T H E S I S

EQUILIBRIA IN THE SYSTEMS, WATER, ACETONE,
AND INORGANIC SALTS.

presented by

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in partial fulfillment of the requirements
for the degree of Doctor of Philosophy.

Degree Granted

1913

A C K N O W L E D G M E N T .

The work in this thesis was done under the direction of Dean George B. Frankforter. I wish to express my appreciation of the assistance and encouragement given.

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Introduction.

In 1874-78, a memoir on the phase rule was published by Willard Gibbs.¹ Owing to its abstruse mathematical nature its appearance attracted but little attention at the time, but in 1887 a new discussion of equilibria dependent on this law was published by Roozeboom.² The value of this rule was then shown by its application to innumerable systems of one, two, three and four components. The discussion of many of these cases and the general development of the subject is given in the following books: Bancroft's "The Phase Rule" (1897), Ostwald's "Lehrbuch" and also "Grundriss der allgemeinen Chemie" (1901) and "Die Heterogene Gleichgewichte" (1901) by Roozeboom. Probably the best treatment of the general subject is given in the concise but comprehensive text Findlay's "The Phase Rule and Its Applications" (1911, 3rd edition). One of its applications, which bears directly on the subject under investigation, is made to physical equilibria appearing in systems of three components, which are called "ternary" systems by Bancroft.³ Bancroft, Roozeboom and his coworker Schreinemakers are the pioneers in this field. Bancroft wished to show that these systems could be classed under another generalization

and believed that their conduct could be fully explained by the Mass Law.⁴⁻⁵ The systems which were only partially investigated included the following sets of two components, water being always the third: alcohol and chloroform, methyl alcohol and acetone, benzene and acetone, benzene and methyl alcohol, benzene and alcohol, ether and alcohol or methyl alcohol, ethyl acetate and alcohol, alcohol and carbon disulfide or methyl or ethyl valerate, etc. Data which are given for water, alcohol and one of the following, mono, di or tri chloroacetic acid, or one of the simple alkyl valerates, acetates, formates, butyrates or propionates, were obtained by Pfeiffer⁶ in work on solutions of limited miscibility. Bancroft concluded that the Mass Law could be applied to these systems and the equilibria in the systems could be represented by the exponential expression $x^{\alpha} y^{\beta} z^{\gamma} = C$, or by some modification of it. x , y and z represented the number of grams in a constant quantity of the solution, and α and β were proportionality factors. His data were not complete enough to justify absolute conclusions. Taylor⁷ and Lincoln⁸ worked along the same line with the same object in view and found that for their data they could apply this law. Bell⁹, in 1905, in work with a series of similar systems came to the conclusions: (1) that the dineric equilibria for two liquids and a solid may be represented by the mass law equation when the components are not electrolytes and when the mass of the solid component is kept constant; (2) that ^{the} mass law equation does not describe the dineric equilibria for salts in an aqueous solution.

Previous to the work of Bancroft, Duclaux¹⁰ expressed the results of his researches in the systems benzene, acetic acid, water; ether,

acetic acid, water; amyl alcohol, acetic acid, water; and amyl and ethyl alcohols and water by means of some mathematical formula which did not admit of general application. A casual glance at the graphic representation of the equilibria which are to be ~~re~~discussed, would lead one to believe that some definite mathematical relationship did exist, but I was unable to develop any definite formula. This side of the subject was not investigated, but more attention was paid to the practical side, with the object of showing the relative efficiency of salts in removing water from acetone.

The dehydration of acetone is very similar to that of alcohol and ether. In most cases where dehydration of organic liquids takes place, the phenomenon of the formation of two definite layers ^{also} takes place. The salts most commonly used for dehydration purposes are CaO , CuSO_4 , CaCl_2 , K_2CO_3 , Na_2SO_4 , MgSO_4 , CaSO_4 , and KCl . CaCl_2 offers disadvantages inasmuch as it frequently forms compounds with the liquids and cannot be used in drying them. The only experiments ¹¹ of value on the efficiency of these drying agents were made by Siebenrock in the drying of ether; Foote and Scholes ¹² in the drying of alcohol; and Frankforter and Frary ¹³ in the drying of alcohol. Siebenrock used the following salts CaCl_2 , K_2CO_3 , Na_2SO_4 , MgSO_4 , KCl , CaSO_4 and carnallite, and found that CaCl_2 and K_2CO_3 gave the best results. Foot and Scholes found that the salt chosen for dehydrating purposes must have a hydrate of low vapor pressure and at the same time of high percentage of water. Included among the salts were CaSO_4 , K_2CO_3 , ZnSO_4 and MgSO_4 . The two latter were used in such quantities that only the monohydrates could be formed with the amount of water present in the liquid to be

dried. CaCl_2 could not be used because it forms a compound with the alcohol. None of the salts mentioned are particularly soluble in alcohol. Frankforter and Frary¹⁴ have recently shown that anhydrous potassium fluoride can be easily placed in the same class as anhydrous potassium carbonate, and that its hydrate is more efficient than the hydrated carbonate.

In the dehydration of acetone containing water it was noticed that two layers were formed when sufficient salt, such as CaCl_2 , KF , K_2CO_3 or NaCl was added. This formation of layers in the addition of a third compound to two solutions is not a new phenomenon, but has been noted from the earliest times. We find the formation of layers when three components are present noted from the times when chemistry was hardly classed as a science. Von Meyer in his History of Chemistry (3rd English Edition, page 60) states that Lully in the 15th Century dehydrated alcohol by the use of fused potashes. Lescœur¹⁵ states that he noted the formation of layers. The exact date cannot be given because the authenticity of most of Lully's works is more or less doubtful because of the vast number that have been accredited to him. This fact was also known to Basil Valentine.¹⁶ In 1824 Firnhaber¹⁷ showed that the addition of sodium sulphate produced layers in aqueous solutions of alcohol, and in 1830 Brandes¹⁸ found that manganous sulphate had the same effect. In 1861 Schiff¹⁹ observed the same fact. Casual observations were made and a series of quantitative results were obtained, though they were not of specific value. In 1864²⁰ Proctor, in a short article in the Chemical News, noticed with great surprise that commercial potassium carbonate would form layers when it was added to an ammonio solution.

He obtained the same effect by the use of potassium phosphate and citrate, ammonium citrate and sodium silicate. His results were qualitative. In 1871, the formation of two layers in mixtures of water, alcohol and carbon disulphide was obtained by Tuchschiidt and Follenius²¹. This shows that the formation of layers is not confined to the third substance being an inorganic salt. In 1872, Berthelot and Jungfleisch²² obtained layers in the systems water, acetic acid, and benzene or amyl alcohol or ether as the third component. In 1877, in a short and incomplete study, Draper²³ noted the distribution of HCl in water and ether layers. In 1887, J. Traube and Neuberg²⁴ found that a large number of salts, including potassium and sodium phosphates, the alkali carbonates, sodium magnesium and zinc sulphates and potassium alum produced the same phenomenon. Bodländer had communicated to them the fact that layers would form in aqueous solutions of alcohol on the addition of ammonium sulphate. They found that with a constant temperature, an increase of potassium carbonate or alcohol to the system of alcohol, water and potassium carbonate would increase the amount of alcohol in the upper layer and decrease the amount of alcohol in the lower layer. The amount of carbonate in the lower layer would also increase. The results given are quantitative. Bodländer²⁵ worked on similar lines in 1891, using ammonium sulphate. In 1892 Linebarger²⁶ obtained two well defined liquid layers, with the following compounds and ethyl alcohol: Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, CaSO_4 , ZnSO_4 , MnSO_4 , NaOH , KOH , Na_2CO_3 and K_2CO_3 . In place of ethyl alcohol he used the organic liquids acetone, propyl and methyl alcohol. The only salt that seemed to salt out methyl alcohol was K_2CO_3 . With propyl alcohol and water, NH_4Cl ,

NaCl, KCl, RbCl, CaCl₂, NaNO₃, Sr(NO₃)₂, Li₂SO₄, Na₂SO₄, (NH₄)₂SO₄, NiSO₄, CoSO₄, CuSO₄, FeSO₄, Fe₂(SO₄)₃, CdSO₄, ZnSO₄, MnSO₄, NaOH, KOH, Na₂CO₃, K₂CO₃, KCN, and K₄Fe(CN)₆ gave two definite liquid phases; with acetone and water the following salts gave two phases: Li, NH₄, Na, K, Rb, Ca, Sr, Co, Cu and Mn (ous) chlorides; K and Mn acetates; no nitrates Li Na, ammonium, Ni, Co, Cd, Zn and Mn sulphates, KOH and NaOH; Na and K carbonates, and KCN. In 1898, Snell,²⁷ found that layers formed in mixtures of water, acetone and the following salts in addition to all the salts used by Linebarger, NaBr, KBr, NH₄Br, MgSO₄, Na₂HPO₄, H₂NH₄NaPO₄, NaNO₃, NH₄NO₃, (NH₄)₂CO₃, NaC₂H₃O₂ and BaCl₂. Snell obtained some of these results at higher temperatures. In 1892, quantitative work was done by McElroy and Krug²⁸ who noted the formation of layers in aqueous carbohydrate solutions such as sucrose, maltose, dextrose, and cane sugar with acetone. In 1887 Parmentier²⁹ noted the formation of layers in crystallized phosphomolybdic acid, ether and water layers, - this is of a slightly different type and hardly belongs to this survey, but in 1896 he noticed similar phenomena in mixtures of alcohol, water and sodium thiosulphate. In 1894, L. Henry³⁰ noted the formation of layers in such systems as water, amines, and KOH. In the same year Schunke³¹ worked with water, ether and hydrochloric acid. In 1898, Cady³² studied the system naphthalene, acetone, water; and Dodge and Gratton³³ obtained layers with difficulty in the systems water, alcohol and KNO₃. In 1900, Newth³⁴ obtained layers in the mixture of K₂CO₃ with ammonia in aqueous solution.

Beginning with the year 1897, Schreinemakers³⁵ published a series of papers dealing with ternary systems in which two layers appeared.

These systems include such components as water, ether or benzoic acid or alcohol or phenol and succinotrile or aniline or NaCl or tartaric or racemic acids etc. In 1912, the liquid phases in the systems water, alcohol and MnSO_4 were studied³⁶. In 1900, deBruyn³⁷ obtained layers in mixtures of water and ethyl or methyl alcohol and potassium carbonate. In 1902 Ketner³⁸ worked with Na_2CO_3 , water and alcohol. In 1904, Herz and Knoch³⁹, in determining the solubility of various salts in aqueous solutions of acetone, found that layers were formed within certain limits with either sodium or ammonium chloride. In 1905, Fleckenstein⁴⁰ obtained layers with water, ethyl alcohol and ammonium nitrate. In 1896, Crismer⁴¹ found that under certain conditions, turbidity appeared in a mixture of petroleum, water and alcohol. In 1905, Bell⁴² worked on systems containing, besides water and acetone, a third substance such as Na_2CO_3 , K_2CO_3 , sugar, naphthalene, anethol, etc. Timmermans⁴³ worked on similar systems as well as those containing antipyrin, water and salts as K_2CO_3 , $(\text{NH}_4)_2\text{SO}_4$ and $\text{Na}_2\text{S}_2\text{O}_3$. He also found the temperatures at which these layers formed and disappeared. W. Lash Miller and R. H. McPherson⁴⁴, in studying the distribution of colloids noted the plait points in the following systems, water, chloroform and acetone; water, ether and acetone; water, chloroform and alcohol; water, ether and alcohol, etc. In 1910, Bonner⁴⁵ made an experimental determination of the binodal curve, the plait point and the "tie lines" of over fifty different systems containing water and two organic compounds. In 1910, Pontein⁴⁶ showed that layers were obtained with amyl alcohol, water

and sodium chloride. J. W. McDavid⁴⁷ obtained layers with quite a different type of components, using water, potassium carbonate and potassium ethyl dipropyl malonate. In 1912, Frankforter and Frary obtained layers in aqueous solutions of ethyl and propyl alcohols with potassium fluoride. Since the potassium fluoride was found to be so effective in salting out the two alcohols, a study was made of its action with aqueous solutions of acetone. A saturated solution of potassium fluoride was added to a solution of acetone in water. A distinct separation into layers took place immediately.

