POTASSIUM CHLORID IN AQUEOUS ACETONE

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I. INTRODUCTION

That potassium carbonate added to mixtures of ethyl alcohol and water will cause them to divide into two layers has been known for centuries, this property of the salt having been utilized by Raymond Lully¹ in the thirteenth century for the preparation of concentrated alcohol. Brandes² and Schiff³ found that manganous sulfate had the same power, Traube and Neuberg⁴ showed that the property was common to a large number of salts, and Linebarger⁵ found that not only could other salts be substituted for the potassium carbonate but other liquids, viz. propyl alcohol and acetone could be used in place of ethyl alcohol. Linebarger found it possible to obtain two-liquid-phase systems in the case of the following salts and bases with ethyl alcohol and water :

Those printed in italics are given also by Traube and Neuberg, while they add to the list the following :

With methyl alcohol and water, Linebarger succeeded in obtaining two layers in the case of potassium carbonate only, though he experimented with a great number of other salts. With

¹ Lescoeur. Ann. Chim. Phys. (7) 9, 541 (1896).

² Pogg. Ann. 20, 586 (1830).

³ Lieb. Ann. 118, 370 (1861).

⁴ Zeit. phys. Chem. 1, 509 (1887).

⁵ Am. Chem. Jour. 14, 380 (1892).

propyl alcohol and water, the following salts gave two-liquid-phase systems :

NH_4Cl , NaCl , KCl , RbCl , CaCl_2 , NaNO_3 , $\text{Sr}(\text{NO}_3)_2$, Li_2SO_4 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, NiSO_4 , CoSO_4 , CuSO_4 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CdSO_4 , ZnSO_4 , MnSO_4 , NaOH , KOH , Na_2CO_3 , K_2CO_3 , KCN , $\text{K}_3\text{Fe}(\text{CN})_6$.

With acetone and water he obtained two liquid phases with :

LiCl , NH_4Cl , NaCl , KCl , RbCl , CaCl_2 , SrCl_2 , CoCl_2 , CuCl_2 , MnCl_2 , $\text{CH}_3\text{CO}_2\text{K}$, $(\text{CH}_3\text{CO}_2)_2\text{Mn}$, Li_2SO_4 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, NiSO_4 , CoSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, CdSO_4 , ZnSO_4 , MnSO_4 , NaOH , KOH , Na_2CO_3 , K_2CO_3 , KCN .

I have confirmed Linebarger's results with acetone in the case of the italicized substances. His negative results, however, are not to be taken as conclusive. His procedure was to take a saturated solution of the salt in a test-tube and add the organic liquid till layers formed or the salt precipitated, and then to repeat the experiment using a salt solution of one-half the concentration. He does not state that he heated the tubes, but in some cases (e. g. KCl) he must have done so in order to obtain the separation. In open tubes I have succeeded in obtaining two layers in the case of the following substances which he gives among those that do not form two layers with acetone and water: NaNO_3 , NH_4NO_3 , $(\text{NH}_4)_2\text{CO}_3$, $\text{CH}_3\text{CO}_2\text{Na}$, also with BaCl_2 in presence of solid salt. I have also observed the phenomenon in the case of the following salts, which he did not use :

NaBr , KBr , NH_4Br , MgSO_4 , Na_2HPO_4 , $\text{H}_2\text{NH}_4\text{NaPO}_4$.

In some other cases, e. g. KNO_3 , $\text{Ba}(\text{NO}_3)_2$ and KClO_3 , I find, in agreement with Linebarger, that solid salt is precipitated by addition of acetone to the aqueous solutions of the salts, but it is possible that in some of these cases the formation of two layers may take place at higher temperatures. For, while it is impossible at room temperature to get two liquid phases in the system potassium nitrate, ethyl alcohol and water, I have succeeded in obtaining the division by heating a complex of the

three components in a sealed tube (see below, p. 464). On the other hand I got negative results in the case of potassium nitrate with methyl alcohol, and in the case of potassium chlorid with either methyl alcohol or ethyl alcohol. The experiments were made in each case with fifty percent aqueous alcohol and a quantity of salt considerably in excess of the amount that would dissolve at room temperature. In the case of potassium nitrate and methyl alcohol, the salt dissolved completely even when it was so greatly in excess that at room temperature it was merely wetted by the liquid. Potassium chlorid neither dissolved completely nor gave two liquid layers in either solution, though the tubes were heated to 195°.

The influence of temperature on these systems has, indeed, been a matter of common observation. Thus Schiff noticed that at room temperature the mixture of alcohol and water that divided into two layers on saturation with manganous sulfate lay between 15 and 50 percent, while at higher temperatures 13, 14 and 60 percent alcohol could be made to divide; Traube and Neuberg found that the concentrations and relative volumes of the two layers in unsaturated solutions of ammonium sulfate in aqueous ethyl alcohol varied with the temperature; and Linebarger observed that "a fall of a few degrees of temperature will bring about the characteristic cloudiness in a solution of potassium carbonate in a mixture of alcohol and water on the point of forming layers, and this cloudiness will disappear on warming to the previous temperature." Linebarger's deduction from this behavior of one system, that "in general, it may be stated that the lower the temperature the more water is needed to bring about the disappearance of the layers", is, however, unjustified. For with certain other systems or even with some complexes of this same system, he would have found that a *rise* of temperature would cause clouding which would disappear on recooling, and that therefore at a *higher* temperature a greater addition of water would be necessary to cause the disappearance of the layers. Indeed, with acetone and water, the latter seems to be the more common case, for of the salts with which I have ex-

perimented I have found only four (Na_2SO_4 , Na_2CO_3 , Na_2HPO_4 , NaNH_4PO_4) whose solutions in mixtures of acetone and water clouded on cooling.

