has taken place. From then on the fall of temperature will again become uniform.

The length of time during which the temperature remains constant at the eutectic point is known as the eutectic halt. The length of the eutectic halt will depend on the amount of solution which remains unsolidified when the eutectic point is reached. If equal amounts of solution are taken, having different initial composition, then it can be seen that the time of the eutectic halt will be greatest when the composition of the solution is the same as the composition existing at the eutectic point.

If one obtains the cooling curve of different mixtures and notes the arrest points, that is, the points where a break in the curve occurs, it is possible to map out the equilibrium diagram of the system. Also from the cooling curve information can be obtained as to the nature of the solid phases. When one plots the duration of the eutectic halt against the original composition of the mixture and obtains a simple curve with the time maximum at the eutectic composition then it is certain that the pure components occur only as solid phases.

(b) Thermal Analysis.

The method of following the nature of a mixture as the temperature is lowered, briefly outlined above, is known as the method of thermal analysis. The method may be summarised as follows:

Mixtures of the two components in various proportions are made up, melted, and cooled down slowly and the temperature obtained at short intervals of time. From the data obtained a curve is plotted showing the relation between time and temperature. From this curve the melting point, the point where the curve first breaks; and the point of complete solidification, the point where the curve breaks again to resume its normal course; is obtained. These two points are then transferred to a separate graph where they are plotted against the original composition of the solution. From the shape of the curve so obtained it can be determined whether the solid components occur in the pure state or whether they form a compound.

(c) Types of Curves Obtained.

(i) Components do not form a compound.

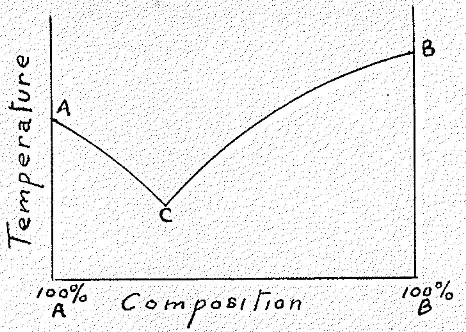


Fig. 1

If the components do not form a compound the equilibrium curve assumes the general form shown by the diagram. A is the melting point of pure A, B is the melting point of pure B, and C is the eutectic point, at which point a eutectic conglomerate composed of certain proportions of A and B separate out. The curve AC gives the composition of solutions of A and B in equilibrium at different temperatures with A as the solid phase. The curve BC gives the composition of solutions in equilibrium at different temperatures with B as the solid phase.

(ii) Components from a compound with a congruent melting point.

When the two components can form a stable compound with a congruent melting point a third equilibrium curve, that for compound in equilibrium with liquid solution, must be added to the two curves already discussed. A compound with a congruent melting point is one that can exist as a solid compound in equilibrium with a liquid of the same composition. Since the compound has a definite melting point this temperature will be a maximum on the equilibrium curve since the melting point of the compound will be lowered by dissolving in the solution either of the pure components. The general form of the equilibrium curve is given by the following figure:

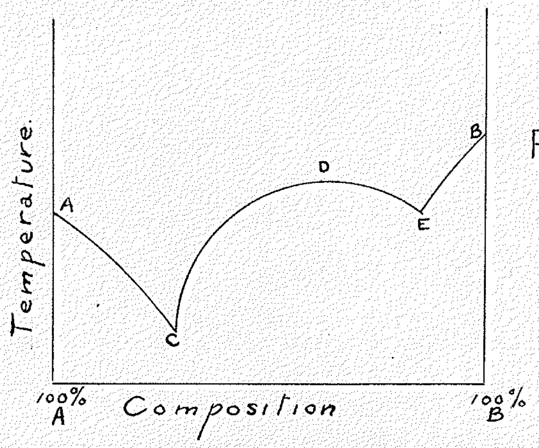


Fig. 11

A is the congruent melting point of pure A, B is the congruent melting point of pure B, and D is the congruent melting point of the compound, which may be given the formula A_xB_y. The curve AC gives the composition of solutions of A and B in equilibrium at different temperatures with the component A as the solid phase. The curve EB gives the composition of solutions of A and B in equilibrium at different temperatures with the component B as the solid phase. And the curve CDE gives the composition of solutions in equilibrium with the compound as the solid phase. C and E are the eutectic points at which solid A and compound and solid B and compound can exist in contact with solutions of definite composition. If it is possible for more than one compound with congruent melting point to form, then a series of curves similar to curve CDE will be obtained, one curve for each such compound. As in the case of the curve CDE the maximum point on the curves will give the composition of the compounds. If there is a sharp bend to the curve CDE it means that the compound is dissociated to a considerable extent in the liquid state. The flatter the curve the less is the degree of dissociation. Thus from the shape of the curve it is possible to obtain the degree of dissociation of the compound in the liquid state approximately.

(iii) Components form a compound with an incongruent melting point.

However the compound formed may not have a congruent melting point, but it may undergo decomposition with formation of another solid phase at a temperature below the congruent melting point of the compound. Such a compound is spoken of as having an incongruent melting point. If such a compound exists then the equilibrium diagram will take the form shown in the figure below:

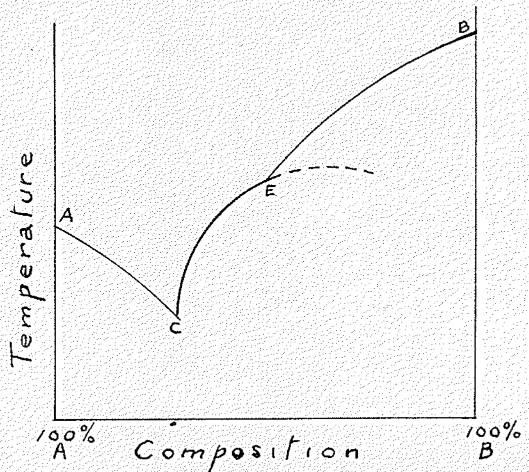


Fig. III

The dotted continuation of the curve CE indicates that the compound is unstable along this portion of the curve. The summit of the curve would be the congruent melting point of the compound. However before this temperature can be reached the compound undergoes decomposition into another solid phase and liquid at the point E. The new solid phase may be another compound or it may be one of the pure components. The liquid which is formed by the decomposition of the compound, which may again be represented by the formula A_xB_y, has not the same composition as the compound itself. Therefore the compound is spoken of as having an incongruent melting point. The point E represents the limit of existence of the compound under the particular constant pressure which is assumed. If it is possible for a series of compounds to form, each of which possess an incongruent melting point, then a series of curves similar to the curve CE above will be obtained, none of which will possess a temperature maximum and there will be only one eutectic point.

Since the compound does not possess a congruent melting point the temperature maximum on the equilibrium curve will not be obtained and it is not possible to determine the composition of the compound from the freezing point curve or the equilibrium curve alone. However in this case the method of thermal analysis may be used.

IV. The Method of Cooling.

1. Method of Tammann.

The method of cooling used was the one developed by Plato. The older method used by Tammann[1] (1905) was the method of free cooling. That is he took a mixture which he desired to investigate, put it in a furnace fitted with a thermocouple and raised the temperature until all was molten. Then the heating was cut off entirely and the melt allowed to cool. Temperature readings were then taken at intervals of time. Tammann's method has the advantage that it is very rapid as the furnace cools off in a very few minutes. Cooling takes place according to Newton's law of cooling and plotting the results a curve such as is shown in figure four is obtained.

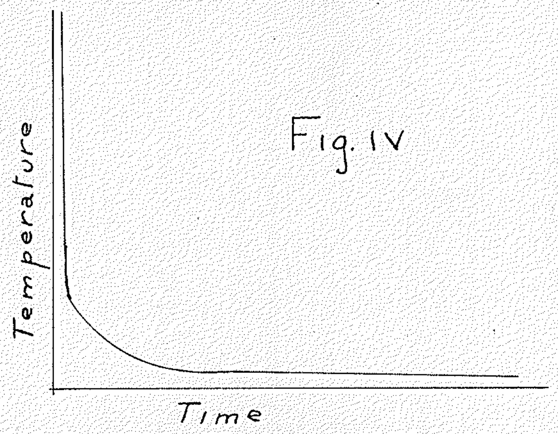


Fig. IV

Such a curve would be obtained in the case of a body which is cooling down, and in the process no change is taking place. It is a straight case of cooling, no solidification or any other phenomena takes place.

2. Method of Plato.

Plato[2] however, used a slightly different method to that of Tammann. He attached to the furnace a rheostat, and instead of switching the current off completely when he wished to cool the furnace down he progressively increased the resistance by moving the slider on the rheostat along a certain measured distance at constant intervals of time and then taking the temperature readings. Then the cooling mass, provided nothing happens such as solidification, would give a curve like this on plotting temperature against time:

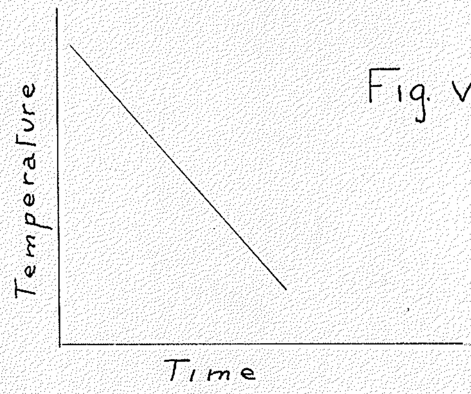


Fig. V

On a curve like this it would be much easier to spot the point at which any change takes place in the melt. It would show up as an outcrop or a kink in the curve. If the heat evolved in the process was small it might be completely overlooked using Tammann's method of cooling because it is much more difficult to distinguish a slight change of direction in a curved line than it is in a straight line as is obtained above.

3. Types of Curves Obtained Using Plato's Method.

Using Plato's method of cooling the following types of curves can be obtained.

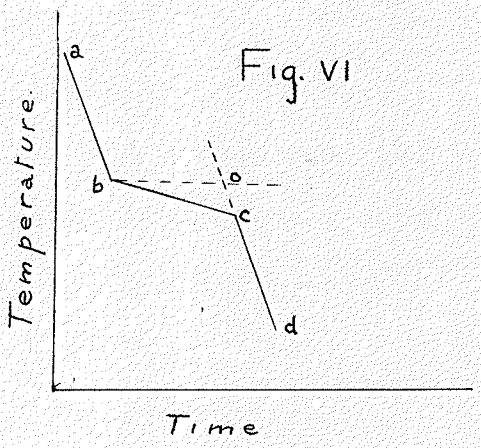


Fig. VI

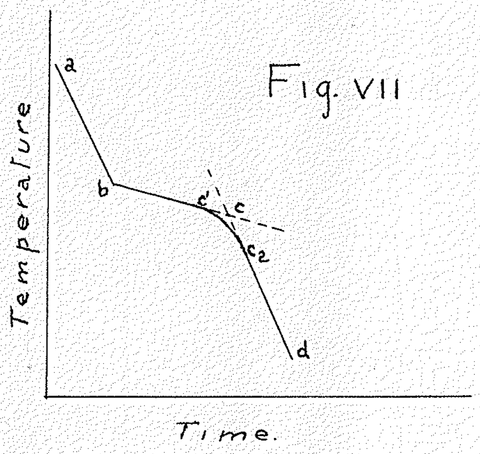


Fig. VII

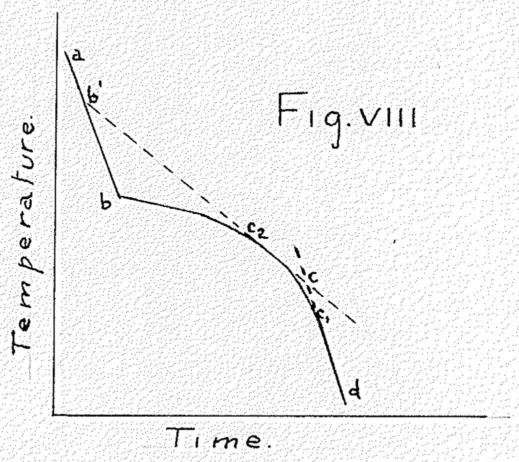


Fig. VIII

Figure VI represents the ideal case. The temperature readings are started at the point "a". Cooling is uniform until the point "b" is reached and here the first trace of solid makes its appearance. From here cooling continues along the line "bc" until the point "c" is reached. At this point everything has been completely converted to solid. And from here on the cooling is again uniform. The temperature of "b", which is the temperature at which solidification commences, and the temperature of "c" at which solidification is complete, are readily obtained from the diagram and can be plotted on the phase diagram. Also the composition of the original mixture is known so three points are known which may be plotted on the phase diagram. The points "c", "b", and "x", where "x" is the original composition of the mixture. Further the solidus and the liquidus lines must meet at the melting point. The time of eutectic halt can also be obtained by producing "cd" back and drawing a horizontal from "b" to meet "cd" produced. The time of the eutectic halt will be measured by the length of the line "bo". Using mixtures of various original compositions the complete phase diagram may be built up.