A study of the equilibrium in this system at the ordinary room temperature was undertaken. In connection with this a study was also made of the systems containing potassium carbonate, water and acetone; calcium chloride, water and acetone; and sodium chloride, water and acetone.

Some quantitative work was done by Linebarger⁴⁸ on the potassium carbonate system, while Bell⁴⁹ made a more complete investigation. The data of Herz and Knoch⁵⁰ in the last system are given in a form that has no practical value.

Theory.

The theoretical side of systems containing three components which can have two liquid and one solid phase has been the subject of a series of investigations by F. A. Schreinemakers⁵¹. Application of the general principles has been made to the systems under discussion. In these systems we have the following conditions:⁽¹⁾ two liquids which are miscible in all proportions, and which in the absence of a third substance do not form layers under any conditions, (2) a salt which is soluble in the water but not in the organic liquid, (or the amount of the salt which dissolves in the organic liquid is practically negligible). This salt does not cause layer formation when added to any one of the two components in the absence of the other. The phases possible under these conditions are: (1) a homogeneous mixture of all three components, (2) two liquid phases, (3) a solid and two liquid phases, (4) a solid phase and one liquid phase. In case the hydrate is formed "4" represents two solid phases and one liquid phase. The graphic representation of these systems is not original with Schreinemakers, but is derived from the original diagram of Gibbs,⁵² which was modified by Roozeboom,⁵³ and further explained by Bancroft⁵⁴. An equilateral triangle is used whose vertices represent the three components, the length of each side of the triangle being equal to 100. If only two components are present, the position of the point representing the amount of each component present will be located on the side of the triangle. If three components are present, the composition will be represented by a point within the triangle, as P in figure 1. In the triangle.

A = 100 grams of salt, B = 100 grams of acetone, C = 100 grams of water. Lines are drawn through P parallel to the three sides of the triangle⁵⁵, the distance of the point to any side representing the amount of the component at the opposite vertex of the triangle. P is therefore made up of a' parts of A, b' parts of B and c' parts of C, as indicated by the parallel lines in figure I. Bancroft has given three different methods for the direct reading of any point within the triangle. The graphic presentation of the systems studied is given in figure II, A, B and C representing the same components as A, B and C in figure I. D represents the solubility of the salt in water. The salts used are practically insoluble in acetone, so this point L almost coincides with B. H represents the composition of the hydrate at the temperature conditions of the experiment. The lines D E and F B are saturation curves of the solid salt in acetone and water, D E representing the solubility of the salt in a water acetone solution and F B representing the solubility of the salt in an acetone water solution. Starting with the solution represented by B, additions of acetone to this solution will not cause the formation of layers until the position in the diagram represented by E is reached. In a similar manner, if water and minute portions of salt are added to a 100 per cent. acetone solution, the solubility of the salt in the acetone and water will be represented by the line F B and layers will not form until the concentration represented by the point F is obtained. The points E and F are quadruple points and represent concentrations of two solutions which are in equilibrium

Fig II

with each other and the solid hydrate phase. If the acetone, water and salt contents of any solution are represented by any point on the curve between E and F, addition of a sufficient quantity of the solid salt will cause the solution to separate into three phases, solid salt and two liquids. The composition of the two solutions will then correspond to the two points E and F. E will represent the lower layer and F will represent the upper layer. This diagram represents an isotherm. therefore, the temperature is a constant. In the experiment it is kept at 20°. The pressure and the vapor phase are constants. The system represented by E and F must then be invariant. No degrees of freedom being present, E and F are therefore quadruple points. The curve E P F is called the binodal curve. Any point on this curve represents a homogeneous solution, but if to any of these solutions salt is added separation into two liquid phases takes place at once. The binodal curve is composed of two parts, E P and P F. P, which is the plait point, represents a homogeneous solution which will separate into two liquid phases with the composition represented by the two points x' and y' which are on the curve immediately to the left and right of the point P. If more salt is added to either of these two solutions, a separation of two liquids takes place, the composition of one of the layers is represented by a point on the curve E P and the composition of the other layer by a point on the curve between P and F. These two solutions are in equilibrium with each other, and are called conjugate solutions, the line connecting a conjugate pair of solutions as in X Y is called a tie line. By the addition of more salt to the solution at P,

different sets of conjugate solutions are formed. At the final point where no more additional salt will go into solution, the two conjugate solutions represented by E and F or the quadruple points are obtained. All the solutions on the binodal curve represented by points on the line E F have a high water content, while those on the line F F have a high acetone content. Starting out with the concentration of the solution given by E, addition of acetone to this solution will cause the formation of definite layers. The composition of the lower layer will be represented by some point on the curve E F and the composition of the upper one will be represented by some point on the curve F F. Water is now added until the two liquid phases just disappear, and a point on the curve between E and F will represent the composition of the solution. By adding more acetone and more water, the concentration of the solution of the plait point P can be obtained experimentally. The volume of the lower layer has always been greater than the volume of the upper layer, and ^{at} the points of the two conjugate solutions immediately next to the plait point the volume of the upper and lower layers is nearly the same and their density is nearly the same. From this point on, as the acetone content increases, the lower layer diminishes in volume. At the point immediately following E on the binodal curve, addition of acetone to the solution will give an upper layer represented by a mere film and just preceding F the additional acetone will cause the lower layer to be merely visible, or the volume will become very small. Every point on the part of the binodal curve E F is in equilibrium with some point on the other part of the binodal curve F F. A second quadruple point is formed when the anhydrous salt and the hydrate are in equilibrium with the solution.

At this point Q_2 only one liquid phase is possible. In the diagram, all parts of the area B C D E P F B are homogeneous. This is an unsaturated area. The field enclosed by A H D E P F B A is heterogeneous. The area E P F E is heterogeneous and is made up of systems composed of two liquid phases. The triangle H D E is heterogeneous. Any point within this triangle is represented by the solid hydrate and a solution given by the line D E. If the hydrate does not form we have the triangle A D E, any point in this triangle representing solid salt A and a solution on the line D E. The triangle H E F H is also heterogeneous, points within it being represented by the hydrate H and two solutions. If the hydrate is not formed this triangle is replaced by the triangle A E F, also a heterogeneous area made up of the solid salt and two liquid phases. H F O H is a triangle which contains the system, hydrate and solutions represented by the line F Q. Points in the triangle A F B A separate into anhydrous salt A and solutions of the salt in acetone and water given by the line F B.

Experimental.

The following determinations were made in all the systems studied:

1. Solubility of the salts in various concentrations of aqueous acetone, ranging from 90 to 100 per cent, acetone.
2. The binodal curve.
3. Tie lines.
4. Approximate positions of the plate point.
5. Quadruple points.
6. Some temperature effects.

Solubility. In the determination of "1" the method used was not always satisfactory. In all cases, except that of calcium chloride, the salt was carefully heated to a dull red heat for about ten minutes, then it was partially cooled in a desiccator and added while still warm to the different acetone water solutions.

The acetone solutions ranged in concentration from 95 to 100 per cent. and were made by carefully weighing the water in an erlenmeyer flask provided with a ground glass stopper. The volume of acetone needed for a given concentration was carefully calculated from the specific gravity. This was added to the water and the contents of the flask were again weighed, giving the actual weight of acetone and water present. After the salts had been added to the solutions, the mixtures were heated to about 35--40°. The solutions remained in intimate contact with the salt for periods ranging from one week to

to ten days. Incidentally, as all the experimental work was done at 20°, the room temperature was kept as near 20° as possible. It ranged at times from 18° to 26°. In the case of sodium chloride the period of contact was much shorter. The salt solutions were shaken from time to time. The source of error in this method was due to the fact that if not enough salt was added the solution would not be saturated, and if too much salt was added the solution separated into two layers, giving entirely different concentrations of acetone than the ones under investigation. After standing for a given time the solutions were decanted off and weighed quantities of the solutions were transferred to weighed platinum dishes and evaporated over water baths or on the radiator, to dryness. The radiator heat was more satisfactory than the water bath, as the acetone passed off less rapidly and did not spurt out of the dish. The residue was weighable only in the case of calcium chloride and in all other cases it was negligible. The solubility of the salts in water was not determined, but the following solubilities were used: 92.3 grams of potassium are soluble in 100 grams of water, but this is an inconvenient form, the percentage of the anhydrous salt in 100 grams of the saturated solution being more convenient to work with. This is equivalent to 48 per cent. of anhydrous salt.⁵⁶ The solubility of potassium carbonate is 112 grams of the anhydrous salt in 100 grams of water at 20°, or 53.06 per cent. carbonate.⁵⁷ For calcium chloride, the solubility used is that given by Roozeboom⁵⁸. 74.5 grams of CaCl_2 in 100 grams of water, which is equal to 42.69 grams of CaCl_2 in 100 grams of the solution. The solubility of NaCl used was 35.79 grams in 100 grams of water or 26.35

per cent. of the solution as sodium chloride.⁵⁹ The following method was employed in determining the binodal curve: An erlenmeyer flask of about 400 c.c. capacity, provided with a carefully ground glass stopper, was used in all the determinations. A side neck was blown into the flask at such an angle that a short thermometer could be inserted into the neck by means of very thin rubber cork thus allowing the bulb of the thermometer to be constantly immersed in ^{the} solution. The thermometer was calibrated by comparison with a standard certified thermometer. The flask was carefully dried and weighed. The salt that was to be used, except in case of the calcium chloride, was heated to red heat for about ten minutes, cooled in a desiccator, rapidly transferred to the weighed flask and weighed immediately. Water from the burette was added, all the salt was completely dissolved and the flask with water was again weighed. The difference in the last two weights showed the amount of water. The indicator was then added. As it was difficult to see the appearance and the disappearance of two phases, the same indicators used by Frankforter and Frary were again used, spirit blue for all the systems except the potassium carbonate. In the carbonate system, on account of the bleaching action of the alkaline solution on the spirit blue, solid particles of phenolphthalein were used. In all cases precautions were taken not to use too much of the indicator, because with excess of the indicator the end point would be more obscure than if no indicator at all were added.

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Bonner is the only other investigator of binodal curves who introduced an indicator, making use of small quantities of lamp black.

The colored indicator is more convenient than the lamp black indicator.

After the addition of the indicator a very small quantity of acetone was added. If two layers did not appear more acetone was added until there was a second definite layer present. The additional acetone was then weighed and water was carefully added from the burette until the two layers just became homogenous. The water was added very carefully and the contents of the flask were thoroughly shaken and allowed to stand; otherwise too much water would be used, nullifying results. The additional water was weighed, and more acetone was added to form a second layer. This was weighed and water added as before until the second layer just disappeared. Series of determinations were made, starting out with saturated salt solutions, continuously adding water and acetone until the flask would hold no more of the solution. The concentrations ranged from the concentration at the part of the quadruple point E up to about 1 per cent. of the salt, or near the other part of the quadruple point at F. The appearance of layers at E was not difficult to determine, but the appearance of those at F was, - it being rather difficult to distinguish between the cloudiness due to two layers and a type of cloudiness of the saturated acetone, salt, water solution itself.

In determining the binodal curve, the temperature was kept at 20°, no particular difficulty being found as the temperature of the solution could be read during the whole course of the experiment.

The temperature changes of a few degrees around 20° were very noticeable in the system of calcium chloride. They were less marked in the case of potassium fluoride, and with certain concentrations, were not at all noticeable with potassium carbonate. In changing the temperature from 5° to $+40^{\circ}$ in the latter system no particular effect was noticed in determining points on the binodal curve. This can also be seen in figure V, where the points determined by Bell⁶¹ are plotted beside the binodal curve obtained at 20° . Bell's results are for an isotherm at 25° . In determining points on the binodal curve the phenomenon of "foam building" mentioned by Ostwald⁶² was noted. According to Ostwald all aqueous solutions above their saturation temperatures are inclined to form foams, no foams being found in heterogeneous mixtures. When the solutions containing two layers were shaken the bubbles quickly disappeared, but on the immediate formation of a single layer the foam was easily obtained.