II. THEORY

No two of the three components of a system of this class form two liquid layers at ordinary temperatures. The organic liquids are consolute with water; they reach their critical points far below the melting-points of the salts, so a two-component system with two liquid phases cannot be obtained in the case of any of these organic liquids with any salt, and water and salt do not form two liquid layers. As, however, it is most reasonable to ascribe the cause of the appearance of the two layers to the immiscibility of the salt with the organic liquid, we may for theoretical purposes regard these two components as forming (at a high temperature) the invariant system, solid salt, two solutions and vapor. On the other hand, in view of the complete miscibility at high temperatures of potassium, sodium, and silver nitrates and of potassium chlorate with water,¹ we may regard salts in general as miscible in all proportions with water at their melting-points. These two assumptions bring the systems into Class 1 of Bancroft's classification of three-component systems in which two liquid phases appear.² For, A being salt, B organic liquid, and C water, we have: melting-point of A higher than that of B, A and B forming the binary invariant system solid A, two solutions and vapor, A and C and B and C not forming two liquid phases and C increasing the miscibility of A and B. One condition of the classification is not necessarily fulfilled by such systems, viz. that the components form no compounds, for in some cases hydrates of the salts may appear. Provided, however, not more than one hydrate can exist in equilibrium with the two liquid phases, we can bring the system under Class 1 so far as this particular equilibrium is concerned by taking the hydrated salt instead of the anhydrous salt

¹ Étard. *Comptes rendus*, **108**, 176 (1889).

² Jour. Phys. Chem. **1**, 647 (1897).

as component A. If, now, we have the further condition fulfilled that ice and salt (or ice and hydrate) cannot coexist in equilibrium with two solutions and vapor, no "secondary" quintuple point is possible and the system falls into Sub-class 1c. All the above conditions are fulfilled in the case of the system that forms the special subject of this research, the solid that appears in equilibrium with the two liquid phases being in this instance the anhydrous salt. The subsequent treatment will be with special reference to this system, but it may be generalized for all systems fulfilling the same conditions. Some applications of the theory to other systems will be introduced.

The temperature-concentration diagram for a system of this nature is represented in perspective in Fig. 1 and in horizontal projection in Fig. 2, the theoretical assumptions as to the miscibility of the components at temperatures not actually attainable being therein embodied. The concentrations represented upon such a diagram are those of the liquid phases. Consequently, at temperatures above which no liquid phase can exist (critical temperatures), the system becomes incapable of representation on the diagram. Each complex of a three-component system having its own critical temperature, the actual diagram would have a surface as its upper termination. Because, however, we have no measurements of the critical phenomena of three-component systems having two liquid phases and also because the theoretical relations are hereby more clearly indicated, I have thought it better to draw the diagram as if no critical points appeared.

It may be well to point out the distinction between this diagram and that employed by Schreinemakers.¹ His diagram represents the temperature-concentration conditions of equilibrium *at constant pressure*, while this represents those conditions *at the equilibrium pressure of the system*. This diagram is, therefore, the strict analogue of the plane temperature-concentration diagram commonly used for two-component systems. It should also be mentioned that my experiments were made under condi-

¹ Zeit. phys. Chem. 23, 429 (1897).

tions not exactly those for which the diagram calls. Some of them were conducted in corked bottles and test-tubes, the rest in sealed tubes from which no attempt was made to expel the air. In the first instance we have atmospheric pressure instead of the equilibrium pressure of the system, and in both cases air is present as a fourth (more strictly a fourth and fifth) component.

Fig. 1

In Figs. 1 and 2, H represents the cryohydric point for the three components, h , h' and h'' are the cryohydric points of the three binary systems and $p\sigma p'$ is the boundary curve for salt, two solutions and vapor. In the solid figure, M, M' and M'' being the melting-point of the pure components, hM is the

jugate point of equal temperature upon the same curve, the two representing the two solutions which at that temperature can coexist in equilibrium with solid salt and vapor. By drawing the tie-lines joining these successive pairs of conjugate points, we obtain a ruled surface $p'Sp\sigma$. In other words, the ruled surface is developed by a horizontal line whose motion is guided by the curves $pP\sigma$ and $p'P'\sigma$. Between the ruled surface and the dineric surface is enclosed the region of temperature-composition conditions for the formation of two liquid phases and vapor. That is to say, any complex whose composition at a given temperature falls within this enclosed space is instable as a homogeneous system and will divide into two liquid layers and vapor. The enclosed space may therefore be appropriately termed the *dineric space*. Beyond the dineric surface is the region of unsaturated solutions, and beyond the ruled surface lies another enclosed space representing instable complexes dividing into solid salt, two liquid phases and vapor. This we may call the *stereo-dineric space*. Its boundaries are the ruled surface of the boundary curve and another ruled surface developed by the motion of a horizontal line guided along the straight line AA' and the curve $p\sigma p'$ as directrices. The latter ruled surface separates the stereo-dineric space from the two divisions of the region of supersaturated complexes that divide into solid, one liquid phase and vapor.

The results of an experiment with a complex of potassium nitrate, ethyl alcohol and water may serve to illustrate the changes that take place along a temperature ordinate that passes through all the spaces into which the triangular prism is divided by the surfaces. At room temperature, the complex consisted of a saturated solution of potassium nitrate in 50 per cent alcohol and a quantity of solid salt in excess. When this complex was heated in a sealed tube, the following states were realized:

(1) The complex consisted of three phases — solid salt, one solution and vapor.

(2) The liquid divided into two layers, making the total number of phases four.

(3) The salt dissolved completely, leaving the three phases — two solutions and vapor.

(4) The two liquid phases coalesced, leaving only one — liquid and vapor.

Thus the temperature ordinate for the complex traverses:

(1) The region behind the surface $l_1' l_1'' l_1'$, (the region of supersaturated solutions).

(2) The stereo-dineric space.

(3) The dineric space.

(4) The region of unsaturated solutions.

Every point of the dineric surface has a conjugate point at the same temperature, the two representing the compositions of the coexistent liquid phases. But along a limiting curve $\sigma S'S$, which we may call the *crest-curve*, the two conjugate points for any given temperature coincide, that is, the composition of the co-existent phases are identical and therefore equal also to that of the whole liquid. The point σ is the *plait-point* of the surface. Its temperature is the minimum temperature at which two liquid phases can coexist in stable equilibrium with vapor, and as the point lies also on the curve $p\sigma p'$, solid salt can exist in equilibrium with the two solutions and vapor at this minimum temperature.