However, using Plato's method of cooling one will usually get a curve like that shown by figure VII. Theoretically cooling should follow along "c_1c" but instead it follows along "c_1c_2". At "c_2" all is solid, this point corresponds to "c" on the ideal diagram. Further cooling follows along "c_2d". Producing "c_2d" back and "bc_1" out to meet it the point "c" is obtained, which is the point which would have been reached if the cooling had not taken place irregularly towards the end of the crystallization. This point "c" gives the true temperature of complete solidification. The point "b" is called the solidifying point although by no means is everything solid at this point. It is the temperature at which the first particle of solid makes its appearance.

Figure VIII is the kind of curve which is obtained when a little super-cooling takes place. In this case a temperature below the point "b", the solidifying point, is reached before the curve breaks. The heat of fusion is then given out so that the first point "bc_2" is almost horizontal owing to the delayed heat of fusion being suddenly liberated. Then a straight portion following "c_2" is obtained, which then rounds off to a shoulder down to "c_1" as before. Extrapolating back "c_1d" and also extrapolating the straight portion containing "c_2" until it meets "c_1d" produced, will give the point "b'", the temperature at which the first trace of solid would have made its appearance if super-cooling had been absent.

V. <u>The Softening-Melting Point Method of Investigating Binary Systems.</u>

1. Disadvantages in the Use of Thermal Analysis.

In non-metallic systems thermal analysis meets with many objections. In the system under investigation at about 40% Rochelle Salt the system had become very viscous which would lead to the danger of super-cooling taking place. In addition to the above objection, there is another drawback to the use of thermal analysis although it does not apply in the present case. This is that thermal analysis requires large quantities of the substances under investigation for the successful investigation of the system. In many cases sufficiently large quantities are not available.

This method, the softening melting point method for the investigation of binary systems, was developed by Heinrich Rheinholdt,[3] and he considers three cases.

2. Types of Curves Obtained.

For the present let us assume that the components in the molten state are completely miscible. As a second assumption let us assume that the solids are mutually insoluble, that is, that they do not form solid solutions. Then we will only have pure component A, pure component B, and pure compound if a compound is formed.

(a) The components form no compound with one another.

The discussion will be easier to follow by making use of this diagram:

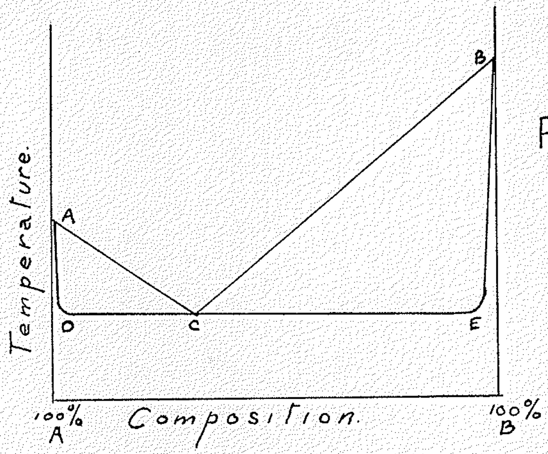


Fig. IX

In the area above the curve ACB all is liquid. The area ADC is the area of component A + melt, the area CEB is the area of component B + melt, and the area below the horizontal DCE all is solid.

For such a diagram as the above there will be only three points at which a sharp melting point occurs. That is the point representing pure A, the point representing pure B and the point representing a eutectic mixture of A and B. All other mixtures will melt with previous softening. For every mixture, theoretically, melting will commence at the temperature of the eutectic. No matter what the composition of the mixture is as a whole, a certain percentage of it will have the composition of the eutectic. The mixture will not melt as a whole, but only that part of it which can be looked upon as having the eutectic composition will melt at the temperature of the eutectic. Due to this partial melting the whole mass takes on a dewy appearance. This is the softening point. This softening will always take place at the eutectic temperature no matter what the original composition of the mixture was. The mixture begins to melt at the eutectic temperature. It will be completely molten when the temperature passes the liquidus line, that is, the line ACB, and every mixture will have a different melting temperature. So by applying the softening point and the melting point one can obtain an outline of the liquidus curve and a horizontal at the temperature of the eutectic. When the mixture consists of almost pure A or pure B, that is, when one is well over to the left or the right of the diagram, owing to the fact that the proportion of the mixture having eutectic composition is so small the temperature is certain to go past the temperature of the eutectic before any dew can be detected by the eye, because the amount of "dew" formed will be so small. So that just before reaching the limits of the diagram the softening curve ascends abruptly.

(b) The components form a compound with congruent melting
    point.

In this case a diagram such as the following is obtained:

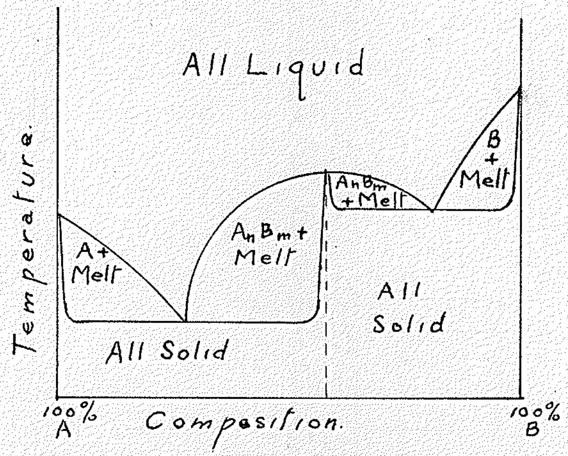


Fig. x

The various stable systems are represented in the areas in which they are stable. From the diagram it can be seen that there are now five points at which melting will occur at a definite temperature in contrast to only three points in the case of a simple eutectic. The five points are as follows: melting point of pure A, melting point of pure B, melting point of the compound which may be represented as A_nB_m, and the two eutectic points. Therefore at these points the softening line will always meet the melting line. By determining the eutectic horizontals even by a few experiments, the softening curve would give a definite answer to the question as to whether or not a compound was formed. If a few experiments were done with various mixtures and only one horizontal was obtained then it would be certain that the two components did not form a compound. However if two eutectic horizontals were obtained then one would be able to say definitely that a compound was formed. Doing a few more experiments in the region where the eutectic horizontals approach one another would give the composition of the compound as is seen from the dotted line in the figure X.

(c) The two components form a compound with an incongruent melting point.

Making up mixtures of various composition and finding the softening and the melting point a diagram like the following is obtained:

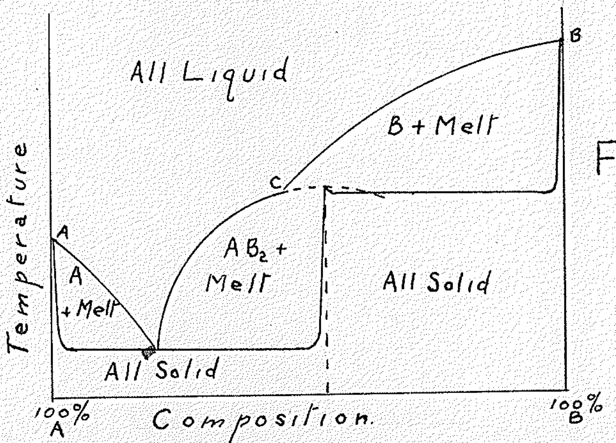


Fig. XI

As before the various stable systems are shown in the areas in which they are stable. Just as in the case where there is no compound formation there are now three points where melting occurs at a definite temperature. These points are the melting point of pure A, the melting point of pure B, and the one realizable eutectic. Therefore there are only three places where the softening and the melting curves coincide. Unless the point of inflection is very marked there is the danger of overlooking it altogether and accepting the diagram as one with only a simple eutectic. However, this difficulty is got around by the fact that although there is only one eutectic there are two eutectic horizontals. Once again the composition of the compound can be obtained from the softening curve because it ascends very rapidly in the neighborhood of the composition of the compound as can be seen. Dropping a vertical from this point to the composition axis will give the composition of the compound.

3. Advantages of the Method.

The advantages of the softening melting point method over that of thermal analysis may be stated as follows:

1. By the combination of two curves and the corresponding determination of the eutectic horizontals the certainty of the investigation is increased.

2. Resulting from the above statement the testing of a few proportions is sufficient if it is only to find out whether or not a compound is formed and it is not desired to determine its composition.

3. It is impossible to super-heat a solid, that is, there is no phenomenon analagous to super-cooling. This is a termendous advantage, especially in working with organic substances, since super-cooling will make the determination of the curve inaccurate.

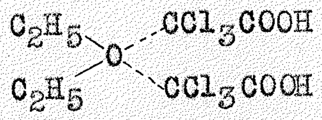
4. It is possible to take a fraction of a gram of a substance and obtain a whole state diagram. In this way many substances can be investigated which it would be impossible to investigate otherwise.

VI. Measurements of Viscosity.

Owing to the unsatisfactory results obtained from the method of thermal analysis it was decided to measure the viscosity of different mixtures of sodium hydroxide and Rochelle salt to determine whether or not a compound was formed.

1. Work of Guye.

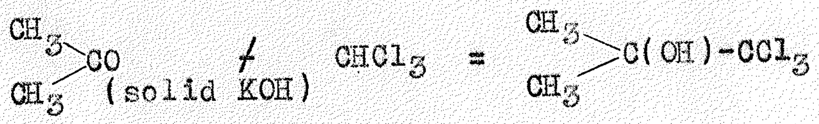
Guye[4], who investigated a large number of systems by the method of thermal analysis with a view to giving a definite answer to the question as to whether or not a compound was formed, found that in some systems the viscosity of the system became so great that it was not possible to determine the freezing point curve with exactness because of the phenomenon of super-cooling. As an example the system ethyl ether--trichloracetic acid may be taken into consideration. The oxygen in the ether has a tendency to throw out two more valencies towards a radical which is acidic in character. Trichloracetic acid is a very strong organic acid and it might be expected that a compound something like this would be formed:



In this case the mixture became extremely viscous and would not crystallize but set to a glass. But the very fact of the sudden increase in viscosity is evidence that a compound is formed. This will be discussed below.

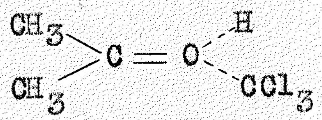
2. Work of Tsakalotos.