Tie Lines. The binodal curve is then the locus of all saturated homogeneous liquids, the effect of adding a particle of salt causing the formation of two layers. The composition of these two layers can then be determined and tie lines drawn. The tie lines are not necessarily parallel, though the tendency toward this is noted in lines near the plait point. The composition of these two solutions, which are called conjugate solutions, was determined in the following manner: The solutions were transferred to a separatory funnel, the upper and lower liquids separated and weighed. Portions of each evaporated to dryness. This gave the amount of salt in the upper and lower layers, respectively. By reference to the

tables for the different binodal curves, the percentage composition of the two solutions can be easily determined. A straight line drawn between these two points on the binodal curve representing the conjugate solutions is called the "tie line".

Plait Point. When the solutions are more nearly of the same composition the tie lines become shorter and disappear when the plait point is reached. The definition of the plait point has been given in the previous discussion. Difficulty was experienced in determining some of the plait points, because as the solutions have more nearly the same composition, their densities approach each other in value and the layers, while they do form, do not separate out so quickly, one solution being held in fine suspension in the other. Instead of determining the plait point directly several tie lines were located, and by interpolation the plait point was determined. It could have been determined directly.

Quadruple Points. These were determined by the following methods: A saturated aqueous solution of the salt was made and acetone was added until two very distinct layers appeared, the volume of each being equal to at least three hundred cubic centimeters. Additional salt was then added, and the flask was warmed to get more of the salt into the solution. The flask and contents were then ^{cooled} cooled to 20° and in most cases crystals of the hydrate appeared in a very short time. The solutions were kept in contact with each other for periods exceeding a week, and the contents of the flask were shaken at frequent intervals. In some instances a shaking machine was used.

Weighed portions of both the upper and lower layers were transferred to weighed platinum dishes and the contents of the dishes evaporated to dryness. Their salt content was thus determined and expressed in grams per hundred grams of the solution. In determining the acetone content of the upper layer, the solution was distilled and the distillate collected in a Will-Varrentrapp apparatus which was kept cold with salt and ice. This prevented the rapid volatilization of the acetone. The contents of the distilling flask were distilled to dryness. There is a slight loss by this method, because when practically all of the liquid has distilled over, traces of the acetone decompose giving rise to slight errors. The specific gravity of the acetone is then determined, and from the table given by McElroy and Krug⁶³ the amount of acetone present is obtained. Another method that might be used would be to make up a series of solutions with varying water and acetone content, saturate them with the given salt and determine the specific gravities of the solutions. The series of specific gravities could be plotted and used as standards of comparison. The same method could be used in determining the exact composition of the lower layers, but difficulties are encountered in determining the acetone content. When salts such as potassium fluoride or carbonate were used the amount of acetone in the lower layer was slight. Therefore very large quantities of the lower layers had to be used. With sodium and calcium chloride the lower layers had a tendency to bump. In determining the acetone content, two to four hundred grams of the solution were transferred to a weighed flask, weighed and then placed in a distilling flask, and water was added to lower the density of the solution. The contents of the flask were then distilled over

into either a weighed flask or Will-Varrentrapp bulbs, which were kept cool by salt and ice. To be sure that all the acetone had passed over, the distillation was always continued from five to ten minutes after the thermometer registered from 98-100°. If the volume of the distillate was not sufficient for specific gravity determinations, more distilled water was added. It was not desirable to add much water as the acetone content was not high. The distillate was weighed and the specific gravity determined, from the tables the amount by weight of acetone present in the distillate found, and from this ^{was obtained} the amount of acetone present in the original amount of solution taken. Concrete illustrations are given in the various systems studied. The data at hand were then the concentration of acetone in the water and salt solution and the amount of salt present. From these data the position of E and F were indicated on the figures.

A second quadruple point was determined when the salt used formed a hydrate. This point determined the dehydrating power of the anhydrous salt. To an aqueous solution of acetone, such as the one from the distillate of the upper of the first quadruple point, excess of the anhydrous salt was added. After the flask was warmed and then cooled, part of the salt appeared as the hydrate and part was still anhydrous. There were four phases present, hydrate, anhydrous salt, one liquid phase and the vapor. The temperature was fixed, so the system was invariant. The acetone content of the liquid phase was determined in the same manner as the acetone content of the upper layer of the first quadruple point. The solution was decanted off from the solid salt and distilled to dryness. The percent. of acetone present

in the distillate was obtained by determining its specific gravity. The amount of salt present in the liquid layer was determined by the evaporation of a weighed quantity of the solution, and ^{the} weight of the residue was obtained. Traces of the salt were found only in the case of calcium chloride. With the carbonate and fluoride practically nothing was left in the dish after evaporation.

Temperature Effects. In determining points on the binodal curve for all the systems, the temperature was kept as near 20° as was possible. The changes produced by variations in temperatures were not so marked in dilute solutions as in concentrated solutions of the various salts. Absolute determinations of the upper and lower critical solution temperatures were not made. Homogeneous solutions of the salts in water and acetone were made at temperatures as low as 5° and the solutions were gradually warmed through five degrees, and if clouding took place water was added until the cloud disappeared. The excess of water was then weighed. Heat was again applied, and the change produced by the next five degrees was noted. This process was repeated until temperatures of 40° were reached. The temperature effects above 40° were not noted at this time. A more complete discussion is given farther on. Work will be continued along this line.

Materials.

Calcium Chloride. The calcium chloride used was Merck's purified especially for analytical purposes. Five grams of the calcium chloride dissolved in 25 c.c. of water did not give a clear solution and the solution was slightly alkaline. Even though the slight amount of calcium oxide present might not affect the experimental data, the cloudiness of the solution would interfere with end point determinations of positions on the binodal curve. The alkalinity was removed by a process described a little farther on. With hydrochloric acid, hydrogen sulphide and ammonium sulphide no precipitate was obtained. One part of the salt practically dissolved in ten parts of absolute alcohol, only a faint opalescence was noted. In a 1:20 solution, to which a few drops of hydrochloric acid and barium chloride were added, no precipitate formed, even on allowing the solution to stand. When the solution was boiled with sodium hydroxide, no test for ammonia was obtained. Baryta water gave no precipitate in a 1:20 solution. With a similar solution, no precipitate was formed when calcium sulphate was added nor did this turn cloudy when ammonium hydroxide was added. The calcium chloride contained some water. When calcium chloride containing one molecule of water is heated, hydrochloric acid is given off and the basic salt is formed.⁶⁴ To prevent the formation of the oxychloride and to remove the water, the following methods were used:

The calcium chloride was fused and while in a state of fusion a current of dry hydrochloric acid gas was introduced. The fused salt was then cooled in a desiccator and was ready for use. It was difficult to prepare large quantities of calcium chloride in this

fashion, so after a trial the method was discarded and the following one substituted in the preparation of all the calcium chloride used. A hydrochloric acid generator was connected with a drying bottle containing concentrated sulphuric acid and then to two calcium chloride drying towers. From the last drying tower a delivery tube was placed in an erlenmeyer flask which was immersed to the neck in a porcelain air bath. The calcium chloride was powdered and from two to three hundred grams were placed in the flask, the temperature of the air bath ranging from 160 - 220°. The hydrochloric acid gas was passed into the heated chloride and was stirred frequently to insure contact of the gas with all of the chloride. At the end of an hour no more moisture formed in the neck of the flask. The chloride was then heated two or three hours longer, the heat was then removed and the generation of the gas was stopped. When the contents of the flask were cooled to 100 degrees, the chloride was transferred to a desiccator containing pumice stone well sprinkled with phosphorus pentoxide. The salt, when dissolved and tested with phenolphthalein, gave a neutral reaction. A solution containing over two grams of this salt turned pink when one drop of N/10 sodium hydroxide solution was added.

The requirements of the experiments did not demand calcium chloride of the purity used by Richards and Honigschmid⁶⁵ in their atomic weight determination of calcium.

Potassium Fluoride. This salt was labeled "Merck's chemically pure potassium fluoride." It gave an acid reaction. The acidity was removed when the salt was heated to red heat, all the excess hydrofluoric acid being driven off. The potassium fluoride did not dissolve completely in water before it was heated, the solution being cloudy. After

the salt had been heated the aqueous solution was clear, indicating that the original salt contained free acid which attacked the glass.

Potassium Carbonate. Pure potassium carbonate was not available, so the salt was made from the bicarbonate. The bicarbonate was dissolved in boiling water, boiled for half an hour, the boiling solution cooled, and the crystals that separated out were dried by suction. The object of boiling was to convert some of the salt into the carbonate. The salt was dried several hours in an electric drying oven at 160°. As complete decomposition takes place at 190°, the salt was then transferred to a platinum dish and heated to red heat until the excess carbon dioxide and water had passed off. The temperature was kept below fusion to prevent the formation of potassium hydroxide and the loss of carbon dioxide.⁶⁶ The potassium carbonate was always reheated and cooled in the desiccator before being used for determinations.

Sodium Chloride. Kahlbaum's chemically pure sodium chloride was used. Its solubility was 35.74 grams of salt in 100 grams of water. The salt was powdered and heated to red heat for a few minutes until all the "crackling" stopped. It was then cooled and used.

Methyl Alcohol. Kahlbaum's absolute methyl alcohol, 100 per cent. pure, was used, specific gravity 0.79576, 0.795875 and 0.79877 at 15.55/4°, boiling point 66.6°.

Acetone and its Purification. Although acetone was discovered by Boyle⁶⁷ in the products given off when sugar of lead was heated, its actual composition was not known until the time of Liebig. Liebig⁶⁸ described its composition and gave a method for obtaining the pure compound. He used anhydrous calcium chloride and allowed the acetone to remain in

contact with it for several days. He distilled the liquid and found its boiling point to be 55.6° and the specific gravity at 18° , 0.7921. He stated that it did not dissolve even a trace of calcium chloride. Subsequent investigators obtained different physical properties. There does not seem to be a general agreement in regard to ^{either} the boiling point or the specific gravity. Dumas⁶⁹ called acetone "l'esprit pyroacetique" and obtained 56° as the boiling point with a pressure of 760 m.m. Peau de St. Gilles⁷⁰ recommended the use of potassium permanganate in the cold for the purification of acetone. Schiff⁷¹ converted acetone into the sodium bisulphite compound and then decomposed this with ether, washed and dried the product, and from it obtained a liquid boiling at 56° . Lime has been used for the first dehydration, then the product has been kept in contact with calcium chloride, fractionated, converted into the bisulphite compound, decomposed with sodium carbonate and redistilled. Bancroft⁷² found no difference in two samples of acetone, one of which he converted into the bisulphite, decomposed, dried over potassium carbonate and ^{and then} calcium chloride/ fractionated; and the other which he treated directly with calcium chloride and fractionated. A third sample could not be purified by either of these methods, and he discarded this lot. Klar⁷³ purified acetone which had been obtained from methyl alcohol by drying with quick lime and then fractionating.

McElroy and Krug⁷⁴ redistilled crude acetone, boiled it over calcium chloride with a reflux condenser for three days and then distilled. The product boiled at 56.4° . They obtained identical results by converting acetone into acetone bisulphite/^{of} soda, liberating the acetone with sodium carbonate, distilling, dehydrating and again distilling.

They also purified acetone by the use of potassium permanganate, allowing the acetone to remain in contact with permanganate one day, when it was dehydrated and distilled. They did not obtain a product any more satisfactory by this method. Snell⁷⁵ merely dried his acetone over calcium chloride and fractionated. Bell⁷⁶ boiled the acetone over fused calcium chloride and fractionated. A yellow, oily residue was left behind. The specific gravity of the acetone at 19.8° was 0.79179. The boiling point was not given.

The acetone on which this work was begun came from the establishment of C.A.F. Kahlbaum of Berlin, and represents his purest quality prepared from the bisulphite compound. In testing the purity of this substance it was found to contain some water in addition to very small quantities of other impurities. It was necessary to purify it before the salting out processes could be satisfactorily carried out.

Fractional distillation failed to remove the last traces of impurities. Calcium chloride and potassium carbonate were tried, but were found unsatisfactory. Magnesium amalgam was next tried, with better results, but was abandoned on account of the loss of acetone during the process, as the amalgam held mechanically a considerable quantity of the acetone. Finally sodium amalgam was used successfully after the acetone had been first dried for some time with calcium chloride. So satisfactory was the sodium amalgam method that it was used later for preparing chemically pure acetone from the commercial product. The method of purification consisted in simply treating the acetone with calcium chloride, decanting off the dried acetone, treating it with sodium amalgam and finally decanting off the acetone and redistilling.