A peculiarity common to many, if not to all, of these systems of salt, water and organic liquid is that the dineric surface extends out so far as to overhang the boundary curve $p\sigma p'$. This is indicated in Fig. 2 where $p\sigma p'$ is the horizontal projection of the boundary curve, while $pS'p'$ is the projected limit of the dineric surface. (I have assumed that the two curves meet in p and p' . It is possible, however, that they may meet in some other conjugate points of σp and $\sigma p'$. No experiments have been made to settle the question.) The physical fact expressed by this property of the surface is that certain solutions unsaturated with respect to the salt can be made to divide into two layers by heating. For example, a complex of the composition,

water 51 g, acetone 39 g, potassium chlorid 10 g, forms a homogeneous solution at 30° and at 40°, but is divided into two liquid layers at 50°. The temperature ordinate for this composition must therefore pass through the dineric surface at a point between 40° and 50°. The same behavior may be observed in the case of many other salts with acetone and water. This peculiarity in the form of the dineric surface distinguishes the systems possessing it from some others belonging to Bancroft's Sub-Class 1c. For example, with naphthalene, acetone and water Cady¹ found no unsaturated solution that formed two layers on heating. In such a system the limit of the dineric surface does not overhang the boundary curve. The difference between the two varieties of systems is expressed in the projected diagram (Fig. 2) by the presence or absence of the curve $pS'p'$.

From Fig. 1 it would appear that by following up the temperature ordinate for water 51 g, acetone 39 g, potassium chlorid 10 g, we should eventually pass through the dineric surface a second time and come back into the region of unsaturated solutions. In other words, the complex that divided into two liquid layers below 50° would become homogeneous again at some higher temperature. This I have not been able to realize with the system acetone, water and potassium chlorid. On account of the steepness of the dineric surface, the temperature at which the liquid becomes homogeneous lies so high (at any rate in the case of the complexes used in the few experiments made) as to be unrealizable by my method of experimentation (see p. 479). But by taking 11.6 cc water, 3.7 cc absolute alcohol and 2.93 g potassium carbonate (= 66.40 g water, 16.8 g alcohol and 16.8 g salt to 100 g solution), I obtained a complex which is an unsaturated solution below 40° and above 70° and a two-liquid-phase system between these two temperatures. With such a system it is possible to realize in an open test-tube the formation of two layers on heating and their disappearance on further heating.

It will be observed that in systems of this class the plait-

¹ Jour. Phys. Chem. **2**, 168 (1898).

point is the point of minimum temperature for the coexistence of solid and two liquid phases (and also for that of two liquid phases), while in the system water, sodium chlorid and ethylene cyanid studied by Schreinemakers¹ it is the point of maximum temperature for this equilibrium.² The latter system belongs to a different class, for here the appearance of the two layers is due to the incomplete miscibility of water and ethylene cyanid and the third component is such as to *decrease* the miscibility of the other two. If we neglect the possibility of the recurrence of two liquid layers at a higher temperature (due this time to the incomplete miscibility of sodium chlorid with ethylene cyanid), this system comes under Sub-class 3a of Bancroft's paper, A being ethylene cyanid, B water and C sodium chlorid. The experimental data of Schreinemaker's paper fulfil the predictions of Bancroft that in the projected temperature concentration diagram for systems of this Sub-class, (1) the two branches of the boundary curve for solid A, two solutions and vapor will diverge as they leave the side AB of the triangle; (2) the temperature will rise along this curve as we pass away from the side of the triangle; and (3) the temperature will rise from the quintuple point along the two branches of the boundary curve for solid C, two solutions and vapor, the curve having therefore a point of maximum temperature.³ For while the concentrations of the ethylene cyanid in the two liquid phases at the binary quadruple point (on the side of the triangle) are:

Upper layer 72 g-mols to 100 g-mols in all
Lower " 2.5 " " " " " "

at the ternary quintuple point they have diverged to

Upper layer 82.79 g-mols to 100 g-mols in all
Lower " 1.99 " " " " " "

The temperature of the quadruple point is 18.5° and that of the quintuple point 29° , a rise as we pass from the side of the triangle. And, finally, the temperature rises as we pass from the

¹ Zeit. phys. Chem. 23, 417 (1897).

² See diagram in Schreinemaker's paper, p. 429.

³ Bancroft. Jour. Phys. Chem. 1, 655 (1897).

quintuple point along the boundary curve for solid sodium chlorid, two solutions and vapor, and reaches a maximum at 145.5° . In assigning this system to Sub-class 3a, we have assumed that sodium chlorid and ethylene cyanid do not form two liquid phases. It would be more consistent, however, to make the same assumption in this case as in that of the acetone and potassium chlorid, i. e. to regard the two components as forming two layers at a temperature not actually realizable. This assumption would require that there should proceed from the AC side of the triangle a second dineric surface, which would be analogous to that of Fig. 1, for here, as there, the effect of the third component, water, is to render the other two more miscible. Though it seems probable that not far above 145.5° chemical action between water and ethylene cyanid will occur to such an extent as materially to alter the nature of the system, still it is just possible that a portion of the second dineric surface may be realizable; in other words, mixtures of ethylene cyanid, water, and sodium chlorid that clear at or below 145.5° may cloud again at higher temperature. But Schreinemaker's work shows that at least this second dineric surface does not cut the first. The lower dineric surface will therefore not differ in any respect from that of systems of Sub-class 3a and this application of Bancroft's predictions is legitimate.

The Isotherms and Isothermal Planes

An isothermal plane is, of course, a horizontal section of the triangular prism and the *isotherm* is made up of the curves of intersection of this plane with the dineric and solubility surfaces. For temperatures, at which only one solid and one liquid phase exist, the isotherm is a single curve (an element of the surface, $ll'l'$) representing the solubility of the salt in varying mixtures of acetone and water. For temperatures at which one solid and two liquid phases can appear, the isothermal plane has the form of Fig. 3, the isotherm consisting of the three curves LP, PSP' and P'L'. The solubility of the salt A in water at the given temperature is represented by the point L and the

Fig. 3

solubility of the salt in the organic liquid by L' . (As the diagram is drawn to represent the system alcohol, water and manganese sulphate, the point L' is practically coincident with B . The same is true in the system acetone, water and potassium chlorid). The field $CLPSP'L'BC$ is a section of the region of unsaturated solutions, $PSP'P$, a section of the dineric space, and the triangle APP' a section of the stereo-dineric space. Therefore at the temperature of the isotherm, complexes whose compositions are represented by points within the field $CLPSP'L'BC$ are stable as homogeneous liquid (and vapor); complexes within the fields, ALP , $AL'P'$ are instable as homogeneous liquid and break down into solid salt and solution represented by points of the curves LP , $L'P'$ respectively; complexes within the triangle APP' break down into solid salt and two solutions having the composition P , P' , and complexes within the dineric field $PSP'P$ break into two solutions represented by conjugate points

of the dineric curve PSP' . S being the *crest-point* — the point of the crest-curve for this temperature — the composition of the lower layer in a system of two liquid phases and vapor will be denoted by a point X between S and P , that of the upper layer by the conjugate point X' between S and P' , while the composition of the whole complex will be denoted by that point of the tie-line XX' , which would be the center of gravity of the whole mass if the mass of the lower layer were situated at X and that of the upper layer at X' .