Tsakalotos[5] in 1909 also published a paper on the viscosity method and showed that when the compound was formed there was a maximum on the viscosity curve. He worked with the system chloroform-acetone and got a curve like figure XII. It has been shown that in the presence of solid KOH, acetone and chloroform react to give this

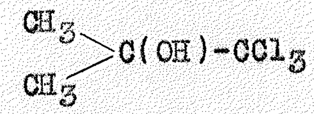


$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>CO \underset{\text{(solid KOH)}}{+} CHCl_3 = \begin{matrix}CH_3\\CH_3\end{matrix}\!\!>C(OH)-CCl_3$$

The solid KOH is necessary. Tsakalotos has shown by his viscosity measurements that an addition product is probably formed. Guye suggests acetone and chloroform unite to form an addition compound of the following formula:



Then under the action of the solid KOH tautomerization takes place giving the following:



3. Work of Faust and Tammann.

Guye states as a result of his investigations that every time components separate solidified in the crystalline state while their mixture gives rise to the phenomenon of vitreous solidification this fact may be considered as revealing the existence of one or several compounds between the components. Vitreous solidification is simply an extreme case of super-cooling. Super-cooling has gone so far that a liquid of very high viscosity is obtained. Compound formation between two liquid components will in general increase the viscosity because it will increase the particle size. This effect will be most marked where the viscosities of the components are close together as is shown in figure XII below.

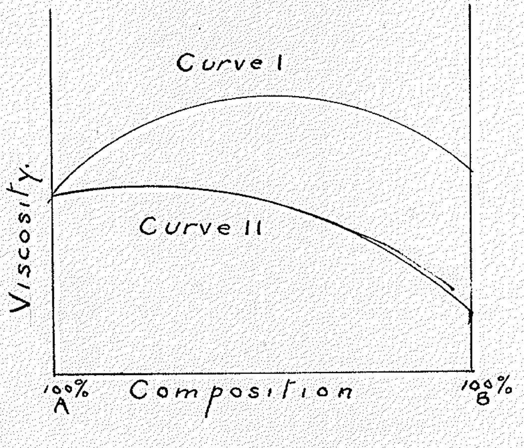


Fig. XII

If the viscosities are very different the curve may only show a sort of bulge rather than a distinct maximum. Curve II. Faust and Tammann[6] in a paper on super-cooling showed that spontaneous crystallization is due to two factors. These two factors are the nucleur number and the velocity of crystallization. The nucleur number is the number of spontaneously formed nucleii per unit of volume per unit of time. These nucleii cannot be seen but they are able to grow and this is where the second factor, the velocity of crystallization comes in. The state of permanent super-cooling may be due to two factors,

1. Reduction of the nucleur number to zero, or

2. The reduction of the velocity of crystallization to zero, or both. Under ordinary circumstances the nucleur number is never reduced to zero although it may be greatly reduced by cooling. The velocity of crystallization is much the more sensitive of the two factors and it is greatly reduced by a fall in temperature.

The work of Faust and Tammann indicates that the reduction in crystallization is due to the increased viscosity which results from the reduction of temperature not from the reduction of temperature itself.

The addition compound increases the viscosity and from the above it can be seen that this favors the super-cooling.

Another method of determining whether or not a compound is formed between two components may be briefly mentioned although the method was not used in this investigation. Konowaloff[7] investigated the system acetone-chloroform from the point of view of the vapor pressures. He measured the vapor pressures of various mixtures of acetone and chloroform. He obtained a curve which may be represented thus:

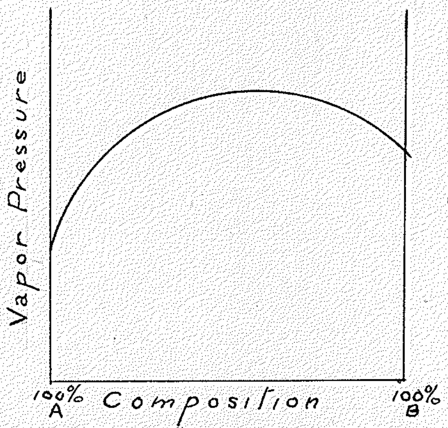


Fig. XIII.

The existence of a maxima or minima is presumptive evidence of the existence in the body of the liquid of compound molecules.

- EXPERIMENTAL -

I. Previous Work on the System NaOH-Rochelle Salt.

Before going on to a detailed outline of the experimental procedure followed in this investigation it might be well to discuss briefly the work which has already been done on this problem.

It has been observed by Campbell and Campbell[8] that the racemisation of Rochelle salt by caustic soda is accompanied, and probably conditioned by complex formation. They investigated the specific rotation of Rochelle salt with increasing concentrations of alkali and found that the specific rotation of the Rochelle salt finally becomes negative. They came to the conclusion that a complexx is formed which is laevorotatory, and the progressive reduction in the rotation of the Rochelle salt is due to increasing formation of complex with the addition of alkali.

Further work by the same investigators[9] showed that as they used sodium hydroxide solutions of increasing strength the specific rotation of the Rochelle salt became less and less. The solutions were always molar with respect to Rochelle salt. Their results are given in the following table. The figures at the head of each table gives the number of the light filter used

Strength of NaOH, N	Specific rotation at 22.2° Filter Nos.				
	2	3	4	5	6
0.0 (water)	25.2	26.8	28.1	28.5-	28.5
1.10	23.3	25.2	26.3	26.8	27.1
1.907	21.7	22.9	24.0	24.4	24.5
2.72	19.7	20.8	21.7	22.1	22.1
5.16	13.1	13.7	14.4	14.8	14.9
6.97	6.68	6.99	7.2	7.4	7.5
9.36	-0.43	-0.91	-1.12	-1.22	-1.26
14.18	-10.9	-12.0	-12.7	-12.7	-12.8

Making the two laevorotatory solutions acid the potassium hydrogen tartrate was precipitated. This was then dissolved in cold water and the specific rotation of the solution of the mother liquor, taken. It was found that both were dextro-rotatory. From the observed dextro-rotations the amount of Rochelle salt was calculated. It was found that this was always much less than the original. That means that considerable racemisation had taken place simply as a consequence of dissolving the Rochelle Salt in cold sodium hydroxide.

Investigation of the density, viscosity, refractive index, and heat of solution, of the various mixtures of sodium hydroxide and Rochelle salt was also carried out.[10] The results may be summarized in the following table. The temperature at which the measurements were made was 30°.

TABLE I.—Physical Properties of Rochelle Salt in NaOH.

Solvent.	Density.				Viscosity in c.g.s. Units.			Refractive Indices.						Heat of Solution.
	NaOH.	NaOH + R.S.	Calc.	Diff.	NaOH.	NaOH + R.S.	Diff.	NaOH.		NaOH + R.S.		Differ.		
								N_C.	N_F.	N_C.	N_F.	N_C.	N_F.	
Water (d = 0·9957)	—	1·129	1·087	+0·040	0·00801	0·01335	0·00534	1·3300	1·3359	1·3585	1·3649	0·0285	0·0290	−1·152 K (anhydrous) −8·8 K (hydrated)
0·97 N NaOH	1·038	1·160	1·115	+ ·045	·0097	·0162	·0065	1·3415	1·3475	1·3661	1·3727	·0246	·0252	−0·895 K
1·94 N "	1·078	1·195	1·155	+ ·040	·01130	·0210	·0097	1·3500	1·3561	1·3732	1·3801	·0232	·0240	−0·49 K
3·03 N "	1·120	1·224	1·190	+ ·034	·0154	·0273	·0119	1·3602	1·3669	1·3808	1·3874	·0206	·0205	−0·455 K
3·92 N "	1·151	1·249	1·230	+ ·019	·0193	·0344	·0151	1·3653	1·3722	1·3844	1·3920	·0191	·0198	−0·21 K
4·90 N "	1·187	1·283	1·235	+ ·048	·0255	·0465	·0210	1·3743	1·3815	1·3931	1·4005	·0188	·0190	−0·25 K
5·92 N "	1·213	1·312	1·270	+ ·042	·0330	·0618	·0285	1·3827	1·3900	1·3984	1·4061	·0157	·0161	−0·263 K
6·70 N "	1·237	1·324	1·290	+ ·034	·0372	·0689	·03168	1·3837	1·3913	1·4004	1·4086	·0167	·0173	−0·215 K
7·88 N "	1·276	1·359	1·325	+ ·034	·0525	·1000	·0475	1·3920	1·3998	1·4079	1·4161	·0159	·0153	−0·275 K
8·95 N "	1·317	1·392	1·360	+ ·032	·0765	·1400	·0695	1·4004	1·4086	1·4135	1·4220	·0131	·0134	−0·14 K
9·80 N "	1·388	1·455	1·430	+ ·025	·0866	·1646	·0780	1·4038	1·4120	1·4155	1·4238	·0117	·0118	−0·125 K
10·9 N "	1·428	1·492	1·460	+ ·032	·1220	·2277	·1057	1·4086	1·4165	1·4172	1·4274	·0086	·0109	+0·187 K
12·15 N "	1·455	1·518	1·480	+ ·038	·1447	·3042	·1595	1·4142	1·4230	1·4255	1·4334	·0113	·0104	+0·35 K
14·5 N "														+1·25 K

From these figures the heat of hydration is calculated as + 7·65 large calories.

Examining the table it is seen that the density is not affected by increasing concentration of NaOH, as regards obedience to the mixture rule. The property that demands the most attention is that of viscosity. When the difference between viscosity of solvent and solution is plotted against concentration of sodium hydroxide the following graph is obtained.

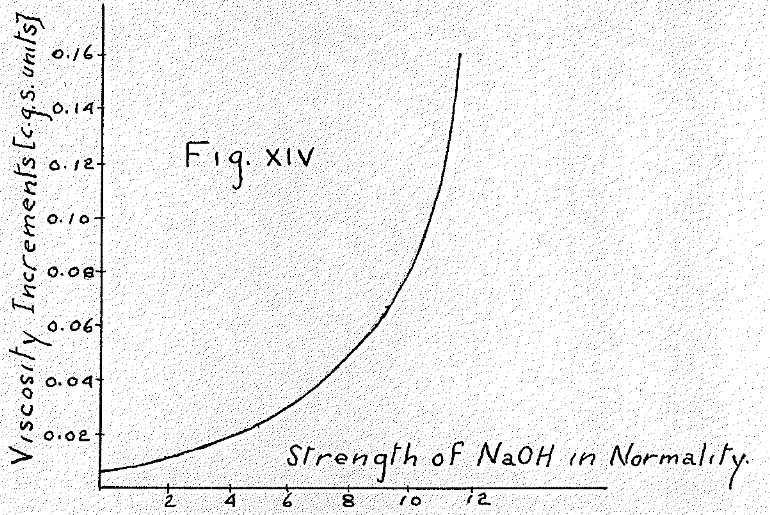
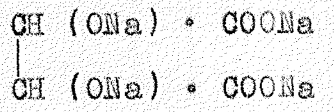


Fig. XIV

From the figure it can be seen that the increment in viscosity produced by dissolving a constant weight of Rochelle salt is about thirty-two times as great in 12.15 N NaOH as it is in water, and about twenty three times what it is for .97 N NaOH. This would indicate that there is increasing association of Rochelle salt molecules with the NaOH molecules. Quoting from the paper of Campbell and Campbell, "The difference in refractive index produced by dissolving Rochelle salt shows a small but distinct decrease. Perhaps this might be taken to indicate that the "complex" is more than a mere loosely associated compound, and that a chemical rearrangement takes place.

Similarly with the heat of solution, there is a small but distinct change from a small negative to a small positive value."