The residue was reddish-brown. The residue obtained by Bell's method was yellow, which may have been due to decomposition, as it was found that acetone which stood in the sunlight gradually turned yellow. This method of treatment gave strictly pure acetone even from the commercial product, hence practically all of the material used in this work was prepared from the crude product by the above method.

R. Bacon and Paul C. Freer⁷⁷ found that sodium reacted with acetone forming C_3H_5ONa , a white flocculent precipitate which turned red on exposure to the air. Whether the red color found in the residue, after the distillation of the acetone which had been treated with this sodium amalgam, is due to a sodium compound is not known, as the residual solution has not as yet been investigated. The formation of this sodium compound is doubted by Taylor⁷⁸.

Physical Constants. That the Kahlbaum acetone was impure was shown by the fact that in the distillation the first part began to distill over at 56° and the last at 57.5° , a variation as great as that found in the commercial acetone, which was later used for purification. The specific gravity and the index of refraction also changed slightly in the purification.

Specific Gravity	Kahlbaum	Kahlbaum's Purified	Commercial Acetone	Purified Commercial Acetone
$15.5^\circ/4^\circ$	0.79846	0.79812	0.79832	0.79818
$20^\circ/4^\circ$	0.79286	0.79264	0.79323	0.79261

Index of Refraction.

Pulfrich Refractometer Used, (latest model). Temperature 20°.

	α	β	γ
Commercial Acetone	1.36309	1.34882	1.33999
Purified Acetone	1.36213	1.34834	1.339506
Kahlbaum's Acetone Purified	1.36219	1.34823	1.33943

Brühl⁷⁹ obtained the following results:

d 20°/4° 0.7920 $\alpha = 1.35715$ $\beta = 1.36392$ $\gamma = 1.36780$

Brühl⁸⁰ used commercial acetone and obtained the following data:

Specific gravity of the acetone used 19.9°/4° 0.8005

H α	H β	H γ
1.36010	1.36674	1.37064

The data given for the specific gravity and the boiling point of acetone by different investigators do not generally agree. The boiling point of the acetone used by Snell and Bell is not given. The acetone used in this work had a boiling point of 56.3-4°. Other boiling points have been given for acetone. Landolt and Börnstein in their physical and chemical tables give 56.3°. Kopp⁸¹ gives the same at a pressure of 763 m.m. Timmerman⁸² gives 56.1°. Regnault⁸³ gives 56.3°; Thorpe,⁸⁴ 56.53°; Beckman,⁸⁵ 56.3°; Kossakowsky,⁸⁶ 56.5°; Krauch,⁸⁷ 56-57°; Korber,⁸⁸ 56.2-3°, 760 m.m. pressure.

For specific gravities variations are found. Squibb's⁸⁹ tables are given for 4°/4°, 15°/15°, and 25°/25°. An average of the last two gives fair agreement with McElroy and Krug's⁹⁰ tables. An average of the last two for 100 per cent. acetone gives 0.7918, while McElroy and Krug give 0.79197 for 20°. Landolt, 20°/20° gives 0.7931, at

19.8° 0.7919. Liebig⁹¹ gave 0.7921 at 18°; ~~Sapozhnikov~~⁹² 0.79905 at 15°/4°; E. Conrady,⁹³ 0.7920 at 20°/4°. Krauch gives 0.797--0.798.

Systems.

Potassium Fluoride Water and Acetone. This system is one that has never been studied, because the use of potassium fluoride has but recently been shown by Frankforter and Frary.⁹⁴ In 1912, they found that the addition of potassium fluoride to ethyl or propyl alcohol mixtures with water would cause the separation of the two miscible liquids into layers. The potassium fluoride would salt out the alcohol, and as a dehydrating agent the saturated solution of the hydrate of the fluoride was better than a saturated solution of the hydrate of potassium carbonate, owing to the lower vapor tension of the solution of the fluoride. It is true that the potassium carbonate hydrate removes more water than the hydrate of potassium fluoride. There is a similarity in their action with acetone, though it is less noticeable with acetone than with alcohol. The conduct of acetone and water with either potassium carbonate or fluoride is very similar to that of alcohol and water with the same salts. The fluoride is soluble to some extent in alcohol, 4.79 grams per hundred grams of the solvent. In acetone the fluoride is practically insoluble. The anhydrous fluoride was heated for about ten minutes, allowed to cool, and while still warm was added to the anhydrous acetone. The acetone was shaken from time to time, after standing in the room at about 20° for over three days, the amount of the potassium fluoride in a known weight of the solution was determined by conversion of the potassium fluoride into the chloride by addition of hydrochloric acid and sub-

sequent evaporation. Care was taken in this determination as potassium chloride is rather volatile. It was rather difficult to determine the solubility of the salt in the less concentrated solutions of acetone, because if too much salt was added the salt took up the water and two layers were formed. In general, the acetone layers in no case gave any perceptible amount of potassium fluoride in the solution. Therefore, potassium fluoride can be classed as a salt that is insoluble in acetone. In the study of this system the two quadruple points, tie lines, binodal curve and the approximate plait points were determined. A few experiments were made to show the temperature effect, within narrow ranges of temperature. The method used in determining the points on the binodal curve and the quadruple points has been already described. The data for the binodal curve are given in Table I and the positions of the other points are given in figure III. The first quadruple point determined is the one where the hydrate, water, acetone and vapor are in equilibrium at 20°. According to the phase law, if the temperature is kept constant the system is invariant and is in equilibrium. The composition of both layers was determined by the potassium fluoride and acetone content in both the upper and lower layers. When from twenty to thirty grams of the upper solution were treated with hydrochloric acid to prevent loss of the chloride, and the solution was evaporated to dryness, no appreciable residue was found. This indicated a potassium fluoride free upper layer. The rest of this upper layer was carefully distilled. A 150 c.c. distilling flask was connected with a condenser and then to a Will-Varrentrapp "U" tube, which was kept in a freezing mixture of salt and ice. The latter was used to prevent the loss of any vapors

of acetone as the acetone has a high coefficient of expansion. The contents of the flask were distilled to dryness and the distillate from the "U" bulb was transferred to an erlenmeyer flask. The temperature at which the distillate passed over was practically 56° until over 5/6 of the solution had passed off, when the temperature rose rapidly to 85-90°. The last trace of the distillate came off at 98-100°. Several fractions were distilled and thoroughly mixed. One slight source of error is noticed at the end of the distillation, the acetone traces turning brown, and a very slight resin is left behind. This decomposes at a high temperature, giving off an unpleasant odor. The specific gravity of this distillate was then determined. In determining specific gravities a 50 cc. pycnometer was used. It contained a ground glass capillary tube with cap ground to fit the capillary, and a ground glass thermometer. The capacity of the pycnometer was determined by carefully cleaning, drying and weighing the pycnometer while empty and then weighing it full of redistilled water at 4°. Several determinations were made. The thermometer in the pycnometer was standardized by comparing it with a certified standard which was graduated to 0.02°. The thermometer in the pycnometer was graduated to 0.2°. Care was taken to read within 0.1° degree. To insure the same temperature in all parts of the pycnometer it was rapidly rotated. 20° was a comparatively easy temperature to control, so the pycnometer was again carefully cleaned, dried and weighed, then filled with distilled water at 20° and again weighed. McElroy and Krug⁹⁵ have determined the data for a table of specific gravities for acetone at 20°/4°. This table gives points for acetone water solutions ranging by five degrees from 0 of one component

to 100 of the same. In order to determine intermediate points this table was plotted, the rectangular coordinates giving per cents. and specific gravities. From the diagram the per cent. of any acetone solution could be obtained from its specific gravity. In the determination of the specific gravity of the acetone obtained from the upper layer, 0.798 at 20° was obtained. This corresponds to 98 per cent. acetone. A saturated solution of potassium fluoride will then dehydrate acetone to the extent of 98 per cent. The amount of potassium fluoride in the lower layer was next determined. 32.679 grams of the lower layer were transferred to a weighed platinum dish and sufficient concentrated hydrochloric acid was added to convert all the fluoride into the chloride. This is done to prevent the loss of hydrofluoric acid, as the salt hydrolyzes. 19.625 grams of potassium chloride were obtained, which is equivalent to 46.3 grams of potassium fluoride in 100 grams of the lower layer. The acetone content of the lower layer was not measurable according to the specific gravity tables of McElroy and Krug. 106 grams of this solution were placed in a distilling flask and distilled, and the temperature rose at once remaining at about 100° for over ten minutes. The distillate was weighed and its specific gravity was determined and found to be 0.9994 at 20°/4°. This shows that only traces of the acetone are present.

In determining the second quadruple point, where the anhydrous potassium fluoride, the hydrate, $\text{KF} \cdot 2\text{H}_2\text{O}$, acetone layer and vapor are in equilibrium at 20°, the acetone from the previous determination was used. It was kept in contact with the hydrated fluoride and the anhydrous salt at room temperature for over a week. The flask was shaken from time to time to insure complete contact, the acetone was decanted

off and several determinations of the specific gravity were made at 20°/20°, giving the value 0.7932 or 97.9 per cent. pure acetone. This would indicate that with potassium fluoride practically anhydrous acetone can be obtained. Landolt and Börnstein tables give the specific gravity of 100 per cent. acetone 20°/20° as 0.793.

In determining the plait point and the tie lines a series of conjugate solutions were made and the potassium fluoride content of the upper and the lower layers determined.

	Amount of Solution	Grams KCl	Grams KF in 100 gr. of solution
(Upper layer	45.98	0.0295	0.05
(Upper layer	39.37	0.03	0.059
I. (Lower layer	53.936	16.006	23.12
(Lower layer	55.81	16.64	23.23
II. (Upper layer	33.869	0.710	1.634
(Upper layer	32.5315	0.6818	1.633
(Lower layer	19.7548	2.744	10.94
(Lower layer	23.1605	3.25	10.94
III. (Upper layer	15.1210	0.1095	0.5642
(Lower layer	19.5975	3.717	14.78
IV. (Upper layer	19.933	0.86	3.36
(Lower layer	18.133	1.862	8.00

From these tie lines, the approximate position of the plait point was found.

Comparison of the carbonate with the fluoride curve shows that it was easier to obtain the plait point on the fluoride curve.

The effect of temperature. In studying the system of $\text{CaCl}_2 \cdot \text{H}_2\text{O}$ and acetone, it was noticed that the just homogeneous solution at 20° became cloudy when the temperature increased even one-half of a degree. With potassium fluoride, water and acetone this clouding effect was not so evident. The temperature effects within narrow limits were determined and are discussed later on.

TABLE I.

Table for the Binodal Curve of Potassium Fluoride Water
and Acetone at 20°.