If, to a mixture of organic liquid and water, whose composition is represented by a point K between Y and Z , we continuously add salt, the composition of the mixture will vary along the line KA until it reaches the dineric curve PSP' , where the solution will divide into two liquid phases of compositions represented by conjugate points of the dineric curve. As the composition of the whole complex proceeds along the line KA , the two layers will differ more and more in composition, the conjugate points separating farther and farther. At the same time, the relative *masses* of the two layers will vary continuously, because they must always be such that their center of gravity will lie at the intersection of the tie-line with the line KA . When the composition of the whole has reached the value R , the compositions of the two layers will be P, P' , and their masses as $P'R:PR$. Further addition of salt will have no effect on either the composition or the relative masses of the two phases. It is evident also that mixtures of the organic liquid and water having compositions between C and Y or between Z and B cannot be made to divide into two layers by addition of salt. In both cases we should get first a homogeneous solution, then a solid salt in equilibrium with a homogeneous solution of a composition represented by a point of the curve LP in the one case or of the curve $L'P'$ in the other. In like manner, N and M being the points of intersection of BP' and BP with the side AC , it is evident that we get different results by continuous additions of organic liquid to aqueous salt solutions of different concentrations. In the case of the most dilute solutions, C to N , we

get first homogeneous solutions, then solid salt and a solution of the curve P'B. More concentrated solutions, M to N, give first homogeneous liquid, then two liquid phases of changing composition and relative masses, then solid salt and two liquid phases of constant composition but varying relative masses, and finally solid and solution of the curve BP', the mass of the lower layer having now become zero. Solutions of concentrations between M and L (the latter being the composition of the saturated aqueous solution) give first homogeneous liquid, then solid salt and solution of the curve LP, then solid salt and two solutions, the mass of the lower layer continuously decreasing, and finally solid and solutions of the curve BP', the lower layer having disappeared.

Very few quantitative experiments have been made with systems of this class. Of measurements at constant temperature there are a few by Schiff,¹ Traube and Neuberg,² Bodländer,³ and Linebarger.⁴

Schiff observed that at room temperature aqueous alcohol of from 15 to 50 percent strength separated into two layers on saturation with manganous sulfate. Table I gives his measurements of the percentage weight of crystallized salt ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$) in the saturated solutions. The data for this system are represented in Fig. 3, where the hydrated salt is taken as one of the components. As Schiff's measurements were of saturated solutions in all cases, they give the points P, P' and points of the curves LP and P'B. They can be immediately plotted on the diagram from the figures of Table I by marking off the given percentage of salt on the straight line joining the point A with the point for the strength of alcohol. If more accurately made, Schiff's measurements of the compositions of the two layers would undoubtedly have been exactly the same in the 20, 30, and 40 percent alcohol. A few points of the dineric curve are obtained from the measurements of Linebarger. As he worked

¹ Lieb. Ann. 118, 370 (1861).

² Zeit. phys. Chem. 1, 509 (1887).

³ Zeit. phys. Chem. 7, 318 (1891).

⁴ Am. Chem. Jour. 14, 380 (1892).

at 20° his results may fairly be plotted on the same isotherm as Schiff's. Table II gives Linebarger's results, recalculated on the basis of grams water, alcohol and hydrated manganous sulfate respectively to one hundred grams solution. The letters in Table I and II, refer to Fig. 3. The position of the point P' is uncertain. I have plotted Linebarger's last determination as probably the nearest approach to that point, though he does not mention that salt was precipitated in the experiment. As already intimated, Schiff's analyses of the upper layers in the 20, 30 and 40 percent alcohol do not accord with the theory. The same is true of his analysis of the 50 percent alcohol solution. But the discrepancies may easily be due to experimental error.

It appears from the diagram (points N and M) that the range of manganous sulfate solutions that can be made to divide into two layers at room temperature by addition of alcohol is very wide, running from solutions containing about 3 to solutions containing over 51 percent of the tetrahydrate, i. e. 2 to 34 percent solutions of manganous sulfate. Schiff's observation that in presence of the crystals the volume of the upper layer is the greater the stronger the alcohol is evidently in accord with the theory. For the nearer the point K approaches Z, the greater is the ratio $PR:PR'$.

Traube and Neuberg determined a number of conjugate points of the dineric curve of the 33° isotherm of the system alcohol, water and ammonium sulfate and Bodländer determined the position of the intersections of the dineric with the salt solution curves (i. e. points P, P' , Fig. 3) on the 15° isotherm of the same system. The methods of the phase rule having been already applied to these measurements by Schreinemakers,¹ it is unnecessary to discuss them here.

Linebarger conceived of the layer formation as taking place in systems of salt, an organic liquid and water only within certain limits of composition and defined the "upper" limit as "the limit attained when the formation of a layer is rendered impossible by the presence of too much organic liquid", and the

¹ Zeit. phys. Chem. **23**, 657 (1897).

"lower" limit as "the point where a layer ceases to form on account of the presence of an excess of water." His method of determination of the lower layer was as follows: "Varying quantities of organic liquid and water were added from burettes to a titrated solution of a salt until a drop of water would clear up the milkiness caused by a drop of alcohol." It is evident that this procedure gives a point of the dineric curve. For he begins with a point on the side AC of the triangle and proceeds in a straight line toward B (by adding alcohol) till he has overstepped the dineric curve, then he proceeds in a straight line towards C (adding water) until he has again overstepped the curve and so moves in an ever-narrowing zigzag until he has approached so close to the dineric curve that a drop of one liquid causes a change in one direction and a drop of the other causes a change in the other direction. The tables given in Linebarger's paper are therefore data of the dineric curve of the 20° isotherms of the various systems. His measurements are limited to a small portion of the curve and no conjugate points are determined.