In this paper the following formula was provisionally assigned to the complex, $C_4H_6O_6 \cdot 4NaOH$ that is perhaps



$$\begin{array}{l} \text{CH (ONa)} \cdot \text{COONa} \\ | \\ \text{CH (ONa)} \cdot \text{COONa} \end{array}$$

The solid phase obtained by Campbell and Campbell in their experiments was a gelatinous sticky mass. Attempts were then made to isolate this complex. The gelatinous mass was filtered by suction, and analysed for sodium hydroxide by titration with acid, and for Rochelle salt by precipitation as silver tartrate. The following results were obtained: 34.8 per cent NaOH, 52.1 per cent Rochelle salt, or 40.3 per cent NaOH, 59.7 per cent Rochelle salt on the dried specimen.

Subsequent determinations of the percentage of NaOH yielded the following results: 40.3 per cent; 37.0 per cent; 36.5 per cent; 37.0 per cent, 24.6 per cent; 28.6 per cent. Another determination was made washing with 95 per cent alcohol and drying. The per cent of NaOH obtained in this way was 21.3 per cent. A final determination was made refluxing the preparation for several hours with 500 c.c. of 95 per cent alcohol. Analysing for NaOH gave 16.0 per cent. If the sodium hydroxide had merely been adsorbed on the Rochelle salt it seems fairly certain that this treatment would have removed it. The conclusion was reached that the complex had a sodium hydroxide content of between 20 and 40 per cent, that is, that it contains either two, three or four molecules of NaOH per molecule of Rochelle salt.

II. Thermal Analysis.

1. Initial Trials.

It was originally planned to use a large size Pyrex test-tube as a receptacle for the NaOH and the Rochelle salt. Asbestos paper was wrapped around the test-tube and then it was wrapped with Nichrome wire, #22 gauge, obtained from the General Electric Company. A coating of water-glass was then put on, and another layer of asbestos paper added. Two rheostats, one 6.5 ohms, 8.3 amps; and the other 97 ohms, 2.2 amps; were connected in series with the wiring on the Pyrex test-tube. The full 6.5 ohms was left in the circuit all the time. The other rheostat was calibrated by placing on it chalk marks as closely spaced as possible. Also the slider of the rheostat had a corresponding chalk mark on it. The test-tube was fitted with a tube bent at right angles and a piece of thick hard glass tubing to act as a sheath for the thermometer, reading from 0° to 350° C and graduated in degrees. Enough mercury was placed in this sheath to allow the thermometer to float at a height convenient for reading. The open end of the sheath was fitted with a piece of rubber tubing and a pinch-cock to prevent the mercury vapor from escaping into the air when the temperature of the NaOH was raised. The piece of tubing bent at right angles was connected to a drying train and through this to the Hy-Vac pump.

A fresh unopened bottle of Mallinckrodt's U.S.P. sticks of NaOH was obtained and about 100 grams weighed out in a stoppered conical flask. In order to keep the air from the NaOH as much as possible and so prevent it from taking up water, the caustic alkali was placed in the flask as quickly as possible until it was judged that 100 grams were present and then this was weighed in the stoppered flask. This NaOH was then placed in the Pyrex test-tube and the heating current started. When the sodium hydroxide was melted the Hy-Vac pump was started and in this way any water which may have been present in the NNaOH was pumped off. The pumping was continued for several hours. When no more moisture was given off the temperature was raised to above the melting point of the NaOH. However, here the experiment had to be stopped as the heat caused the rubber stopper in the neck of the flask to melt.

Next a hard glass distilling flask of 125 c.c. capacity was obtained. This was fitted with a one-holed rubber stopper and in it was placed about 100 grams of NaOH. Next the side-arm of the flask was bent so that it was standing vertically. Then a tin-can with a lid was obtained. The can was of such a size that the 125 c.c. flask would just fit snugly inside it leaving the neck of the flask projecting. Two holes were punched in the lid of the can, one to allow the neck to go through and the second to allow the side-arm to pass out. The flask was then placed in the can which had been previously wrapped with Nichrome wire and asbestos paper, and the lid was put in place. In order to keep the rubber cork from melting, rubber tubing was wrapped around the neck of the flask and attached to the water tap and a continuous supply of water was passed through. Heating was commenced using the same two rheostats as before and the pump was attached to the upright side arm of the flask and the vapor pumped off. Pumping was continued for several hours. However, it was seen that the heating up was going to take too long so the current was switched off and the space between the tin and the flask was packed with powdered asbestos in order to cut down the radiation as much as possible. Heating was then resumed and it was found that this time the temperature rose much more rapidly than before. However, looking at the flask next day it was found that on allowing it to cool down it had cracked.

A new flask was obtained and prepared in exactly the same way as the one mentioned above only this time the side arm was not bent, but a slit was cut in the side of the can and the side arm was allowed to project through this. In this way it was easier for any moisture present to escape by running down the side arm when the whole thing was heated up and then pumped down with the Hy-Vac. Exactly the same procedure was followed as in the previous case. This time the alkali attacked the flask rather readily and the bottom fell out of it. When the solidified alkali was examined it was observed to have a distinct greenish tinge.

2. The Copper Flask.

Finally a pear-shaped copper flask, of about 700 c.c. capacity was obtained. The neck, with the side arm, was cut from a hard glass distilling flask of 250 c.c. capacity. Fortunately this fitted the neck of the copper flask quite well when wrapped once with asbestos paper. To make it more secure a paste of water -glass and calcium fluoride was made up and applied to the join. Instead of pumping the flask down to remove any water vapor, air was blown through the flask and out the side arm. This was done because in the pumping down the molten alkali was drawn up the side arm in the previous cases causing it to become plugged when it solidified, as it did almost immediately in contact with the comparatively cold glass. The air, before passing into the flask, was dried by passing it through a drying train consisting of a tube of soda and lime, two tubes of $CaCl_2$, one tube of P_2O_5, and then bubbling it through concentrated H_2SO_4. The neck of the distilling flask was fitted with a two-holed rubber stopper. One hole carried the glass tube through which the air was blown.

3. Measurement of Temperature.

Using the copper flask the thermometer went so far down into it that it could not be read, so a thermocouple was used to overcome this difficulty. This consisted of two wires, one of constantan and the other of iron. These two wires were insulated from one another by passing one through a narrow piece of glass tubing. They were twisted together at their lower ends. Then they were placed in a wider piece of glass tubing which served as a sheath, which was in turn inserted through the second hole in the rubber stopper mentioned above and so down into the melt in the flask. The other ends of the two wires were connected to the proper binding posts on a potentiometer which was graduated in 10° F and could be estimated to 1° F.

NaOH was weighed out and placed in the flask which was then put in a tin which had previously been wrapped with Nichrome wire and asbestos paper. The heating current was started using the same rheostats as before, however, the temperature could not be raised to the point of the NaOH.

At this stage it was decided to wrap the flask itself with wire. Two windings of wire were put on, the two wrappings being placed in series and insulated from one another and from the flask by two thicknesses of asbestos paper. The bottom of the flask was heated as well as the sides. Still the temperature could not be raised high enough without burning out the wiring on the flask which occurred several times. Next the flask was placed in a can of suitable size and the space between the can and the flask was packed with powdered asbestos. Still the temperature could not be raised high enough. Then the can mentioned above was given a heavy coating of asbestos paper made into a paste by adding water. The copper flask was placed in the can and the space between the can and the flask was again well packed with powdered asbestos. This time a temperature high enough to melt the NaOH was obtained.

The cooling was brought about by progressively putting in the 97 ohm resistance, moving the slider along to the next chalk mark at certain intervals of time. However, the full 97 ohms had been put in the circuit and even then cooling was not complete. Consequently the experiment had to be stopped until another rheostat could be obtained and placed in position. A 96 ohm rheostat was obtained, calibrated in the same manner as the 97 ohm rheostat and attached in series to it. The NaOH was again heated up and the cooling curve obtained. In a trial previous to this the temperature readings were taken every minute but the cooling was taking place so slowly that in all the latter trials the time between temperature readings were increased to two minutes. After each temperature reading the slider on the rheostat was moved to the next chalk mark and at the end of two minutes the temperature was again read.

4. Proportions of Rochelle Salt.

The first series of readings were for pure NaOH alone. Then Rochelle salt was added in various proportions and the cooling curves obtained in each case, that is, for each separate mixture. The Rochelle salt used was Mallinckrodt's U.S.P. It was dried for four days in an electric oven, powdered, and kept in a sulphuric acid dessicator. It was intended to use the following proportions of Rochelle salt:

TABLE I

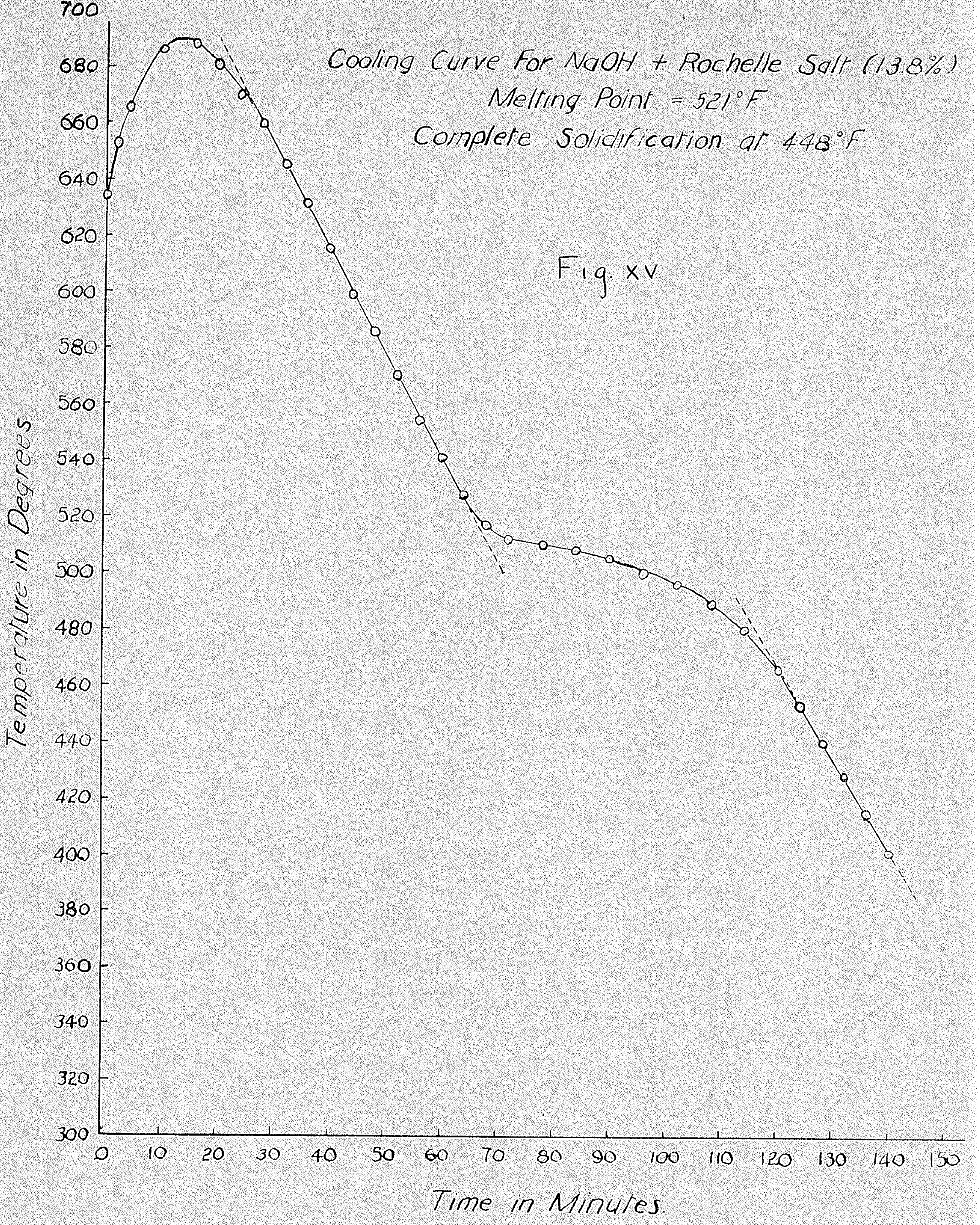
MIXTURE NUMBER	PROPORTION OF ROCHELLE SALT BY WEIGHT
1.	2.0%
2.	3.8%
3.	7.4%
4.	10.7%
5.	13.8%
6.	16.7%
7.	19.3%
8.	24.8%
9.	27.8%
10.	30.0%
11.	40.0%
12.	50.0%
13.	55.0%
14.	60.0%
15.	65.0%
16.	70.0%