Solvent Added			Total weight of substances present			Wt. of substances present in 100 grams of solution.	
Water	Acetone	KF	Water	Acetone	KF	Water	Acetone
50.615	30.361	4.9433	50.615	30.361	5.75	58.91	35.34
4.983	7.897	4.9433	55.598	38.258	5.00	56.23	38.72
11.634	18.237	4.9433	67.232	56.495	3.84	52.25	43.91
12.055	20.903	4.9433	79.287	77.398	3.06	49.05	47.89
9.453	18.358	4.9433	88.740	95.756	2.61	46.84	50.55
10.895	22.112	4.9433	99.635	117.868	2.22	44.79	52.99
79.847	12.346	16.206	79.847	12.346	14.95	73.66	11.39
20.224	12.778	16.206	100.071	25.122	11.46	70.77	17.77
18.888	16.476	16.206	118.959	41.598	9.17	67.30	23.53
15.445	17.761	16.206	134.404	59.359	7.72	64.01	28.27
7.695	11.415	16.206	142.099	70.774	7.07	62.03	30.90
10.230	12.490	16.206	152.329	83.264	6.43	60.50	33.07
33.194	47.528	1.1273	33.194	47.528	1.38	40.55	58.06
8.715	24.505	1.1273	41.909	72.033	0.979	36.42	62.60
11.254	36.286	1.1273	53.163	108.319	0.693	32.69	66.61
9.49	26.795	1.1273	62.653	135.114	0.57	31.50	67.93
44.520	78.942	1.114	44.520	78.942	0.89	35.74	63.36
5.980	18.618	1.114	50.50	97.56	0.75	33.84	65.41
7.708	25.30	1.114	58.208	122.860	0.61	31.95	67.44
8.66	32.572	1.114	66.868	155.432	0.5	29.92	69.58
44.591	1.163	18.163	44.591	1.163	28.42	69.76	1.82
5.686	0.972	18.163	50.277	2.135	25.74	71.24	3.02
9.038	1.651	18.163	59.213	3.786	22.35	72.99	4.66
6.77	1.514	18.163	66.085	5.300	20.28	73.80	5.90
5.843	1.675	18.163	71.928	6.975	18.71	74.10	7.19
10.420	3.844	18.163	82.348	10.819	16.31	73.97	97.2
23.100	12.003	18.163	105.448	22.822	12.40	72.01	15.59
46.814	0.282	24.1185	46.814	0.282	33.36	65.73	0.397
8.300	0.935	24.1185	55.114	1.217	29.97	68.54	1.50
25.178	3.747	24.1185	80.292	4.964	22.05	73.41	4.54
19.882	6.088	24.1185	100.174	11.052	17.82	74.01	8.16
23.044	9.741	24.1185	123.218	20.793	14.34	73.29	12.37
79.437	0.341	63.2847	79.437	0.341	44.24	55.52	0.240
45.205	1.542	63.2847	124.652	1.542	33.34	65.66	1.00
20.566	1.515	63.2847	145.218	3.398	29.86	68.54	1.60
42.104	5.630	63.2847	187.322	8.928	24.38	72.16	3.45

Figure III gives a graphic representation of this system.

Potassium Carbonate, Water and Acetone. Potassium carbonate has been used as a dehydrating agent since the time of Raymond Lully, when he dehydrated alcohol with fused potashes⁹⁶. Since that period, because of the low vapor tension of its hydrate, it has been used to dry many organic liquids, as has been cited in another part of this paper. The most common among these are the alcohols and acetone. That potassium carbonate would form two layers when added to an aqueous solution of acetone has been shown by Linebarger,⁹⁷ Snell⁹⁸ and Bell⁹⁹.

Linebarger's work, although classed as quantitative by Timmermans,¹⁰⁰ was very incomplete and merely shows that two layers are formed when the carbonate is added to the water and acetone. He made only ten determinations on the binodal curve, and these he admits are not very accurate. His measurements are also made on points of the curve that do not give any indication of the general direction of the curve and no tie lines are determined. The method he used in determining the points on the curve was to add varying quantities of organic liquid and water from a burette to a titrated solution of the carbonate until just a drop of water would clear up the milkiness caused by a drop of acetone. I have recalculated the data obtained by Linebarger and tabulated them in parts per 100 grams of the solution. These are given in Table II, while in Figure V, the points on the curve indicated by $\odot$ are those obtained by Linebarger. The temperature used by Linebarger was 20°, the same used in my data.

These points fit in fairly well with the binodal curve, but when one considers the fact that the maximum amount of the carbonate used by Linebarger was 6.67 grams in 100 grams of the solution, and that a saturated solution contains over 53 per cent. of carbonate, the results cannot be

T A B L E II.

Temperature 20° C.

K ₂ CO ₃	Acetone	Water	Total	Per cent. K ₂ CO ₃	Per cent. Acetone	Per cent Water
1	4.8	9.2	15.	6.67	32.	61.33
1	11.4	16.1	28.5	3.51	40.	56.49
1	18.8	22.1	41.9	2.38	44.87	52.75
1	30.8	31.1	62.9	1.59	48.97	49.45
1	43.0	38.5	82.5	1.21	52.11	46.68
1	5.4	10.2	16.6	6.02	32.5	61.50
1	14.4	18.8	34.2	2.92	42.10	54.98
1	28.2	28.7	57.9	1.72	48.70	49.58
1	50.	38.7	89.8	1.11	55.67	43.23
1	89.7	49.9	141.6	0.7	64.	35.20

considered very satisfactory, especially if one takes into consideration the dehydrating effect of potassium carbonate on acetone.

Bell¹⁰¹ determined points on the binodal curve over a much wider range, his concentrations of the carbonate varying from 2.34 grams in 100 grams of solution to 30.58 grams in 100, while the per cent. of acetone decreased from 42.36 to 1.27. Bell's particular object was not so much the determination of the points on the curve as to prove that the exponential expression of Bancroft¹⁰² $\frac{K^a y^b}{z^c w^d} = K$ would describe the equilibrium in the system, acetone, potassium carbonate and water. By simplifying the above, the equation becomes $\frac{z^a}{y} = K$. z denotes the grams of water per gram of salt and y the grams of acetone per gram of salt. Bell applied this equation to Linebarger's data as well as to his own, and found that it could be applied neither to this system nor to any system containing two consolute liquids and an electrolyte. Bell's data are obtained at 25° C and are given in Table III and plotted in figure V. The points are indicated by X. It is noticed that Linebarger's data and Bell's data combined give a fair idea of the general character of this curve. While Bell's data are obtained at 25°, I have compared them with data obtained at 20°, because the temperature effect between these two points is not very marked. The method Bell employed in determining his points is very similar to the one used in this work. He controlled the temperature effect by the use of an Ostwald thermostat. He did not use any indicator in detecting the presence of the two liquid phases. With extreme concentrations he found difficulty in determining the end points. He detected minute globules of the second phase by holding the flask before an incandescent lamp. With extreme concentrations of carbonate in the water, where only

TABLE III.

Bell's Data			Recalculated in parts per 100 grams.		
Grams K_2CO_3	Grams H_2O	Grams $(CH_3)_2CO$	K_2CO_3	H_2O	$(CH_3)_2CO$
1.456	34.41	26.36	2.34	55.30	42.36
1.924	35.67	23.54	3.14	62.05	37.95
2.257	35.57	21.49	3.80	62.4	33.8
2.251	36.10	19.494	3.89	62.41	33.70
2.746	37.92	20.645	4.48	61.83	33.69
2.694	39.94	19.153	4.36	64.64	31.
3.016	37.87	19.510	4.99	63.43	31.57
3.380	39.25	19.001	5.48	63.68	30.83
3.984	40.13	17.303	6.5	65.45	28.05
4.571	42.89	17.426	7.04	66.10	26.86
4.981	42.81	16.173	7.79	66.93	25.28
6.022	45.17	14.602	9.2	68.5	22.2
7.349	45.	11.078	11.58	70.95	17.47
8.093	49.91	12.339	11.51	70.95	17.54
9.06	50.05	10.246	13.06	72.17	14.77
9.765	50.17	8.940	14.17	72.84	12.98
11.076	39.99	6.802	16.32	73.66	10.02
12.396	50.87	5.572	18.01	73.9	8.09
14.509	50.4	3.656	21.16	73.51	5.33
15.744	51.03	2.966	22.57	73.17	4.26
7.82	50.53	2.143	20.28	71.68	3.04
19.67	50.48	1.563	27.43	70.4	2.17
22.602	50.38	0.940	30.58	68.17	1.27

traces of acetone were present, little trouble was found in distinguishing the vanishing point of the two layers because the little globules of the second liquid phase took up enough of the indicator phenolphthalein to color them a dark violet. These globules formed on the surface, and, owing to surface tension, collected around the thermometer stem and the side of the flask, and when the contents of the flask were shaken, the globules were quickly set in motion and their presence readily detected. With concentrations exceeding 60 per cent. acetone and less than 0.5 per cent. potassium carbonate, the cloudiness was difficult to perceive, but by holding the flask to the sunlight the cloudiness was detected by transmitted light. Some of these last determinations are not so accurate as the first for this reason.

In the system potassium carbonate, water, acetone, the points on the binodal curve given in Table IV were determined--two quadruple points, several tie lines, and, indirectly, the plait point. These are plotted on the triangular diagram of figure V. Spirit blue could not be used as an indicator because the carbonate bleached it, but tiny particles of solid phenolphthalein proved satisfactory. Potassium carbonate was found to be practically insoluble in acetone, and was also found to be practically insoluble in solutions of 95-100 per cent. acetone. The method used in determining the solubility of potassium carbonate in aqueous solutions of acetone, ranging from 90 percent of acetone to 99 per cent. is not very satisfactory, because unless almost the exact amount of salt is used, it withdraws water from the solution, forming the hydrate, and if sufficient salt and water are present two liquid phases will form, the upper one being a dehydrated solution of acetone containing very little of the salt. The determination of the solubilities

up to 92 per cent. are best obtained from the binodal curve.

In determining the tie lines, analyses of five sets of conjugate solutions gave the following results:

		Grams of Solution	K ₂ CO ₃ found	Total K ₂ CO ₃ in 100 grams
I.	Upper layer	15.61	0.1111	0.7117
	Lower layer	24.268	5.9271	24.40
II.	Upper layer	15.85	0.0062	0.039
	Lower layer	24.627	8.0373	32.63
III.	Upper layer	73.29	0.9967	1.36
	Lower layer	57.43	13.1613	22.91
IV.	Upper layer	11.169	0.511	4.57
	Lower layer	14.939	2.534	16.92
V.	Upper layer	11.645	0.812	6.97
	Lower layer	12.315	1.819	14.77

A glance at figure IV will show the position of the east tie line relative to the curve, and the difficulty in obtaining the plait point. When the upper and lower layers have approximately the same composition and specific gravity, the two layers separate with difficulty. The plait point is then determined approximately. The plait point in the system potassium fluoride, acetone and water lies in a relatively different position on the curve and is more easily obtained. The calcium chloride, acetone and water tie lines are as difficult to obtain as the potassium carbonate. In determining the two quadruple points the method described in the potassium fluoride system was again used. The saturated solution of potassium carbonate was kept in contact with acetone and the hydrate of potassium carbonate for over a week. At the end of that period the solution was distilled, and the specific gravity

of the distilled acetone was found to be 0.8037 at $20^{\circ}/4^{\circ}$. Reference to the tables in use give an acetone content of 96.4 per cent. 29.09 grams of the original solution of the upper layer gave a carbonate content of only 0.0007 grams, or 0.0024 grams in 100 grams of solution. No attention is given to this result as it practically coincides with the point of 100 per cent. acetone on the triangle.

400 grams of the lower layer which had a distinct acetone odor were used to determine the amount of acetone in the lower layer, but, despite this large amount, it was not, apparently, possible to obtain enough acetone to determine the amount in the solution. The specific gravity of the weighed distillate from 400 grams of the solution was 0.9994, although acetone was present. In the reference tables 0.994 gives zero or negligible quantities of acetone. It is not zero, however. (Note in figure IV, the point Q should be nearer the outside of the triangle as the per cent. of acetone is less than one.) In this solution, evaporation of 29.503 grams gave 15.4567 grams of potassium carbonate, which is equivalent to 52.38 grams of potassium carbonate in 100 grams of the solution. This shows that at the quadruple point, the lower layer is nearly a saturated solution of potassium carbonate. Frankforter and Frary found the solubility of potassium carbonate to be 53.05 or 53.07 grams in 100 grams of the carbonate solution.

The second quadruple point was obtained in a manner similar to the second quadruple point of the fluoride system. The acetone which had been obtained from the distillation of the upper solution was added to anhydrous carbonate, and a little water was added to insure the formation of $2K_2CO_3 \cdot 3H_2O$. More of the anhydrous salt was added until

the four phases were formed, the two solid phases, hydrate and anhydrous salt, one liquid and one vapor phase. The contents of the flask were frequently shaken and were then decanted off and distilled to dryness. The specific gravity of the distillate at 20° was then determined. The acetone content was found to be only 98.3 per cent. This acetone was again kept in contact with more of the anhydrous salt and the hydrate and the solution was frequently stirred. At the end of the second week the distillation process was repeated and the acetone was found to be practically pure. The specific gravity found was 0.7933. This gives 99.8 per cent. acetone. The anhydrous carbonate practically dries the acetone, but the time required for equilibrium to be reached is about twice that required with potassium fluoride. For this reason the fluoride is more satisfactory.

In determining some temperature effects in this system, it was found the temperatures between 5° and 40° had no effect on a solution which contained 2.7 grams potassium carbonate, 29.701 grams water and 12.95 grams of acetone. This solution was just homogeneous at 5°. It was then gradually warmed up to 40° and no effect and no cloudiness was noted. Whether the solubility of the salt in water has any effect is questionable, but it is noticeable in ~~the~~ Table V. ~~that~~ that the solubility of potassium carbonate does not change materially. The slight change in solubility where concentrations are not very strong would not be noticeable.