In attempting to determine the "upper" limit, Linebarger took a certain volume of salt solution and added the organic liquid in small quantities until the volume of the lower layer became zero. A glance at the diagram will show that this result cannot be attained without precipitation of salt unless a line joining some point on AC with the point B has two intersections with the dineric curve and none with the line PP', which can occur only in case the dineric curve which has been tending downward toward the side CB begins to tend upward when we get near the side AB. In general this is not the case and Linebarger found that precipitation of salt prevented his attaining the "upper" limit of layer-formation in all systems but one — potassium carbonate, ethyl alcohol and water. In the case of this system, either the dineric curve has the peculiar form just referred to or, what seems more probable in view of the fact that "crystals appeared as soon as the layer disappeared", Linebarger was really determining points on a metastable extension of the dineric curve.

An interesting confirmation of the theory of the tie-lines is afforded by some measurements by Traube and Neuberg of the variations of the conjugate solutions of a complex of ammonium sulfate, alcohol and water with the temperature. They added 250 cc of 99.6 percent alcohol to 750 cc of a solution of ammonium sulfate, containing 340 g to the liter and analyzed the two layers into which the mixture divided at four different temperatures. Their results recalculated into mass-percentages are given in Table III. According to our theory the tie-lines joining each pair of conjugate points must pass through the temperature ordinate of the composition of the whole complex. In other words, the horizontal projections of the four tie-lines must intersect in the point that gives the composition of the whole complex. If the tie-lines be actually drawn on a triangular diagram they are found to intersect, as nearly as one can tell, in the point

Water 58.7 Alcohol 18.1 Salt 23.2

Taking the specific gravity of the ammonium sulfate solution used as 1.168 and that of the alcohol as 0.795, I calculate for the composition of the complex as made up by Traube and Neuberg :

Water 57.86 Alcohol 18.42 Salt 23.72

The diagram shows also that with rising temperature there is an increase in the relative mass of the lower layer, i. e. the ratio $R'X':R'X$ (Fig. 3) increases as the temperature rises, and Traube and Neuberg found that with increasing temperature the lower layer increased in volume, while the upper layer decreased.

TABLE I
Manganous Sulfate, Alcohol and Water — Schiff

Strength of alcohol	Pct $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$		Point on Fig. 3
0	56.25		L
10	51.4		<i>l</i>
	Upper layer	Lower layer	
20	2.2	47	
30	1.66	48	P
40	1.37	48.6	
50		2.0	
60		0.66	<i>k</i>

TABLE II

Manganous Sulfate, Alcohol and Water — Linebarger, 20° C

g water	g alcohol	g salt ($\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$)	Point on Fig. 3
55.86	30.03	14.11	<i>a</i>
52.25	43.59	4.16	<i>b</i>
49.41	47.66	2.94	<i>c</i>
45.34	53.00	1.66	<i>d</i>
42.56	56.24	1.20	P'

TABLE III

Ammonium Sulfate, Ethyl Alcohol and Water — Traube and Neuberg

Composition of 100 g solution

Temp	Upper layer			Lower layer		
	g water	g alcohol	g salt	g water	g alcohol	g salt
16.6°	52.80	40.21	6.99	60.33	10.19	29.48
33.0°	47.99	46.75	5.26	61.02	9.80	29.18
41.8°	47.34	47.67	4.99	61.16	9.74	29.10
55.7°	45.90	49.47	4.63	61.59	9.46	28.95

III. EXPERIMENTS

In order to gain a more accurate knowledge of the shape of the dineric surface for the system acetone-water-potassium chlorid, I have made the following experiments:

I. A series of measurements of the temperatures at which different unsaturated solutions of the system divide into two layers, i. e. a determination of the points at which given temperature-ordinates cut the dineric surfaces and so pass from the region of unsaturated solutions into the dineric space.

II. A few experiments to discover whether divided solutions become homogeneous again at higher temperatures, i. e. whether the temperature-ordinate passes a second time through the dineric surface—this time from the dineric space to the region of unsaturated solutions.

III. Measurements of the temperatures of division of saturated solutions, i. e. determination of points of the boundary curve.

IV. Measurements on the 30° and 40° isotherms.

The Materials

The potassium chlorid used in all the experiments described in this paper was carefully purified by three recrystallizations, then fused in a platinum dish. It gave no reactions for sulfate and none for magnesium and an analysis by precipitation with silver nitrate gave:

KCl taken	AgCl found	Calc. for pure KCl
0.5359 g	1.0313 g	1.032 g

One portion used in some of the experiments of Series III was made from acid potassium carbonate. Analysis of this portion gave:

KCl taken	AgCl found	Calc. for pure KCl
0.7360 g	1.4125 g	1.418 g

The acetone was dried over calcium chlorid and fractionated. The portions used distilled within half a degree.

(a) Temperature of Division of Unsaturated Solutions

The salt was weighed out from weighing tubes and the water and acetone added from burettes. The complex was then heated and the temperature at which the clouding took place noted. Where the temperature of division was low, the measurements were made in a wide test-tube provided with a cork through which the thermometer passed. For higher temperatures, pressure flasks were tried at first, but, these proving leaky, sealed tubes were used, the tubes being heated in a water- or oil-bath.¹ Here, of course, the temperature measurement was not as accurate as for the lower temperature, the thermometer being immersed in the bath instead of in the inner liquid. In all cases a number of observations of the temperature of division were made. For the lower temperature, these observations did not in general differ from one another by more than a few tenths of a degree, but in the case of the solutions in 30 percent acetone the clouding was indistinct and the temperature of division, therefore, much harder to distinguish. The error in all the

¹ For the temperatures above 150° an air-bath was used.

temperature readings for this strength of acetone and in the higher reading for other mixtures may amount to more than one degree. The results are given in Tables IV–IX. They show that with rising temperature the dineric surface approaches the

Fig. 4

acetone-water plane of the triangular prism. Table X shows the nearest approaches to that plane that were realized and so gives an approximation to the position of the limit-curve of the projected diagram—the curve $pS'p'$ of Fig. 2. The limit-curve as thus approximately determined is shown together with the boundary curve in Fig. 4.