MIXTURE NUMBER	PROPORTION OF ROCHELLE SALT BY WEIGHT
17.	80.0%
18.	90.0%
19.	100.0%

5. Method of Procedure.

About one series of readings could be made in a day. That is, it would take one whole day to get the series of readings for any given percentage mixture. Coming back the next day the melt would, of course, be much too solid to allow the stopper to be taken from the neck of the flask in order that more Rochelle salt could be added, even with a small heating current going all night. Consequently, the mixture had again to be heated up until the mixture was molten so that the rubber stopper could be removed. Then the appropriate amount of Rochelle salt was weighed out for the next mixture. This could not be added to the molten mixture as considerable charring would have taken place. The mixture in the flask was allowed to cool down to a considerable extent and then the Rochelle salt was added gradually. Then the mixture was heated up very gradually to prevent charring of the Rochelle salt. When all these precautions were observed, little or no charring took place, more especially in mixtures where the percentage of Rochelle salt was small.

As mentioned earlier, temperature readings were taken every two minutes. Then temperature was plotted against time, a separate graph being made for each mixture. From these graphs the melting point and the point of complete solidification of each of the mixtures was obtained. A sample graph is shown



Cooling Curve For NaOH + Rochelle Salt (13.8%)
Melting Point = 521°F
Complete Solidification at 448°F

Fig. XV

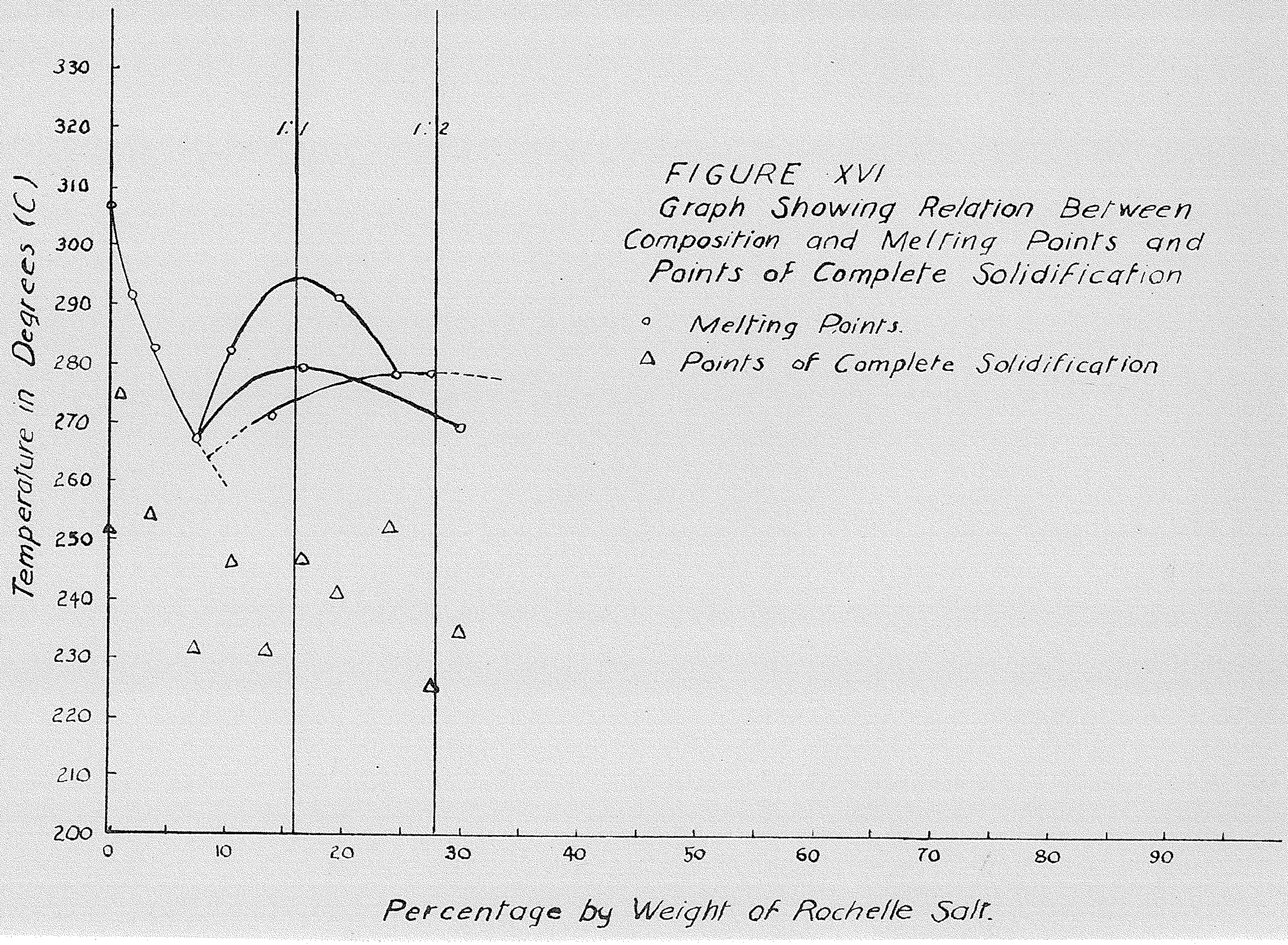


FIGURE XVI
Graph Showing Relation Between Composition and Melting Points and Points of Complete Solidification

in figure XV. Then the melting point of each mixture was taken and plotted against the composition. In this way the liquidus curve was obtained. Also the point of complete solidification for each mixture was plotted against composition on the same graph. It was thought that this was the solidus curve but it appears to be due rather to super-cooling. The complete curve of composition against melting points and points of complete solidification is shown in figure XVI. It was plotted from the following data:

TABLE II

TOTAL % ROCHELLE SALT	MELTING POINT	COMPLETE SOLIDIFICATION
0%	306.7°C	251.7°C
2%	291.1°C	274.4°C
3.8%	282.8°C	254.4°C
7.4%	267.0°C	231.6°C
10.7%	282.2°C	246.1°C
13.8%	271.7°C	231.1°C
16.7%	279.4°C	246.7°C
19.3%	291.1°C	240.6°C
24.2%	278.9°C	252.2°C
27.8%	278.9°C	225.0°C
30.0%	268.9°C	233.9°C

For mixtures beyond 30.0% of Rochelle salt the cooling curve could not be obtained because beyond this concentration the mixture became extremely viscous and in the process of heating it up it frothed up so violently that it forced the rubber stopper out of the neck of the flask. This meant that the thermocouple was also forced out and it was impossible to obtain the temperature. It was thought that as the heating was continued the frothing might die down, but this was found not to be the case. If anything it became worse.

The figures given in Table I, are for total percentages. The amount of Rochelle salt to be added to one mixture to bring it up to the composition of the next mixture was calculated from the following formula:

$$\text{Required percent} = \frac{X \times 100}{\text{total amount of NaOH} + X}$$

Knowing the percent that was required and the total amount of NaOH originally present, the equation was solved for X, the amount of Rochelle salt that would make a mixture of the required percent. However, from this value of X there must be subtracted the total amount of Rochelle salt which had been added up to this point.

III. Softening-Melting Point Method.

1. Initial Attempt.

A Pyrex distilling flask of about 250 c.c capacity was obtained and half filled with concentrated H_2SO_4. Then a melting point tube was made by drawing down some soft glass tubing. The capillary had a somewhat larger bore than has the ordinary melting point capillary.

Then some fresh sodium hydroxide was weighed out in a weighing bottle and placed in a test tube. The test tube was fitted with a one-holed rubber stopper and connected through a drying train to the Hy-Vac pump. The pump was started and the test tube was then heated until the sodium hydroxide had melted. The pumping was continued for some time, the sodium hydroxide being kept in a molten condition all the time, in order to allow the water vapor to be pumped off. When the vapor had all been pumped off, the test tube was allowed to cool and then it was broken and the solidified sodium hydroxide taken out and rapidly put into the capillary. One end of the capillary had, of course, been previously sealed.

When the capillary was about half filled with the NaOH the other end was then sealed and the capillary attached by means of a piece of platinum wire to a thermometer near the bulb. The thermometer was graduated in degrees from 0° to 350°C. The thermometer was then inserted through a one-holed rubber stopper which closed the neck of the flask. The thermometer was inserted far enough into the flask so that the melting point tube was almost completely immersed in the acid. The sulphuric acid fumes were allowed to escape through the side arm of the distilling flask. The whole thing was then placed on a sand bath and heat applied. After a considerable time the temperature was raised to the melting point of the sodium hydroxide. This temperature was noted. In the case of a pure component, which is what we have here the softening point and the melting point will be one and the same.

2. Apparatus of Rast.

However, it was seen that by this method the heating up of the mixtures was going to consume too much time. It was decided to use an apparatus similar in type to that used by Rast.[11]

A solid piece of brass about 2½ inches in height and 1½ inches in diameter was obtained. Down through the center of this a hole was bored of such diameter that a thermometer with the capillary melting point tube attached could pass down into it with ease. This hole was not quite bored to the bottom of the cylinder of brass. About half way up the brass cylinder a second hole was bored cutting the first hole at right angles. In this case the hole was bored clean through the brass. The whole thing was then wrapped with asbestos paper and Nichrome wire and supported on a suitable stand. A hole was punched through the asbestos paper to correspond with the second hole in the brass cylinder.

3. Method of Procedure.

The mixtures of sodium hydroxide and Rochelle salt were made up, as before, the sodium hydroxide being melted in a test tube, the water vapor pumped off and the Rochelle salt added in the proper proportions. Heating was continued for some time to ensure complete mixing of the two components. The test tube was then allowed to cool, broken and the mixture put into the capillary melting point tube until it was about half full. The melting point tube was then attached to the thermometer, which, as before, was graduated in degrees from 0^{o} to 350^{o} Centigrade. The thermometer with its attached capillary was then placed in the brass cylinder to such a depth that by looking through the second hole bored in the cylinder the melting point tube and its contents could be seen. The heating current was then started and the temperature rose rapidly. By using a hand glass and watching the mixture through the hole in the brass cylinder, any changes with rise of temperature could be observed. In this way the softening point of the first mixture was noted but unfortunately before the melting point could be reached the mixture charred very badly and became useless.

Consequently this method was abandoned as a means of investigation.

IV. Measurement of Rotation.

Since neither the method of thermal analysis nor the softening melting point method gave very satisfactory results it was next decided to measure the specific rotation of various mixtures of sodium hydroxide and Rochelle salt.