TABLE IV.

System Potassium Carbonate, Water and Acetone.

Solvent Added		Total weight of substances present.			Per cent. in 100 gram solution.		
Water	Acetone	K ₂ CO ₃	H ₂ O	(CH ₃) ₂ CO	K ₂ CO ₃	H ₂ O	Acetone
55.107	5.971	14.189	55.107	5.971	18.84	73.22	7.94
20.984	10.344	14.189	76.091	16.315	13.32	71.38	15.30
8.29	5.063	14.189	84.381	21.378	11.83	70.34	17.83
12.307	7.827	14.189	96.688	29.205	10.13	69.03	20.84
19.355	12.955	14.189	116.043	42.16	8.24	67.31	24.45
13.606	10.46	14.189	129.649	52.62	7.22	65.99	26.79
21.642	16.884	14.189	151.291	69.504	6.04	64.39	29.57
89.28	2.65	37.125	89.280	2.65	28.87	69.08	2.05
22.871	3.714	37.125	112.151	6.364	23.94	71.93	4.08
13.973	3.576	37.125	126.124	9.94	21.52	72.75	5.73
13.072	3.967	37.125	139.196	13.907	19.6	73.10	7.3
47.797	20.627	4.7235	47.797	20.627	6.46	65.34	28.2
3.905	2.911	4.7235	51.702	23.538	5.91	64.65	29.44
2.128	2.114	4.7235	53.830	25.652	5.60	63.93	30.47
5.010	4.487	4.7235	58.840	30.139	5.04	62.80	32.16
5.624	5.529	4.7235	64.464	35.668	4.50	61.48	34.02
9.890	9.596	4.7235	74.354	45.264	3.80	59.79	36.41
11.950	12.619	4.7235	86.304	57.883	3.18	57.95	38.87
11.342	12.563	4.7235	97.646	70.446	2.73	56.50	40.77
10.32	11.895	4.7235	107.966	82.341	2.43	57.79	42.21
38.055	2.56	11.652	38.055	2.56	22.29	72.31	4.90
9.646	5.885	11.652	47.701	5.885	17.86	73.12	9.02
5.745	2.704	11.652	53.446	8.589	15.81	72.53	11.66
4.757	2.510	11.652	58.203	11.099	14.39	71.89	13.72
20.484	11.849	11.652	78.687	22.948	10.29	69.46	20.25
27.379	22.312	0.969	27.379	22.312	1.91	54.05	44.04
1.671	2.631	0.969	29.05	24.943	1.76	52.86	45.38
2.082	3.288	0.969	31.132	26.231	1.60	51.60	46.8
5.945	8.518	0.969	37.077	36.749	1.29	49.57	49.14
5.810	9.005	0.969	42.887	45.754	1.08	47.86	51.06
5.484	8.412	0.969	48.371	54.166	0.94	46.73	52.33
9.274	16.13	0.969	57.645	70.296	0.75	44.72	54.53
6.383	12.541	0.969	64.001	82.81	0.66	43.31	56.03
4.17	8.485	0.969	68.171	91.295	0.6	42.49	56.91
6.92	12.605	0.969	75.091	103.9	0.54	41.73	57.73
3.288	9.302	0.969	78.319	113.202	0.50	40.69	58.81
5.753	14.7	0.969	84.072	127.902	0.46	39.48	60.52

T A B L E V.

Solubility Table for Potassium Carbonate.

(John Castell-Evans Physico-Chem. Tables)

Grams K_2CO_3 in
100 gr. of Water.

0°	89.4
5°	104
10°	109
15°	110
20°	112
25°	113
30°	115
35°	117
40°	119
50°	121

Calcium Chloride, Water and Acetone.

Although calcium chloride is generally used in dehydrating acetone, the system that it forms with acetone and water has not been investigated. Snell¹⁰³ and Linebarger¹⁰⁴ merely note the fact that calcium chloride as well as certain other chlorides will produce two layers. The limits of the layers, binodal curves, etc. are not given. Calcium chloride is not very soluble in acetone: Liebig,¹⁰⁵ who was one of the first investigators of acetone, stated that not a trace of the salt was found to enter into solution. McElroy and Krug¹⁰⁶ classify calcium chloride among the salts that are very sparingly soluble. In my work I found that the average results of a series of determinations at 20° gave .02 grams of calcium chloride in 100 grams of acetone. The method used has been already described. The solubility of calcium chloride in acetone ranging in concentration from 95 to 100 per cent. acetone gave negligible results at 20°. Not very satisfactory results were obtained in determining the solubility of the calcium chloride in 1 to 10 per cent. acetone water solutions. Unless the calcium chloride is added in very small quantities and the solution quickly cooled, considerable heat is generated and the concentration of the acetone solution changes. The solubility of the anhydrous calcium chloride in 91 per cent. water and 9 per cent. acetone was found to be 40.5 grams calcium chloride in 100 grams of the solution. This gives one point in the line D Q, figure VI. The point D represents the solubility of the salt in water, or 74.5 grams of calcium chloride in 100 grams of water or 42.70 grams of calcium chloride in 100 grams of the solution of calcium chloride in water. The points on the binodal curve were determined in the same manner

as those previously described, and are given in Table VI. Acetone was added to a solution which was saturated with calcium chloride at 20°. The acetone dissolved in the solution and no salt was precipitated. With saturated potassium fluoride and carbonate solutions, very little acetone was required to produce two layers, but with the chloride of calcium over 20 per cent. of acetone was added before a second layer appeared. The end points in this saturated solution were not easy to obtain, being rather obscure on account of the syrupy nature of the liquid. Time was required to obtain satisfactory conditions of equilibrium and realization of a sharp clearing. The points on the other end of the binodal curve are not difficult to obtain. Temperature effects are noticeable with this particular system. From 19-20° there is no appreciable clouding, but when the solution is heated from 20-21°, immediate cloudiness is noted. Unless the bulb of the thermometer was kept immersed in the liquid satisfactory results at this end of the curve were not obtained.

Determination of Quadruple Points. The solution of calcium chloride was saturated with calcium chloride, enough acetone was added to form two layers of over 500 c.c. each. More calcium chloride was dissolved in a very small quantity of hot water and the hot solution was added to the mixture. By repeating this process several times a saturated solution was obtained, and when this solution was cooled to 20°, fine crystals of the hydrate separated out and four phases were present: CaCl_2 , $6 \text{ H}_2\text{O}$ and two liquid layers containing different quantities of acetone water and calcium chloride, and the vapor phase. Owing to an accident one system which had stood over ten weeks was unavailable for analytical purposes. The experiment was repeated, but instead of allowing the

solution to stand, the flask containing the components was well stoppered and placed in a shaking machine. It was shaken and contents brought in intimate contact with each other for a period of over four days. The four Phases and the hydrate crystals were still present at 20°. The contents of the flask were allowed to stand over night and in the morning the upper layer was decanted off. Part of it was weighed and transferred to a weighed platinum dish and the contents of the dish were evaporated to dryness, and then gently heated over the bunsen flame. No weighable results were obtained. Fontein¹⁰⁷ in determining quadruple points for similar systems, determined the specific gravity of such solutions, counting the salt content zero, and from the specific gravity determined the alcohol present. I did not consider this method advisable, and so I distilled about 120 c.c. of the solution to dryness in a distilling flask and collected the acetone in a receiver surrounded by ice and salt. I took the specific gravity of the distillate at 20°/4° and obtained 0.7938. By comparison with the interpolated results of McElroy and Krug's specific gravity tables, the percentage of acetone present was 98.4. A saturated solution of calcium chloride will not remove all the water from the acetone. It is also wasteful as it retains over 20% of the acetone. In the distillation a noticeable resin was left in the distilling flask. This decomposed at 100°, giving rise to dense, white fumes with an intense acrid odor. The formation of the resin may be due to the action of the sunlight on the acetone, as part of the mixture had been exposed to light over ten weeks. The same yellow color was present in the lower solution. To determine the composition of the lower layer, 31.715 grams of the solution were evaporated to

points on the upper part of the binodal curve, though the reentrance is not so marked. If errors are present in this determination, they are due either to changes in temperature or else to the time given for realization of clearing being too short. More work will be done on this system.

The second quadruple point was determined by using the 98 per cent. acetone obtained by distillation of the upper solution of the first quadruple point and adding to it anhydrous calcium chloride, and although an appreciable amount of acetone was present, there did not seem to be any liquid present. The contents of the flask seemed to form a solid white crystalline mass. However, when the contents of the flask were stirred with a glass rod the liquid separated and settled on top. At first it was thought that a compound was formed similar to the compound formed by alcohol and calcium chloride. As far back as 1850, Hlasiwetz¹⁰⁸ stated that powdered calcium chloride formed a compound with pure acetone, which was a dry mass at 100° and only traces of the acetone odor were given off. The formation of this compound is doubtful. After the contents of the flask were stirred repeatedly and kept at 20° for a week the supernatant liquid was decanted off and distilled. Its specific gravity at 24°/4° was 0.7915, which corresponds to 100 per cent. acetone. The amount of calcium chloride dissolved in the acetone solution was practically nothing. Anhydrous calcium chloride will completely dehydrate acetone.

Numerous determinations of the tie lines were made in an attempt to locate the plait point accurately, but separation into distinct upper and lower layers was rather difficult to obtain.

The following results were obtained:

		Amount of Solution	Grams Calcium Chloride	Grams of Calcium Chloride in 100 gr. of solution.
I.	Lower layer	12.102	2.010	16.61
	Upper layer	9.67	0.018	0.186
II.	Lower layer	23.837	3.090	12.97
	Upper layer	17.018	0.107	0.628
III.	Lower layer	11.586	1.228	10.60
	Upper layer	11.600	0.110	0.948
IV.	Lower layer	17.432	1.961	11.25
	Upper layer	9.355	0.092	0.985
V.	Lower layer	20.949	1.960	9.36
	Upper layer	19.080	0.252	1.321

The calcium chloride content of some of the upper layers was determined by titration with a standard N/10 silver nitrate solution. The results did not differ from those obtained by evaporation of weighed quantities of the solution.

T A B L E V I.