TABLE IV
Temperatures of Division
30 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
63.46	27.20	9.36	No division up to 290°
62.00	26.57	11.43	" " " 150°
61.75	26.47	11.79	" " " 290°
61.68	26.43	11.92	103°
61.73	26.46	11.85	100°
61.19	26.22	12.62	81°
60.50	25.93	13.60	67°
60.40	25.88	13.71	62°
59.86	25.64	14.50	48.5
59.98	25.72	14.30	48
59.02	25.31	15.68	36 (?) Metastable
Saturated solution			40°

TABLE V
Temperature of Division
40 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
54.42	36.28	9.28	About 65° (in pres. flask)
54.00	36.00	10.00	49.3
53.84	35.90	10.28	45.6
53.48	35.65	10.87	39.0
53.27	35.51	11.22	35.1
Saturated solution			34.2

TABLE VI
Temperature of Division
50 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
47.48	47.48	5.04	No division up to 150°
47.12	47.12	5.79	97.5°
46.96	46.96	6.09	76
46.66	46.66	6.69	57.2
46.61	46.61	6.80	56
46.54	46.54	6.94	52.6
46.38	46.38	7.23	47.4
46.06	46.06	7.90	35.4
45.75	45.75	8.50	27.4 (?) Metastable
Saturated solution			32.6

TABLE VII
Temperature of Division
60 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
38.80	58.20	2.97	149 ^o
38.42	57.64	3.95	71.5
38.20	57.49	4.32	51.9
38.05	57.24	4.70	45.1
38.04	57.25	4.69	44.4
38.00	57.19	4.79	41.0
37.95	57.11	4.94	39.0
37.78	56.96	5.27	34.0
Saturated solution			33.3

TABLE VIII
Temperature of Division
70.12 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
29.24	68.61	2.13	54.1
29.19	68.50	2.30	47.2
29.16	68.44	2.41	42.6
29.14	68.37	2.48	40.4
29.14	68.33	2.53	39.0
Saturated solution			35.4
70 pct acetone			
Saturated solution			35.6
75 pct acetone			
Saturated solution			39.0

TABLE IX
Temperature of Division
80 pct acetone

Composition of 100 g solution			Temperature of division
g water	g acetone	g salt	
19.90	79.60	0.55	110.5
19.88	79.52	0.65	95
19.84	79.36	0.80	67
19.82	79.29	0.93	55.5
19.80	79.21	0.99	45.8
Saturated solution			45.6

TABLE X
Minimum quantity of salt that will cause division

pct acetone	g salt to 100 g solution
30	11.8
50	Between 5.0 and 5.8
60	2.9
80	0.5

(b) Attempts to Realize Clearing

A number of divided unsaturated solutions were heated to higher temperatures to determine whether the two liquid phases become one again. A beaker was used as an air-bath and the sealed tubes were shaken by means of wires wrapped about them and projecting through the asbestos cover of the beaker. With carefully made tubes, it was found possible to reach a temperature of 250° in this way, but when heated to 300° , the tubes invariably burst. It is not known to what extent decomposition of acetone at high temperatures may alter the equilibrium between the phases. That decomposition does take place to an appreciable extent is shown by the coloration of the liquid in the tubes. The following complexes remained divided at about 300° :

- (1) Water 60.77 g Acetone 26.04 g Salt 13.19 g (30 pct acetone)
 (2) " 46.30 g " 46.30 g " 7.40 g (50 pct acetone)

When the approximate position of the limit-curve (Fig. 4) had been determined, a few complexes in the neighborhood of the curve were chosen in the hope that they would become homogeneous at realizable temperatures:

- (3) Water 47.0 g Acetone 47.0 g Salt 6.0 g (50 pct acetone)
 and
 (4) " 47.1 g " 47.1 g " 5.8 g (50 pct acetone)
 remained divided at 220° – 230° .

- (5) Water 61.68 g Acetone 26.43 g Salt 11.92 g (30 pct acetone)
 which did not divide till it had reached a temperature of nearly 100° appeared to be homogeneous above 180° , no second layer being visible and no clouding being caused by shaking. But

the volume of the upper layer was so very small as to make it difficult to decide whether the two had really coalesced, and the evidences of decomposition were specially marked in this tube. It is therefore not claimed that reclearing has been certainly realized in any complex of the system potassium chlorid, acetone and water. That it can be realized in the analogous systems, potassium nitrate, ethyl alcohol and water and potassium carbonate, ethyl alcohol and water is shown by the experiments described above (pp. 464-466).

(c) Temperature of Division of Saturated Solutions—The Boundary Curve

In determining the temperature of division of saturated solutions, a difficulty is met with. Here one cannot make one's readings by heating the tube containing solution and salt and observing the temperature at which the liquid clouds, for the solubility of the salt increases with the temperature and the chances are that the solution will not be saturated when the clouding occurs. Consequently it is necessary to heat the tube to a temperature above the temperature of division of the saturated solution and then, shaking it as it cools, observe the temperature at which the clouding disappears. If the tube be cooled rapidly, a temperature below that of the boundary curve is reached, a metastable extension of the dineric surface into the region of the supersaturated solutions being realized. Such a state is realizable even in the presence of an excess of solid salt, for the crystals form slowly and a temperature below that of the stable equilibrium is easily reached before clearing takes place.

The compositions and temperatures of divisions of the saturated solutions are given in Table XI. The compositions were derived from the data of Tables IV-IX by plotting the variation of the temperature of division with the salt-content of the unsaturated solutions and extrapolating for the observed temperature of division of the saturated solution. The relative proportions of acetone and water in the solutions were, of course, already known. On the projected triangular diagram the boundary curve, so far as I have determined it, has the position

shown in Fig. 4. The data of Table XI plotted with temperature and strength of acetone as coordinates gives the curves of Fig. 5, which may also be regarded as traced upon the water-

Fig. 5

acetone face of the triangular prism by the horizontal line which moves upon the salt-temperature axis and the boundary curve as directrices. Such a curve might be used in the estimation of the strength of aqueous acetone. The error due to the difficulty of determining accurately the temperature of division of saturated solutions could be eliminated by making the readings always under the same conditions, but at best the method would be applicable only to mixtures of say between 20 percent and 85 percent acetone not containing any third substance and would not be very accurate for mixing between 50 percent and 60 percent acetone because of the flatness of this portion of the curve.