1. Work of Campbell and Campbell.

Campbell and Campbell[12] observed that in measuring the rotation of Rochelle salt in different strengths of NaOH that the specific rotation was very variable with alkali concentration and even changed sign at an alkali concentration of about 9N. Determination of the OH concentration in these solutions also gave indications of complex formation.

The hypothesis has been advanced that variation in the rotation in different media is a consequence of loose complex formation loading the molecule but the experimental evidence to support this is very meagre.

The above investigators decided that the variation in rotation was so large that it might be possible to obtain definite evidence of the formation of a complex.

In their measurements of the specific rotation of Rochelle salt in sodium hydroxide of various concentrations they made use of a 3-field polarimeter and used a 2 dm. tube. A series of Wallace color filters were also used. The results obtained are shown in the following table.

Normality of NaOH	Specific Rotations Filter Number				
	2	3	4	5	6
Pure Water	+ 25.2	+ 26.8	+ 28.1	+ 28.5	+ 28.5
1.10	+ 23.3	+ 25.2	+ 26.3	+ 26.8	+ 27.1
1.907	+ 21.7	+ 22.9	+ 24.0	+ 24.4	+ 24.5
2.72	+ 19.7	+ 20.8	+ 21.7	+ 22.1	+ 22.1
5.16	+ 13.1	+ 13.7	+ 24.4	+ 14.8	+ 14.9
6.97	+ 6.68	+ 6.99	+ 7.2	+ 7.4	+ 7.5
9.36	- 0.43	- 0.91	- 1.12	- 1.22	- 1.26
14.18	- 10.9	- 12.0	- 12.7	- 12.7	- 12.8

The negative rotations were quite stable in the cold, thus showing that in the cold no racemisation takes place.

At the same time determinations of the OH concentration were made and also a phase rule study of the system, NaOH-$NaKC_4H_4O_6$-H_2O, was made. However, for the present purpose this need not be gone into in any detail suffice it to say that in these cases support was lent to the theory that a compound was formed in the process of racemisation. As can be seen from the table, there is a very marked variation in the rotation of the different mixtures of Rochelle salt and sodium hydroxide which, as was mentioned earlier, led to the hypothesis of compound formation.

2. The Polarimeter.

In the present investigations a three-field Hilger polarimeter was used. It was equipped with a scale which enabled the instrument to be read to 0.01 of a degree. The zero reading of the instrument was determined to be 180.03°.

In the solutions containing a low concentration of NaOH a 2 dm. tube was used in making the measurements. However, for solutions having a comparatively high concentration of caustic soda a 1 dm. tube was used, as it was found that the packing of the 2 dm. tube was rather readily attacked by the strong alkali and the solution was discolored, making it difficult to obtain accurate readings with the polarimeter.

3. Light Source.

It was intended to use as a source of light a carbon arc light with a lens to concentrate the light on the monochromator. Considerable difficulty was experienced in settling the monochromator correctly and it was finally abandoned. In its place a sodium flame was used. The sodium flame was obtained by passing air through a bubbler containing a solution of sodium chloride and then passing the vapor up through a lighted Bunsen burner.

All measurements were of course made in a dark room and the following results were obtained. About fourteen readings were taken at each concentration, the average of which is shown in the table. The results under the heading Corrected Value were obtained by subtracting the observed rotation from the zero reading.

4. Results.

100% Rochelle Salt.

Conc. of Rochelle salt	Temp.	Average	Corr. Value	Specific Rotation
10 gms/50 c.c.	26.5°C	191.22°	11.19°	27.98°
10 gms/100 c.c.	26.5°C	185.65°	5.62°	28.10°

Conc. of Rochelle salt	Temp.	Average	Corr. Value	Specific Rotation
90% Rochelle Salt				
9.153 gms/50 c.c.	27.0°C	190.40°	10.37°	27.23°
9.153 gms/100 c.c.	27.0°C	185.46°	5.43°	29.66°
80% Rochelle Salt				
8.572 gms/50 c.c.	28.35°C	189.29°	9.26°	27.01°
8.572 gms/100 c.c.	28.40°C	184.99°	4.96°	29.06°
70% Rochelle Salt				
6.513 gms/50 c.c.	26.9°C	187.02°	6.99°	26.63°
6.513 gms/100 c.c.	26.5°C	183.63°	3.60°	27.64°
65% Rochelle Salt				
7.172 gms/50 c.c.	26.5°C	187.32°	7.38°	25.72°
7.172 gms/100 c.c.	26.7°C	184.00°	4.06°	28.20°
60% Rochelle Salt				
6.105 gms/50 c.c.	26.1°C	183.12°	3.09°	25.30°
6.105 gms/100 c.c.	25.65°C	181.71°	1.68°	27.52°
55% Rochelle Salt				
5.5 gms/50 c.c.	25°C	182.72°	2.68°	24.30°
5.5 gms/100 c.c.	25.5°C	181.63°	1.60°	27.0°

45% Rochelle Salt

Conc. of Rochelle salt	Temp.	Average	Corr. Value	Specific Rotation
4.508 gms/50 c.c.	23.8°C	182.10°	2.07°	22.96°
4.508 gms/100 c.c.	23.8°C	181.33°	1.30°	25.80°

35% Rochelle Salt

3.509 gms/50 c.c.	24.1°C	181.55°	1.52°	21.65°
3.509 gms/100 c.c.	23.9°C	180.87°	.84°	23.94°

25% Rochelle Salt

2.508 gms/50 c.c.	23.9°C	180.94°	.91°	18.14°
2.508 gms/100 c.c.	24.1°C	180.64°	.61°	20.40°

15% Rochelle Salt

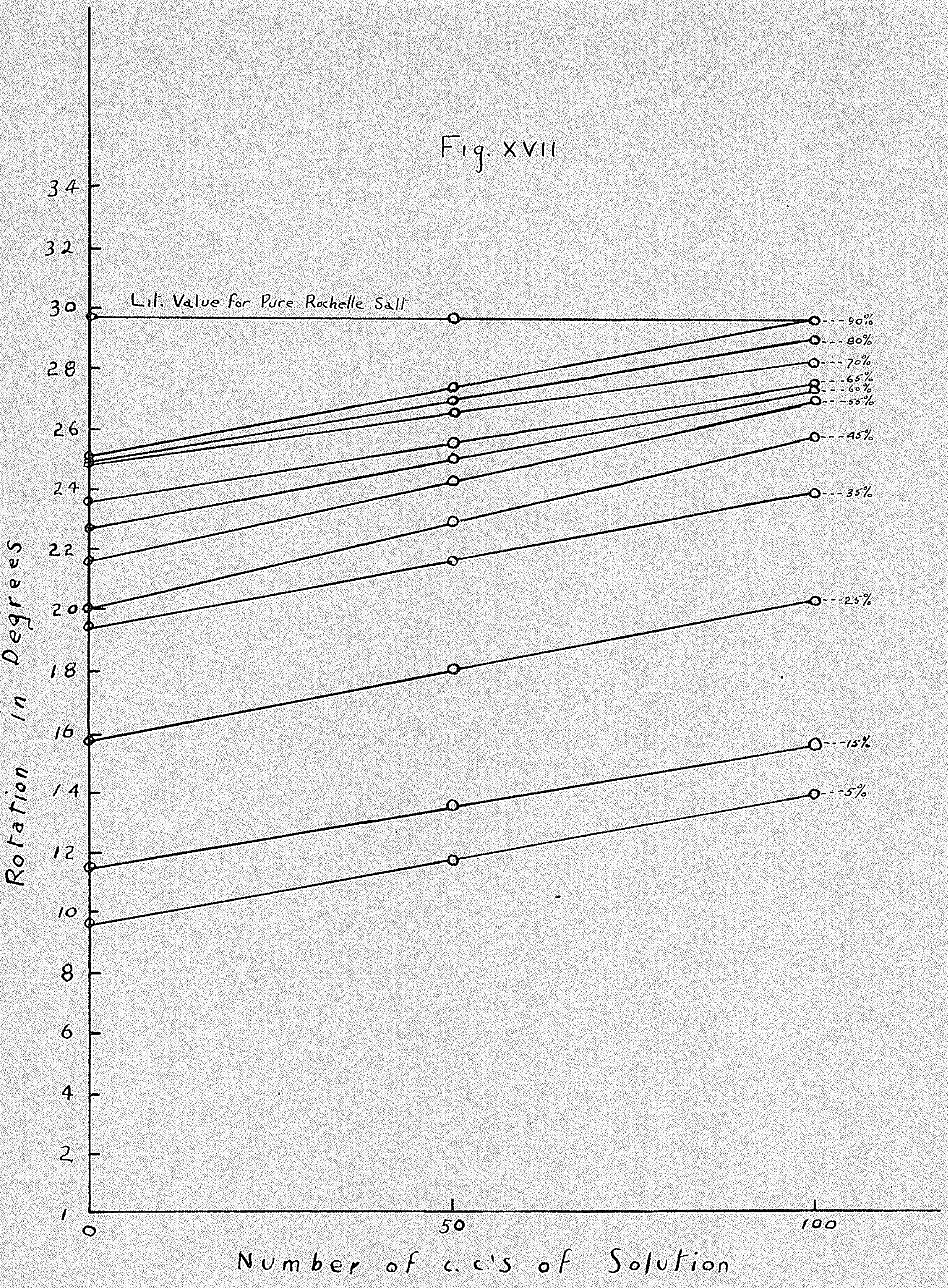
1.509 gms/50 c.c.	23.4°C	180.44°	.41°	13.58°
1.501 gms/100 c.c.	25.0°C	180.21°	.18°	15.60°

5% Rochelle Salt

.503 gms/50 c.c.	24.5°C	180.13°	.10°	9.94°
.503 gms/100 c.c.	24.5°C	180.10°	.07°	13.97°

The results are shown graphically in Figure XVII.

Fig. XVII


Lit. Value for Pure Rochelle Salt
34
32
30
28
26
24
22
20
18
16
14
12
10
8
6
4
2
1
0
50
100
Rotation in Degrees
Number of c.c's of Solution
90%
80%
70%
65%
60%
55%
45%
35%
25%
15%
5%

V. Measurements of Viscosity and Density.

1. Work of Tsakalotos.

Tsakalotos[5] has distinguished three types of curves which may be obtained in the measurement of the viscosity of mixtures of two components in various concentrations.

(a) The normal curves.

The viscosity of different mixtures is equal to, or a little less than, that calculated by the mixture rule. The normal curve corresponds to mixtures, the components of which have no action on one another.

(b) The negative curves.

The viscosity of different mixtures is a great deal less than that calculated by the mixture rule. An example of this type of curve is obtained with systems in which the associated components bring about mutual dissociation.[13]

(c) The positive curves.

The viscosity of different mixtures is a great deal greater than that calculated by the mixture rule. In this case, molecular combination between the two components of the system has taken place. If one of the components is water, the compound formed is in all probability a hydrate.

2. Work of Baker.

Baker[14] has indicated that the complex may be of less viscosity than one or other of the components (assumed to be very associated) in which case a sagged curve or a minimum might be obtained. In fact, he draws the conclusion that in mixtures of alcohol-ether, used for dissolving nitrocellulose, there is a complex existing, but the shape of the curve does not in any way indicate it.

It seems fairly well established that a maximum viscosity does indicate some molecular aggregation, but the mass of evidence is decidedly against any prediction that the position of the maximum point may indicate the composition of the compound.