Solvent Added at one time.		Total amount of components present.		No. of grams of each component in 100 gr. of the solution.			
Water	Acetone	CaCl ₂	Water	Acetone	CaCl ₂	Water	Acetone
26.3245	17.289	6.534	26.3245	17.289	13.03	52.49	34.48
8.3095	17.94	6.534	34.634	35.229	8.5	45.37	46.15
5.82	20.183	6.534	40.454	55.412	6.38	39.51	54.11
3.808	16.937	6.534	44.262	72.349	5.35	35.95	58.75
6.28	29.505	6.534	50.542	101.854	4.11	31.8	64.09
3.98	19.596	6.534	54.522	121.45	3.58	29.88	66.54
1.933	13.026	6.534	56.455	134.476	3.31	28.59	68.10
3.824	13.801	6.534	60.279	148.277	3.04	27.03	69.93
2.61	18.098	6.534	62.879	166.375	2.77	26.67	70.56
41.945	25.595	10.904	41.945	25.595	13.90	53.47	32.63
10.707	18.603	10.904	52.652	44.198	10.12	48.86	41.02
6.027	14.933	10.904	58.679	59.131	8.47	45.59	45.94
6.255	22.49	10.904	64.934	81.621	6.92	41.24	51.84
2.72	12.615	10.904	67.654	94.236	6.31	39.15	54.54
6.898	26.902	10.904	74.552	121.138	5.28	36.09	58.63
2.015	11.945	10.904	76.563	133.083	4.94	34.72	60.34
19.553	35.766	2.525	19.553	35.766	4.37	33.8	61.83
10.116	58.96	2.525	29.669	94.726	1.99	23.38	74.65
4.137	26.917	2.525	33.806	121.643	1.6	21.4	77.00
3.362	25.298	2.525	37.168	146.941	1.35	19.92	78.73
45.72	21.423	15.531	45.72	21.423	18.787	55.301	25.913
19.372	22.765	15.531	65.092	44.188	12.443	52.153	35.404
6.932	13.420	15.531	72.024	57.608	10.70	49.61	39.69
5.274	11.441	15.531	77.298	69.049	9.59	47.75	42.66
3.755	10.413	15.531	81.053	79.462	8.82	46.04	45.14
7.709	23.88	15.531	88.762	103.342	7.48	42.75	49.77
2.546	9.612	15.531	91.308	112.954	7.07	41.54	51.39
2.193	8.985	15.531	93.501	121.939	6.72	40.48	52.8
53.372	22.230	32.4593	53.372	22.230	30.04	49.39	20.57
44.551	25.399	32.459	97.922	47.629	18.23	55.01	26.76
15.278	16.33	32.459	113.2007	63.959	15.49	54.00	30.51
16.151	20.506	32.459	129.352	84.465	13.18	52.52	34.3
13.54	24.925	32.459	142.892	109.390	11.40	50.20	38.40
57.272	22.372	31.13	57.272	22.372	28.09	51.71	20.20
3.11	2.216	31.13	60.383	24.588	26.81	52.01	21.18
16.014	5.166	31.13	76.397	29.754	22.67	55.66	21.67
19.84	14.08	31.13	96.237	43.834	18.189	56.21	25.60
41.367	17.903	26.901	41.367	17.903	31.21	48.00	20.81
24.512	71.611	2.197	24.512	71.611	2.23	24.93	72.84
2.310	19.74	2.197	26.822	91.351	1.82	22.27	75.89
18.55	97.606	0.816	18.55	97.66	0.68	15.87	83.44
2.14	19.48	0.816	20.69	117.086	0.58	14.93	84.49
3.389	35.910	0.816	24.079	152.996	0.45	13.55	86.00
8.2145	48.23	0.2735	8.2145	48.23	0.48	14.49	85.13
4.214	40.096	0.2735	12.4285	88.326	0.27	12.31	87.42
1.090	33.45	0.2735	13.5185	121.776	0.20	9.95	89.85
2.92	43.06	0.2735	16.4385	164.836	0.15	9.05	90.81

Sodium Chloride..Water and Acetone: The systems previously mentioned contain salts whose dehydrating value depends largely on the vapor tension of their hydrates. When two liquids are miscible in all proportions, the addition of a third component will cause the appearance of two liquid phases, and the third component does not necessarily form a hydrate. This is shown in the case of common salt. As sodium chloride is a very common laboratory agent, its efficiency in salting out acetone was determined. Some work has been done along this line. Linebarger¹⁰⁹ and Snell¹¹⁰ have shown that two liquid phases will appear when sodium chloride is added to an aqueous solution of acetone. Work of a quantitative nature was done by W. Herz and M. Knoch¹¹¹ when they determined the solubility of salt in aqueous solutions of acetone. In their paper they note the solubility of the salt and the formation of layers. The work is of little value as their data are in an unavailable form, for example, the solubility of the salt is expressed in millimols, for 100 c.c. of the solution which contains the salt, water and acetone. The solubility is plotted on a diagram and the rectangular coordinates are volumes of acetone and millimols of sodium chloride in 100 c.c. of the whole solution. No densities nor specific gravities are given. The solubility of sodium chloride in water is given as 537.9 millimols in 100 c.c. of the solution, which corresponds to 31.44 grams in 100 c.c. of the solution. The only data which corresponds to this are those given by Bødlander¹¹², who gives 31.6 grams of sodium chloride in 100 grams of the salt solution, the specific gravity of the solution being 1.203. Herz and Knoch give the limits of the layer formation, which would correspond to my quadruple points, as follows: water 68, acetone 32 and salt 18.03 in the lower layer, and water 13, acetone 87 and salt .45 in the upper layer. This

means that in a solution made up of 68 volumes of water and 32 of acetone, salt is dissolved, and 100 c.c. of the salt solution so made will contain 18.03 grams of salt. I made no attempt to realize these conditions in order to make comparison with my data, as the work entailed would not give correspondingly valuable results.

The salt that I used was the chemically pure salt for analytical purposes, prepared by Kahlbaum. Frankforter and Frary had used the same salt and determined its solubility, so no redetermination of this point was made. The solubility is 35.7 grams in 100 grams of water, or 26.3+ grams in 100 grams of solution. This is given by point D in figure VII. Other solubilities given for sodium chloride are those given by Armstrong and Eyre¹¹³, who state that the solubility depends upon the sample of salt used. Their solubilities range from 35.71 to 36.23 grams per 100 grams of water at 25°. In Landolt and Bornstein's¹¹⁴ tables the solubilities given are the following: Andreas gives 35.82 grams of salt in 100 grams of water at 20°, Raupenstrauch gives 35.85 and Taylor 36.1. The salt used was heated to redness until all decrepitation ceased. It was then cooled in a desiccator and a weighed amount dissolved in as little water as possible at 20°. This gave the saturated salt solution. Acetone was then added to the weighed water and salt solution and the salt was immediately precipitated, the acetone seeming to take the place of the salt. The weight of the acetone added was determined by difference and more water was added until the salt layer just disappeared. The last traces of salt did not dissolve very readily. This process was continued until the appearance of two layers without salt precipitation. The points on the binodal curve were determined in the

same manner as in the other systems, and are given in table VIII. Toward the end, as the concentration of the acetone increased, the salt was again precipitated on addition of acetone and water was again added until the salt dissolved. By continuation of this latter process, the solubility of the salt in acetone in concentrations ranging from 86 per cent. of acetone to 91 per cent. was determined. These determinations are given in table VII. The solubilities from 91 to 100 are interpolated. The solubility of BaCl_2 at 100 is zero.

In determining the quadruple point, salt was added to an acetone water-mixture until there was a large excess of undissolved salt in the bottom of the bottle. The bottle containing the complex was placed in a shaking machine which was operated by an electric motor, and after four days of this thorough shaking the composition of the upper and lower layers was determined in the usual manner. 23.545 grams and 23.65 grams of the upper layer gave 0.110 and 0.105 grams of salt, equal to 0.44 and 0.48 grams of salt in 100 grams of solution, and 22.530 grams of the lower solution gave 3.729 grams of salt or 16.55 grams of salt in the lower solution. The specific gravity determination used ^{before} to obtain the amount of acetone in the upper and lower layers was used in this case. The distillation of the upper layer required more attention than the distillation of the other layers. The upper layer, when heated, bumped and frothed. Capillary tubes were used to overcome this tendency, and a very small flame was used. The only other solution indicating a similar tendency, though not in so marked a degree, was the lower solution in the determination of the quadruple point of calcium chloride.

The specific gravity of the solution obtained by complete distillation of the upper layer was 0.8338 which gives an acetone^{content} of 85.8 per cent. Salt dehydrates only to this percentage, showing that it would be of no value in removing water from acetone.

259.79 grams of the lower solution which was distilled until the temperature remained at 100° over five minutes, gave 83.645 grams of the distillate, which had a specific gravity of 0.8810. This corresponds, on the McElroy and Krug tables to 67.9 per cent. acetone; or, in 83.645 grams there are 56.80 grams of acetone, giving the total amount of acetone in the 259.79 grams, which is equivalent to 21.86 per cent. acetone. Then the upper layer contained 85.8 per cent. acetone and 0.45 grams of sodium chloride, while the lower layer contained 21.86 per cent. acetone and 16.55 per cent salt. These points check with the points which were obtained in the determination of the binodal curve. The points on the binodal curve are given in table VIII. Tie lines were determined in an effort to locate the plate point. The solubilities of salt in the different concentrations of acetone, the binodal curve, the quadruple point and the tie lines are all indicated in figure VII.

In determining points on the line DQ, some were obtained by the method used for determination of the binodal curve, but a few were directly determined. To a solution containing 98.6 water and 1.4 acetone by weight, salt was added and the flasks were well shaken. The temperature was kept at 20°. It was found that 25.9^{grams}/salt were present in 100 grams of the salt solution. In a similar manner the solubilities of salt in a 96.10 and a 93.9 per cent. water acetone solution were determined. 24.19 grams of salt were present in 100 grams of a 93.9 per cent water acetone solution and 25.06 grams of salt were present in a 96.10 per cent. solution. These points are given in table VII, which gives the solubility of salts without appearance of layers.

T A B L E VII.

Temperature 20°.

Solubility of Salt in Acetone and Water.

NaCl	Water	Acetone
25.9	73.06	1.04
24.19	71.18	4.03
25.06	72.00	2.94
20.85	66.78	12.37
20.17	66.01	13.82
18.32	63.16	18.52
20.44	66.19	13.37
17.89	62.21	19.90
0.19	10.82	88.99
0.15	9.62	90.23
0.12	8.94	90.94
0.32	13.92	85.76

T A B L E VIII.

 Temperature 20°.

Binodal Curve of Salt, Water and Acetone.

Solvent added			Total amount of		Per cent. Components present in 100 grams of solution.		
			Components present.				
Water	Acetone	Salt	Water	Acetone	Salt	Water	Acetone
3.921	6.606	12.5163	47.085	19.259	15.87	59.71	24.42
13.511	17.608	12.5163	60.596	36.867	11.38	55.09	33.53
3.567	7.366	12.5163	64.163	44.233	10.35	53.06	36.59
3.166	8.134	12.5163	67.329	52.367	9.47	50.92	39.61
2.424	6.567	12.5163	69.753	58.934	8.87	49.39	41.74
3.025	6.336	12.5163	72.778	65.270	8.31	48.33	43.36
3.905	11.80	12.5163	76.683	77.07	7.53	46.12	46.35
3.162	12.25	12.5163	79.845	89.32	6.89	43.95	49.16
1.884	10.454	12.5163	81.729	99.774	6.45	42.12	51.43
3.882	15.40	12.5163	85.611	114.984	5.87	40.19	53.94
8.94	34.928	1.3838	94.551	149.912	4.87	36.79	58.34
16.3322	42.188	1.3838	16.3222	42.188	2.31	27.27	70.42
4.79	23.723	1.3838	21.1222	65.901	1.57	23.89	74.54
2.893	16.897	1.3838	24.0152	82.808	1.27	22.19	76.54
3.99	36.566	1.3838	28.0052	119.374	0.93	18.83	80.24
3.144	25.340	1.3838	31.1492	144.714	0.79	17.58	81.63
7.392	40.153	0.2840	7.392	40.153	0.59	15.46	83.95
4.97	76.208	0.2840	12.362	76.208	0.32	13.92	85.76

Temperature Effects.

Acetone and water are two liquids miscible in all proportions at temperatures at which they exist as liquids. Lowering or raising the temperature will not cause the formation of two layers unless a third substance such as calcium chloride, potassium fluoride or sodium chloride is added. In the discussion of the binodal curve in the calcium chloride system, attention was called to the fact that when a just homogeneous mixture of calcium chloride, water and acetone at 20° (the temperature chosen for this isotherm) was slightly warmed, two liquid phases formed immediately. With solutions containing a high sodium chloride or potassium fluoride content, the same phenomena was noticed. In more dilute solutions the effect was not apparent. Tables IX, X and XI give the results obtained when just homogeneous solutions of these salts and aqueous acetone were warmed from temperatures ranging from 5° to 40°. Temperatures above 40° were not used because acetone is very volatile, and in working at temperatures above 30° there was a loss in acetone. Pressure flasks were not used. It was thought that an increase in the pressure might have some effect on the results. The pressure used in all the experiments was that of the atmosphere.

The method used has been described. A definite amount of salt was weighed in the erlenmeyer flask that contained the thermometer and the same process was used as in the determination of the binodal curve. The temperature of the first determination was kept as near 5° as possible, and water was then added until the two layers just disappeared. The additional water was weighed. The contents of the flask were allowed to warm to 10°, cloudiness appeared, water was added until the cloudiness just disappeared, and the increase in water was determined by weighing. The solution was then warmed to the different temperatures, water being added until homogeneity was obtained at the temperatures given. Variations are noted in the tables.

T A B L E I X.

Binodal Curve Points at Varying Temperatures in the System

Potassium Fluoride, Water and Acetone.