TABLE XI
Temperature of Division of Saturated Solutions

pct ace- tone	Temp of division	Composition of 100 g solution		
		g water	g acetone	g salt
26	46.5			
30	40.0	59.36	25.44	15.20
40	34.2	53.21	35.47	11.32
50	32.6	45.97	45.97	8.06
60	33.3	37.86	56.80	5.34
70	35.5	29.09	68.25	2.66
75	39			...
80	45.6	19.80	79.20	1.00

An experiment to determine the effect of a further increase of temperature on a divided saturated solution may be here described. A portion of 75 percent acetone was heated in a sealed tube with a quantity of salt more than sufficient to saturate it at any temperature realized. About 230° , the upper liquid phase became identical with the vapor, the lower liquid phase remaining. On cooling, the upper phase divided into liquid and vapor with the turbulent clouding characteristic of a critical point.

(d) The Isotherms

THE 30° ISOTHERM

At 30° , two liquid phases do not appear. This isotherm, therefore, consists of a single curve representing the solubility of potassium chlorid¹ in varying mixtures of acetone and water.

In the solubility determinations I used small bottles that had been steamed out. The acetone solutions were made up by weight and with the finely-powdered salt were heated to 40° for seven hours with frequent shaking. The bottles were then transferred to an Ostwald thermostat set at 30° . After they had stood over night, salt had crystallized out from all these solutions, showing that they were saturated. The 40, 50 and 60 percent acetone solutions were still divided into two layers but became homogeneous on shaking. The bottles were left standing in the thermostat two days longer before the analyses were

¹ The solubility of potassium chlorid in water at 30° appears from my measurements as 37.495 parts in 100 parts water. Mulder, Scheik. Verh. 1864, 39, found 37.4, and Andreä, Jour. prakt. Chem. 137, 470 (1884), got by interpolation of his results 37.275.

made. After two days more a second analysis of each was made and the mean of the two determinations is given in Table XII. The analyses were made by evaporation according to the method described by Trevor¹. The isotherm is represented in Fig. 6.

TABLE XII
Isotherm 30°C.

pct acetone	Composition of a 100 g solution		
	g water	g acetone	g salt
0	72.73	0.00	27.27
5	71.45	3.71	25.11
10	70.16	7.42	23.42
20	61.85	14.84	18.69
30	53.54	22.26	15.04
40	45.23	29.68	11.31
50	36.92	37.10	8.04
60	28.61	44.52	5.12
70	20.30	51.94	2.77
80	12.00	59.36	1.07
90	3.69	66.78	0.17
100	0.00	74.20	0.00

¹ Z. phys. Chem., 10, 190 (1904).

THE 40° ISOTHERM.

The isotherm for 40° is represented by Fig. 7 and Tables XIII-XV. The points upon the curve KP and P'B, the solubility curves, were determined according to the same method used for the 30° isotherm. The results are given in Table XIII.⁴ For the points of the dimeric curve I proceeded as follows:

Portions of an aqueous solution of potassium chlorid of known strength were measured out by carefully calibrated pipettes (5 cc in most cases, but in some cases 1 cc) varying quantities of water were added from a calibrated burette and just sufficient acetone run in from another burette to cause permanent separation at 40°. Of course, a number of such experiments were necessary for the determination of each point. A glance at Fig. 7 will show that this method gives points upon

1.

the dineric curve PSP'. For, if to an aqueous solution of potassium chlorid represented by the point M, we continuously add acetone, the composition of the complex will vary along the line MB and the solution will remain homogeneous until the point L is reached, when it will divide into two layers. If, then, we know the composition of the original aqueous solution (M) and the quantity of acetone added, the point L is determined.

The points of the dineric curve so obtained are given in Table XIV. The compositions of the solutions that just divide at 40° are there expressed in two ways: (1) For plotting on rectangular coordinates, as grams water and acetone respectively per gram salt; (2) For triangular coordinates, as grams of each component per hundred grams solution. In calculating these results, the specific gravity of water at room temperature was taken as equal to unity and that of acetone as 0.792, the value given in Landolt and Börnstein's Tables for acetone at 19.8° as compared with water at the same temperature.

A number of pairs of *conjugate* points of the dineric curve were determined. This was done by the following method: The data of Table XIV were used to plot a curve with acetone per gram salt (x) and water per gram salt (y) as coordinates. A two-liquid-phase system having been allowed to come to equilibrium at 40° C, portions of each layer were pipetted off and weighed. Their salt content was then determined by evaporation and the difference gave the number of grams of acetone and water together. Reduced to one gram salt, this gave the value of $x + y$ and reference to the curve enabled one to determine what values of x and y gave the found value of $x + y$. The composition of the conjugate phases is given in Table XV.

An approximation to the position of the point P can be obtained by producing the salt-solution curve, KP, and the dineric curve to their intersection, and in the same way the point P' can be found by producing BP' and the dineric curve. On either the rectangular or the triangular diagram, however, these approximations are very rough. I obtained a more accu-

rate determination of the points by evaporating a portion of each of the two liquid phases that existed in equilibrium with solid salt, so determining what percentage of the solution consisted of water and acetone together, and then finding from Table XI (Fig. 5) what were the *relative* quantities of acetone and water in the solutions that coexist with solid and a second liquid phase at 40° . A direct observation there tabulated gives 30 percent acetone as one of these and interpolation shows that 76 percent acetone is the other. The former will, of course, be the lower layer. Evaporation-analyses of the lower layer were made in the case of the 40, 50 and 60 percent acetone solutions and gave as an average 84.23 as the percentage of acetone and water in this layer. For the upper layer, an average from the 50, 60 and 70 percent solutions gave 98.57 percent. Hence the figures given in Table XV for the composition of these coexistent phases.