3. Method of Calculation.

Suppose that a liquid is flowing along a narrow tube. It will be moving in parallel layers. The layer immediately in contact with the side of the tube is motionless, the next layer is moving slowly, the next layer a little faster and so on. There will be a certain amount of friction sliding liquid upon liquid. The closer one approaches the center of the tube the faster the layers of liquid are moving. The fastest moving cylinder is a cylinder of zero diameter in the center of the tube. There must be some force driving the liquid along the tube. Also there must be some resistance to the motion of the liquid for if such was not the case the velocity would be infinite. This resistance is what is called viscosity or liquid friction. Viscosity varies greatly with the nature of the liquid and it may be measured by applying the following formula:

$$\eta = \frac{\pi P r^4}{8 V l} \times t$$

where η = the viscosity of the liquid in question

P = the hydrostatic pressure in dynes

V = volume of liquid flowing through the capillary in time t

l = length of the capillary

r = radius of the capillary

The absolute viscosity of water is accurately known at all temperature. The absolute viscosity of any other liquid may be obtained by the comparison method and by applying the above formula.

Water is generally used as the standard liquid. Suppose that the same amounts of water and the unknown liquid are put in the viscometer and in each case the time is determined for the liquid to flow from one mark on the viscometer to the other. Then let t be the time in seconds for water and t_x be the time in seconds for the unknown.

$$\frac{\eta_{H_2O}}{\eta_x} = \frac{\pi P_{H_2O} r^4 t_1 \times 8Vl}{\pi P_x r^4 t_2 \times 8Vl} = \frac{P_{H_2O} \times t_1}{P_x \times t_x}$$

The hydrostatic pressure must have some average value. If in each case the same volume of liquid is put into the viscometer then the vertical height at the beginning and the vertical height at the end will be the same for both liquids. Then

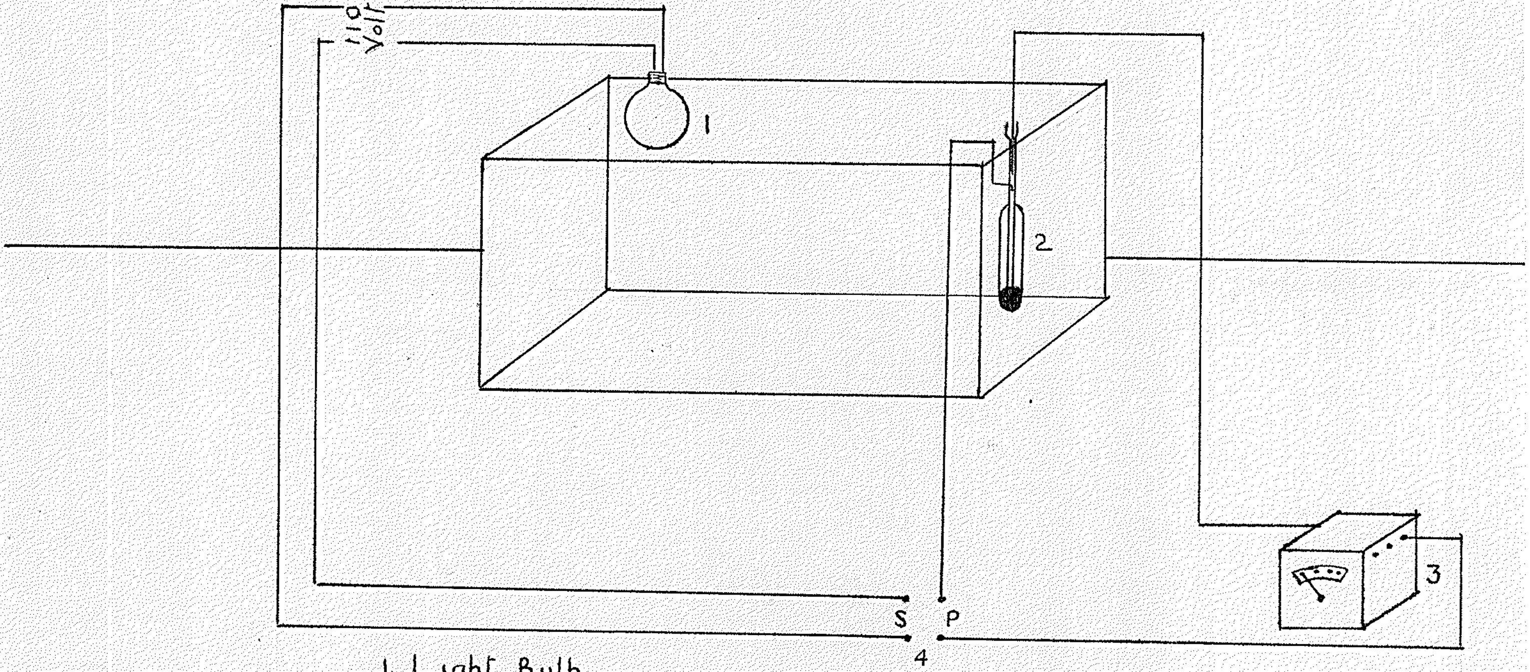
$$\frac{\eta_{H_2O}}{\eta_x} = \frac{h \times d_{H_2O} \times g \times t_1}{h \times d_x \times g \times t_2} = \frac{d_{H_2O} \times t_1}{d_x \times t_2}$$

where d_{H_2O} and d_x represent the density of water and the unknown liquid respectively. Since the density of water is known the density of the other liquid only needs to be found.

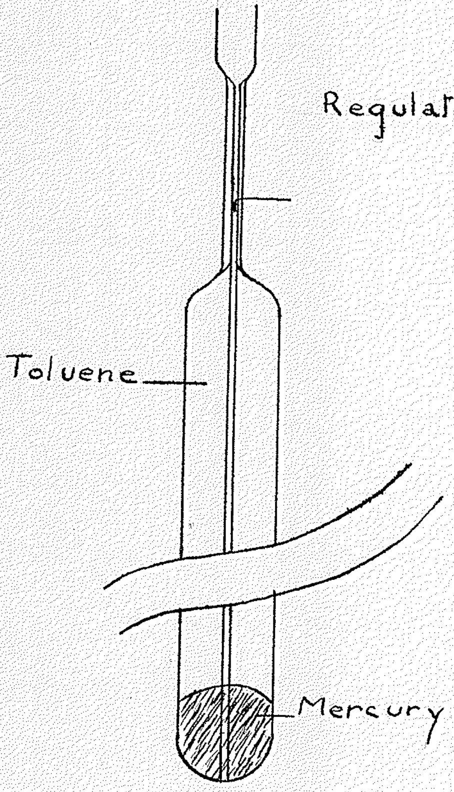
4. The Thermostat and the Regulator.

The discussion of the apparatus used in the viscosity measurements will be simplified by the use of the following diagrams:

Fig. XVIII



1 Light Bulb
2 Regulator
3 Transformer
4 Relay.



Regulator

The water bath was about 22 cms x 40 cms x 26 cms. In it was placed a regulator and an electric bulb of 40 watts which was used as a heating element. Also in the bath was placed a stirrer which kept the water circulating. For the sake of simplicity of stirrer is not shown in the diagram.

The regulator is shown above in more detail. It consists of a bulb which narrows down to a capillary neck and then widens out again. The bulb is filled with toluene. This was done by inverting the regulator in a beaker of toluene and heating it about half way up the bulb. The heat was removed after a while and when the bulb cooled down it became completely filled with toluene. Mercury was introduced through the wide portion at the top. Sufficient mercury was put in so that when the regulator was at a temperature of 25.8°C the mercury was at such a height in the capillary that it just made contact with the wire which was passed down through the wide portion of the tube into the capillary. A second wire is sealed into the glass at about half way down the bulb.

A relay was incorporated into the circuit. It consisted of an electro-magnet in front of which there was an armature attached to a spring, also there were secondary and primary terminals.

The apparatus was set up as shown in the diagram. The regulator was first adjusted by immersing in a beaker of water at about 25°C. In this way it was found just about how high the mercury would rise for this temperature and consequently it was determined just what length of wire would be required to be inserted down into the capillary. The regulator was then immersed in the thermostat and connected up to the transformer and the relay as shown in the diagram. The connections were made in such a way that the transformer was giving 9 volts. Then the electric light bulb was immersed in the bath and plugged into the 110 volt circuit and connected up to the circuit breaker as shown. The stirrer was then connected up through two 96 ohm rheostats and allowed to revolve slowly.

The temperature of the thermostat caused the toluene to expand forcing the mercury up in the capillary and making contact with the wire thus closing the circuit. When this circuit is closed the electro-magnet attracts the armature and breaks the heating circuit. When the bath cools below the required temperature the liquid in the regulator contracts usfficiently to lower the mercury in the capillary tube away from contact with the wire. The electrical circuit is thus broken, the electro-magnet ceases to operate, and the spring pulls the armature back so as to close the heating circuit. The water bath is then heated, and the liquid in the regulator expands until the mercury again contacts the wire and closes the circuit. This alternate closing and opening of the heating circuit continues indefinitely and maintains the temperature within a narrow range.

For the actual measurement of the viscosity the ordinary Ostwald viscometer was used.

5. Experimental Procedure.

5 c.c. of water were measured in a 5 c.c. pipette and placed in the wider limb of the viscometer. By means of a rubber tube on the other end of the viscometer the water was

drawn up to above a scratch on the other limb of the viscometer which for considerable distance was capillary. When the water had fallen to the first mark a stop-watch was started and when it reached a second mark the stop-watch was stopped. Several trials were made and the average gave the value of t_1. The various mixtures of sodium hydroxide and Rochelle salt were made up in a flask calibrated to hold 50 c.c. Each solution was then filtered two or three times through a Gooch crucible and then 5 c.c. was placed in the viscometer which was then placed in the thermostat. The time for each solution to flow from the first mark on the viscometer to the second mark was taken just as in the case of water. The viscometer was carefully cleaned and dried before placing a fresh solution in it.

6. Measurements of Density.

At the same time as the viscosity measurements were being made density measurements were also made of the various solutions. For the measurement of the densities a small bottle was equipped with a small thermometer which fitted into the mouth of the bottle closing it securely. It also had a side tube which was capillary and was covered with a small glass cap. This enabled the bottle to be filled to the top and the thermometer was placed in the neck, thus forcing the excess of liquid up the capillary and out.

The bottle was first weighed empty and then filled with water and placed in the thermostat. When it had reached the temperature of the thermostat it was removed and the excess of liquid wiped off and the bottle was then weighed again. Subtracting the two weighings gave the weight of the water in the bottle. This value was multiplied by 1.00320, the volume of one gram of water at the temperature oft he thermostat. Then the bottle was filled with the various mixtures of sodium hydroxide and Rochelle salt in turn and by the appropriate subtraction the weight of the solution in the bottle was determined after it had come to the temperature of the thermostat. Then the density of the unknown solution was found from the following formula

$$D_x = \frac{W_x}{W_w \text{ x } V_w}$$

This gives the density of the unknown referred to water at 4°C.

where

D_x = Density of the unknown solution

W_x = Weight of the solution in the bottle

W_w = Weight of water contained in the bottle

V_w = Volume of one gram of water at the temperature of the thermostat.