The following deductions can be drawn from the diagram of the 40° isotherm:

1. At 40° aqueous solutions of potassium chlorid of from 5 to 21.5 percent strength can be made to divide into two liquid layers by addition of a sufficient quantity of acetone. From weaker or stronger solutions, salt will be precipitated. We have already seen that the acetone-water mixtures that can be made to divide by addition of potassium chlorid lie between 30 and 76 percent acetone.

2. The crest-point S lies between l and l' . Thus there is a solution of a composition of about 50 percent acetone, 43 percent water, and 7 percent salt that an infinitesimal addition of salt or of acetone will cause to divide into two layers of almost exactly equal composition.

3. The point R being the middle point of the line PP' , the line BR produced cuts the side AC of the triangle at about 17 percent salt, and the line AR produced cuts CB at 55 percent acetone. Therefore, if we begin with a 17 percent solution of potassium chlorid and add acetone till salt just begins to precipitate, we shall have two liquid layers of equal mass, and we

get the same two layers by saturating 55 percent acetone with potassium chlorid. The compositions of the complexes that divide into layers of equal mass without precipitation of salt is given by the middle points of the tie-lines connecting the different pairs of conjugate points.

TABLE XIII
Solubility Curves 40° C

pet acetone	Composition of 100 g solution		
	g water	g acetone	g salt
Curve KP			
0	71.31	0.00	28.69
5	69.62	3.67	26.72
9.09	67.88	6.79	25.33
15	65.15	11.51	23.34
20	62.97	15.75	21.28
Curve P'A			
80	19.81	79.34	0.58
85	14.94	84.66	0.40
90	10.00	89.84	0.16
95	4.97	94.96	0.07
100	0.00	100.00	0.00

TABLE XIV
Dimeric Curve 40° C

Per gram salt		Composition of 100 g solution		
g water	g acetone	g water	g acetone	g salt
3.86	1.95	56.68	28.63	14.68
4.70	3.16	53.05	35.67	11.29
5.12	4.05	50.34	39.82	9.83
5.55	5.11	47.60	43.83	8.58
6.08	6.63	44.35	48.36	7.29
6.50	7.73	42.68	50.75	6.57
7.39	10.79	38.53	56.26	5.21
8.01	12.88	36.59	58.84	4.57
9.39	18.62	32.37	64.18	3.45
10.38	22.52	30.62	66.43	2.95
11.53	28.47	28.12	69.45	2.44

TABLE XV
Conjugate Points of the Dimeric Curve 40°C

Point on curve	Upper layer To 100 g solution			Point on curve	Lower layer To 100 g solution		
	g water	g acetone	g salt		g water	g acetone	g salt
<i>a</i>	55.20	31.82	12.99	<i>a'</i>	28.14	69.42	2.44
	54.27	36.69	12.03		29.45	67.83	2.72
	53.27	35.44	11.29		30.96	65.97	3.07
	51.69	37.76	10.55		31.83	64.83	3.33
<i>e</i>	51.23	48.50	10.27	<i>e'</i>	32.64	63.79	3.56
	50.34	39.88	9.77		34.07	62.01	3.92
	49.08	41.67	9.26		35.27	60.49	4.24
<i>i</i>	48.02	43.18	8.79	<i>i'</i>	37.44	57.67	4.89
	47.62	43.73	8.64		38.00	56.96	5.04
	46.49	45.34	8.17		38.68	56.17	5.25
<i>l</i>	45.65	46.52	7.83	<i>l'</i>	39.98	54.36	5.66
	45.64	46.57	7.79		40.41	53.78	5.81
<i>P</i>	58.99	25.24	15.77	<i>P'</i>	23.66	74.91	1.43

THE 50° ISOTHERM

This isotherm for 50° is represented in Table XVI and Fig. 8. The data for this isotherm are deduced entirely from

the experimental results of Series I and III, with the exception of the point K which is taken from Andreä's measurements of the solubility of potassium chlorid in water. The sources of the figures are indicated in the table. Points *a-f* are obtained by interpolation on curves for each acetone water-mixture, the coordinates being temperature and g salt per 100 g solution. Points P and P' I have located by producing the dineric curve to its intersection with the lines joining the point for pure potassium chlorid to the point for 25 percent and 81 percent aqueous acetone. It will be observed that both the range of acetone-water mixtures that can be caused to divide by addition of salt and the range of aqueous salt solution that can be caused to divide by addition of acetone are greater at 50° than at 40°.

TABLE XVI

Isotherm 50° C

per cent acetone	Point on curve	Composition of 100 g solution			Source of figures
		g water	g acetone	g salt	
Dimeric Curve					
30	<i>a</i>	59.91	25.67	14.42	Table IV
40	<i>b</i>	54.04	36.03	9.93	" V
50	<i>c</i>	46.46	46.46	7.07	" VI
60	<i>d</i>	38.25	57.37	4.38	" VII
70.12	<i>e</i>	29.22	68.56	2.22	" VIII
80	<i>f</i>	19.81	79.25	0.94	" IX
81 ±	<i>p'</i>	Saturated solution			" XI
25-26	<i>p</i>	"			" XI
Solubility curve <i>Kp</i>					
0	<i>k</i>	70.0		30.0	Andreä

SUMMARY

The knowledge thus gained of the form of the dineric surface for the system potassium chlorid, acetone, and water, may be summed up as follows:

The plait-point of the surface lies at a temperature of about 32.5° and a composition somewhere near water 43, acetone 50, salt 7 (saturated solution of the salt in 54 percent acetone at 32.5°). From this point the boundary curve extends in the

direction indicated in Fig. 4, the temperature rising from the plait-point in both directions. From the boundary curve, the dineric surface extends upward and outward toward the acetone-water plane at least as far as the position of the outer curve of Fig. 4 and to temperatures as high as 149° (See Table VII). That at some higher temperature it reaches its actual limit and begins to slope back in the other direction is indicated by the fact that solutions differing very little in composition from others that divide at about 100° can be heated to very high temperatures without dividing and would also seem probable from the fact that in the analogous systems, potassium carbonate, ethyl alcohol and water and potassium nitrate, ethyl alcohol and water, solutions that divide into two layers on heating become homogeneous again at still higher temperatures.

In conclusion, I desire to express my hearty thanks to Prof. Bancroft upon whose suggestion this work was undertaken and whose valuable advice has been ever at my service.

Cornell University, May, 1898