Then knowing the viscosity of water at the temperature of the thermostat the viscosity of the solution was readily found from the following formula:

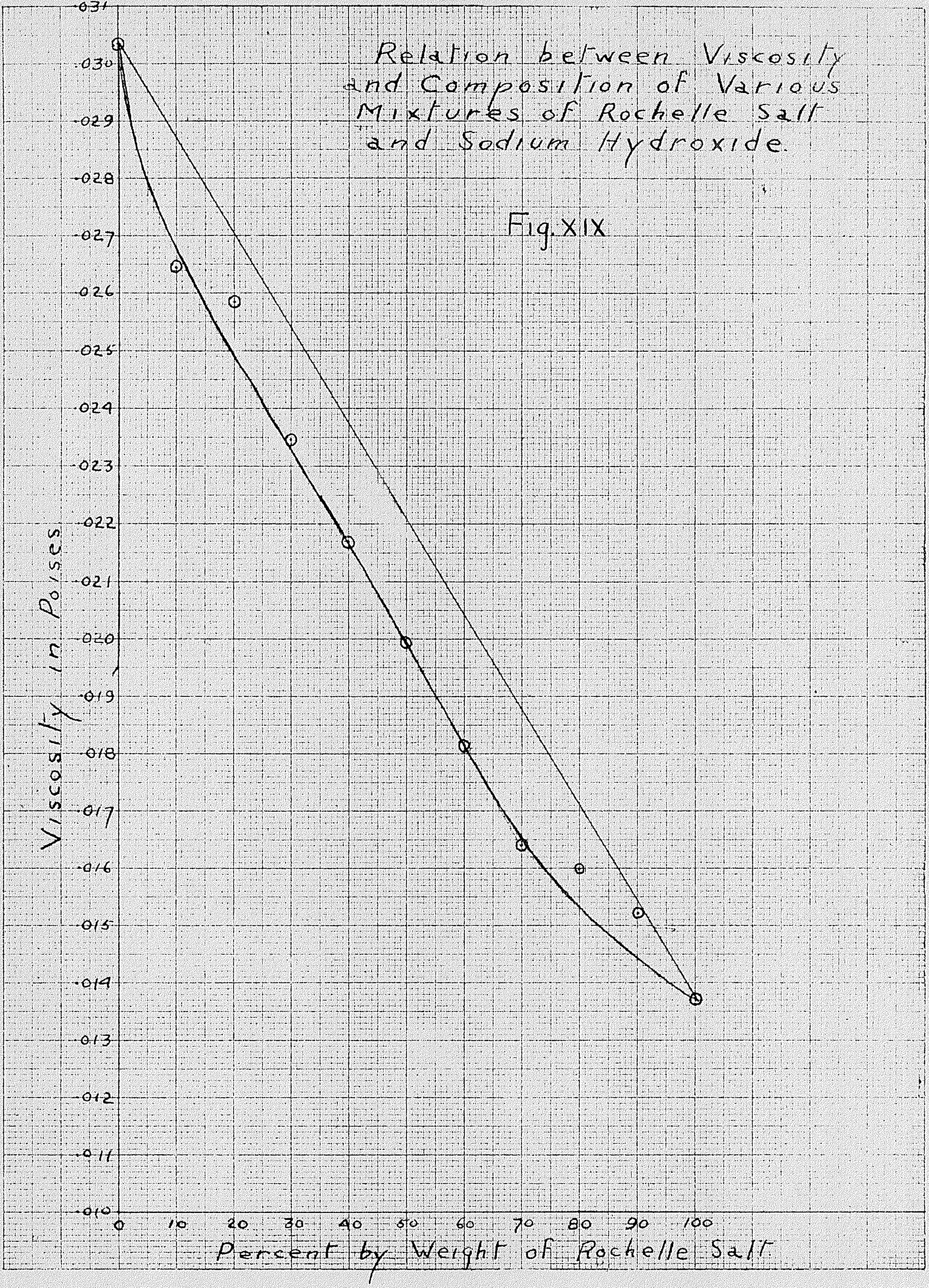
$$\eta_x = \frac{\eta_{H_2O} \; d_x \text{ x } t_x}{d_{H_2O} \text{ x } t_1}$$

7. Results.

The results obtained may be summarised in the table on the following page:-

Per Cent of Rochelle Salt	Temp.	Average Time (In seconds)	Viscosity	Density
Pure H_2O	25.8°C	71.		
100%	25.8°C	100.	.01372	1.115
90%	25.8°C	112.6	.01519	1.096
80%	25.8°C	118.2	.01597	1.097
70%	25.8°C	121.8	.01644	1.097
60%	25.8°C	133.6	.01819	1.106
50%	25.8°C	145.2	.01997	1.118
40%	25.8°C	157.2	.02173	1.123
30%	25.8°C	168.8	.02345	1.129
20%	25.8°C	184.6	.02585	1.138
10%	25.8°C	186.2	.02646	1.136
0%	25.8°C	217.6	.03034	1.135

These results are shown graphically in figures XIX and XX.

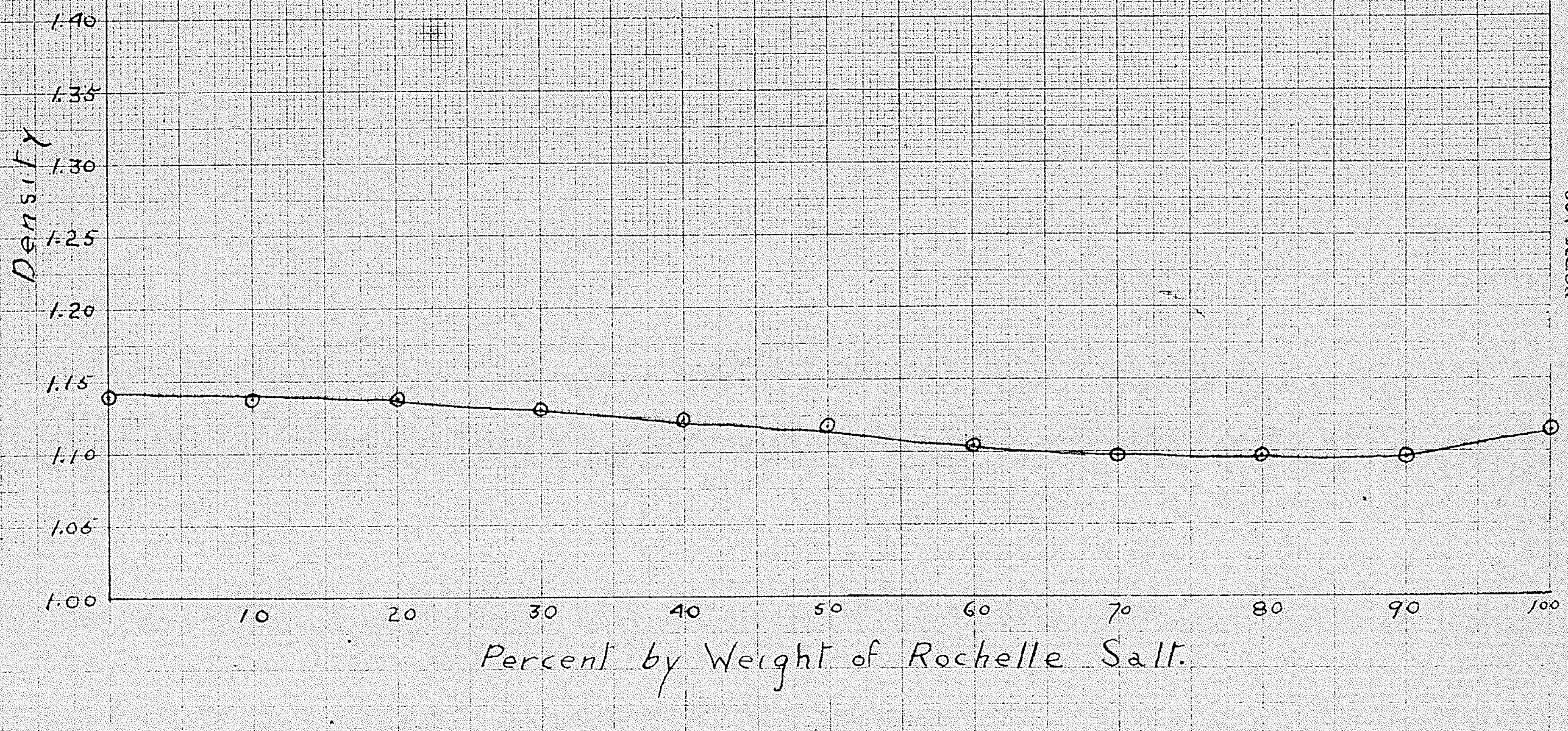


Relation between Viscosity and Composition of Various Mixtures of Rochelle Salt and Sodium Hydroxide.

Fig. XIX

Relation between Density and
Percent of Rochelle Salt in the
Solution

Fig. XX



DISCUSSION OF RESULTS.

DISCUSSION OF RESULTS

Thermal Analysis.

Plotting temperature against composition as is done in Figure XVI, a curve is obtained which seems to point to the formation of a compound in the racemisation of Rochelle salt by sodium hydroxide. After a temperature of about 267° has been reached on the graph the curve may go in three possible directions. In two of these, the curves reach a maximum point when the proportion of NaOH to Rochelle salt is 1:1. In one case the compound would not be very highly dissociated and in the second case it would be a little more so. The third possible curve reaches a maximum when the proportion of NaOH to Rochelle salt is 1:2. In this case the compound would be fairly highly dissociated.

However, the method of thermal analysis cannot be considered to be a very useful one in this case. In the first place copper vessels are readily attacked by evaporating sodium hydroxide in them. As was mentioned in the experimental part of the work air was passed into the flask to drive out the moisture from the molten sodium hydroxide and this is essentially the same as evaporation. Some pieces of pure iron wire were placed in the flask in order to lessen the action but it must still be taken into account.

Further as the Rochealle salt reached a concentration of about 15% charring took place when it was added to the NaOH and heat applied, and this became more pronounced as the concentration of the Rochelle salt was increased.

Measurement of Rotation.

In Figure XVII is shown the relation between the rotation in degrees of various mixtures of NaOH and Rochelle salt and the dilution. As can be seen the curves--more especially those where the concentration of Rochelle salt is high--all tend to approach the value for pure Rochelle salt as the dilution becomes greater. This might be explained by assuming that a complex is formed which is in itself laevorotatory.

Since Rochelle salt is dextrorotatory, as the concentration of the NaOH is increased, that is, as more and more complex is formed the rotation would fall off from that of pure Rochelle salt.

With dilution dissociation would take place and the rotation would once again tend to approach that of pure Rochelle salt.

Although from a dilution of 50 c.c. to a dilution of 0 c.c. the curves are sketched in solid this should not be taken to mean that actual measurements were carried out in this region as such was not the case. The curves were extrapolated back to zero dilution, that is, no water content, to determine what the rotation would be under such circumstances.

Measurements of Viscosity.

In Figure XIX the straight line represents the normal curve, that is, it shows the increase in viscosity as NaOH is added to Rochelle salt assuming the two components have no action on one another. However, the curve actually obtained differs but slightly from this. This would seem to indicate the absence of compound formation. If a compound had been formed the curve should have shown a distinct maximum or, if the compound was less viscous than one or other of the components, a minimum. The curve obtained only showed a slight sag.

Measurements of Density.

Nothing much need be said about the curve shown in Figure XX as the measurement of density is really too coarse to be of much value. However, it may be noted that the density shows only a very slight increase with increase in concentration of NaOH, which is what would be expected in the absence of compound formation.

NOTE. To the discussion of the results obtained from the method of thermal analysis should be added the fact that the temperature of complete solidification was also plotted against composition. It was thought this might give the solidus curve. However such does not appear to be the case. It is probable that these points are due to super-cooling in the melt.

SUMMARY

SUMMARY

1. Various methods were used to determine whether or not a compound is formed in the racemisation of Rochelle salt by sodium hydroxide.

2. Complications arose which rendered the value of the method of thermal analysis doubtful and the softening-melting point method proved to be entirely unsatisfactory.

3. The method of thermal analysis and the measurement of rotation point to the possible existence of a complex in the Rochelle salt solution.

4. Measurements of the viscosity show that complex formation is improbable. Measurements of the density, although not very strong evidence, also point to the absence of a complex in the Rochelle salt solution.

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BIBLIOGRAPHY

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