Temperature	Potassium Fluoride	Water	Acetone	Total	Water added	Per cent. Potassium Fluoride	Per cent. Water	Per cent. Acetone
10°	6.548	41.773	11.426	59.747	41.773	10.96	69.91	19.13
15°	6.548	42.153	11.426	60.127	0.380	10.89	70.10	19.01
20°	6.548	42.663	11.426	60.637	0.510	10.80	70.36	18.84
25°	6.548	43.283	11.426	61.257	0.620	10.68	70.65	18.67
30°	6.548	44.72	11.426	62.694	1.437	10.44	71.34	18.22
35°	6.548	44.87	11.426	62.844	0.150	10.41	71.44	18.18
10°	8.045	69.784	32.481	110.310	69.784	7.29	63.27	29.44
15°	8.045	69.784	32.481	110.310	0.000	7.29	63.27	29.44
20°	8.045	70.069	32.481	110.595	0.285	7.27	63.36	29.37
25°	8.045	71.274	32.481	111.800	1.205	7.19	63.76	29.05
30°	8.045	72.824	32.481	113.350	1.550	7.10	64.24	28.66
35°	8.045	73.884	32.481	114.410	1.06	7.04	64.57	28.39
8°	15.915	81.620	15.41	112.945	81.620	14.09	72.27	13.64
15°	15.915	83.00	15.41	114.325	1.38	13.92	72.60	13.48
20°	15.915	84.69	15.41	116.015	1.69	13.73	72.99	13.28
25°	15.915	86.06	15.41	117.385	1.37	13.56	73.31	13.13
30°	15.915	87.54	15.41	118.865	1.48	13.39	73.65	12.96
35°	15.915	88.58	15.41	119.905	1.04	13.28	73.87	12.85
0°	15.915	90.04	24.34	130.295	90.04	12.22	69.11	18.67
10°	15.915	92.02	24.34	132.275	1.980	12.04	69.56	18.40
15°	15.915	93.84	24.34	134.095	1.82	11.87	69.98	18.15
20°	15.915	96.24	24.34	136.495	2.40	11.65	70.51	17.84
25°	15.915	98.04	24.34	138.295	1180	11.51	70.89	17.60

T A B L E X.

Temperature Effect in the System Sodium
Chloride, Water and Acetone.

Temper- ature	Sodium Chloride	Water	Acetone	Total	Water added	Per cent. Sodium Chloride	Per cent. Water	Per cent. Acetone
13°	14.44	51.96	25.88	92.28	51.96	15.64	56.30	28.06
15°	14.44	52.875	25.88	93.195	0.195	15.50	56.74	27.76
* 20°	14.44	55.760	25.88	96.080	2.885	15.03	58.04	26.93
25°	14.44	56.50	25.88	96.82	0.74	14.91	58.36	26.73
30°	14.44	57.66	25.88	97.98	1.16	14.74	58.85	26.41
35°	14.44	58.71	25.88	99.06	1.08	14.58	59.30	26.12
40°	14.44	60.45	25.88	100.77	1.71	14.33	59.98	25.69
10°	14.44	61.15	43.38	118.97	61.15	12.14	51.40	36.46
15°	14.44	62.25	43.38	120.07	1.10	12.03	51.84	36.13
20°	14.44	64.45	43.38	122.27	2.20	11.81	52.71	35.48
25°	14.44	66.15	43.38	123.97	1.70	11.65	53.36	34.99

* Note. The reading at 20° is too high and at 25° too low, too much water was added at 20°. 3.62 grams of water were added to give homogeneity in the solution in raising the temperature of the solution from 15° to 25°. The temperature effect is most noticeable around 20°.

T A B L E X I.

Temperature Effects in the System
Calcium Chloride, Water and Acetone.

Temperature	Calcium Chloride	Water	Acetone	Total	Water added	Per cent. Calcium Chloride	Per cent. Water	Per cent. Acetone
10°	15.430	34.969	14.86	65.255	34.965	23.64	53.59	22.77
20°	15.430	36.505	14.86	66.795	1.540	23.10	54.65	22.25
25°	15.430	39.045	14.86	69.335	2.540	22.25	56.51	21.44
30°	15.430	40.505	14.86	70.795	1.460	21.79	57.22	20.99
35°	15.430	43.435	14.86	73.775	2.960	20.91	58.95	20.14
40°	15.430	44.675	14.86	74.965	1.190	20.58	59.59	19.83
5°	15.430	53.065	30.89	99.385	53.065	15.52	53.39	31.09
15°	15.430	53.065	30.89	99.385	0.000	15.52	53.39	31.09
20°	15.430	54.695	30.89	101.015	1.630	15.27	54.15	30.58
25°	15.430	57.245	30.89	103.565	2.550	14.89	55.28	29.83
30°	15.430	59.225	30.89	105.545	1.98	14.62	56.11	29.27
35°	15.430	61.715	30.89	108.035	2.49	14.29	57.12	28.59
40°	15.430	64.395	30.89	110.715	2.68	13.93	58.17	27.90

* Note. The change occurred at 18°.

The preceding method was used in trying to determine the critical solution temperature of the various solutions of the salts in water and acetone mixtures. The temperature at which any two conjugate solutions become homogeneous is called the critical solution temperature. A complete discussion of the critical solution temperature is given by Timmermans.¹¹⁵ He states that the elevation of the critical solution temperature of the two liquids through a third substance is proportional to the concentration, when the third substance is soluble in only one of the liquids. If two completely miscible solutions are salted out by the addition of a third substance, there is an elevation of the upper critical temperature.¹¹⁶

When two nonhomogeneous solutions or a pair of conjugate solutions are warmed, the temperature at which the two layers disappear and the solution becomes homogeneous is called the upper critical solution temperature. The lower critical solution temperature is one below which solutions are homogeneous. On cooling the two solutions, they become homogeneous and remain so at lower temperatures. W. Dolgolenko¹¹⁷ states that the lower critical solution temperature of two solutions is due to the presence of an impurity, as a lower critical solution temperature is characteristic of ternary mixtures. V. Rothmund¹¹⁸ states that the clouding is not dependent upon the third substance, but is an optical property. Exception must be taken to this statement, as it seems very evident in the foregoing experiments that the clouding is dependent on the amount of the third substance present.

J. Snell,¹¹⁹ in working with salts and mixtures of acetone and water, found that all of the solutions with which he worked (with the exception

of those which contained the salts, sodium sulphate, sodium carbonate, disodium phosphate and sodium ammonium phosphate) clouded when they were warmed. Linebarger¹²⁰ stated that the lower the temperature the more water is needed to bring about the disappearance of the layers. A fall of a few degrees will bring characteristic cloudiness in a solution of potassium carbonate in a mixture of alcohol and water. Traube and Neuberg¹²¹ show that temperature will affect the composition of two layers when the two solutions are heated, the lower layer increasing in volume and the upper layer decreasing. I made saturated solutions of calcium chloride, sodium chloride and potassium fluoride in water, and added acetone until the concentration of the solutions was that obtained at the quadruple point. Upon increasing the temperature all the lower layers clouded, showing that the room temperature was the lower critical temperature of these solutions. When the upper solutions were heated, neither the calcium chloride nor the potassium fluoride was affected. This would be expected, as practically no salt is in solution in either of these two upper layers. The upper layer of the sodium chloride solution clouded when it was warmed. This was not expected, as it would indicate that the plait point was not independent of the temperature and all the isotherms would not cross at this point.

I changed the concentrations of all my solutions and tried the effect of warming and cooling the different layers. On cooling no effect was noticed, but when any of the solutions were warmed they clouded, and when cooled to the original temperature they cleared. A more thorough investigation of this phenomenon is to be made.

A pair of conjugate solutions of potassium carbonate, water and acetone were warmed and cooled. A slight cloud was noticeable in the lower layer, but on the whole the temperature effects in this system were not very marked.

Quite a number of lower critical solution temperatures for the various systems were determined, but no upper critical solution temperatures were found with the concentrations used. Different concentrations will be tried and the effect further investigated.

Determinations of Acetone. When acetone is made by the dry distillation of the gray acetate of lime, the products in the distillate may contain in addition to the acetone, some aldehydes and some of the higher ketones. None of the alcohols are formed in this process. The acetone is obtained in a nearly pure state by treating the distillate with milk of lime and separating the pure acetone by fractional distillation. Acetone is also prepared commercially by the destructive distillation of wood. It comes over in the same fraction that contains methyl alcohol. Acetone is separated from the methyl alcohol by the use of calcium chloride. Methyl alcohol forms with calcium chloride the compound $\text{CaCl}_2 \cdot 4 \text{CH}_3\text{OH}$ which is stable at 100°C . If acetone does combine with calcium chloride, the compound formed is not stable at 100°C . and the acetone is removed by distillation. Hlasiwetz¹²² is the only authority for the formation of the calcium chloride acetone compound, and according to him 80 per cent. of the acetone is given off when the compound is heated and the distillation would not leave a very pure methyl alcohol: but Veitch¹²³ states that pure methyl alcohol is made by this method. Another method commonly

used to remove acetone from methyl alcohol is to convert the acetone into iodoform with iodine and caustic soda or caustic potash. The iodoform can be mechanically removed from the alcohol.

Methyl alcohol is used as a denaturant of ethyl alcohol and in the specifications adopted by the Treasury Department of the United States¹²³ for methyl alcohol used in denaturing grain alcohol, not less than 15 nor more than 25 grams of acetone, or acetone substances that are determined as iodoform, are to be used in 100 c.c. of the mixture. A good method for the determination of acetone in methyl alcohol and methyl alcohol in acetone is very desirable. There is no satisfactory method for the determination of acetone in the presence of ethyl alcohol, aldehydes and other ketones. Methods for the accurate determination of acetone in pathological cases are very desirable. Many methods have been used in the determination of acetone, none of which has given unqualified satisfaction. Practically all the methods are based on either the Deniges or the Messinger method. The Messinger¹²⁴ method depends on the conversion of acetone into iodoform with iodine and sodium or potassium hydroxide. The iodoform is either dried and weighed or else the iodine in the iodoform is determined by some modified volumetric method. The value of acetone in terms of iodine is represented by the following equation, $3 I_2 = 1 CH_3COCH_3$. In the Deniges¹²⁵ method the ketones are precipitated with mercuric oxide and sulphuric acid. A double mercury salt is formed.

Various modifications of the Messinger method are given by the following:- Robineau and Rollin,¹³⁶ Arachequesne,¹³⁷ J. Squibb,¹³⁸ Geelmuyden,¹³⁹ A.P. Sy,¹³⁰ Kebler,¹³¹ Collischon,¹³² Vaubel and Scheuer,¹³³ Keppeler,¹³⁴ Krauss,¹³⁵ Auld¹³⁶ converts the acetone into bromoform and then estimates the bromine with silver nitrate.

Babington¹³⁷ states that the iodoform test is good when the acetone content is high, but it is inexact with small quantities of acetone.

Oppenheimer¹³⁸ did not obtain satisfactory results when he made use of Deniges' method. Zetsche¹³⁹ and Heikel¹⁴⁰ made use of both methods in expressing their final results. The former obtains good results with the Deniges' method, in aqueous solutions that do not contain over 1 per cent. of ethyl alcohol.

Other methods used in detecting and determining acetone quantitatively are: Jolles'¹⁴¹ formation of the bisulphite, Strache's¹⁴² conversion of the ketone into the phenyl hydrazone, decomposition of the compound and the estimation of nitrogen, thus giving the amount of hydrazine in combination with the ketone, Marsh and Struthers'¹⁴³ determination by the use of $Hg(CH_3)_2$, the acetone forming with it $HgC_5H_8H_2O$.

H.Scott-Wilson¹⁴⁴ uses a similar reaction for acetone in an alkaline solution in the presence of silver nitrate. Donath and Dits¹⁴⁵ determined acetone by its oxidation with permanganate. Conroy¹⁴⁶ states that there is no quantitative relationship between potassium permanganate and acetone.

If salts are added to homogeneous mixtures of some organic liquids and water, the solutions become turbid, sometimes at room temperature and sometimes at higher or lower temperatures. Frankforter and Frary

used this principle in determining the amount of ethyl alcohol in an aqueous solution. Quantitative results were obtained. They added to a liquid of unknown alcoholic contents enough of the salt to cause the solution to separate into two layers and then, by cautious addition of water, made the solution just homogeneous. The salt giving the most satisfactory results was potassium fluoride. Snell¹⁴⁷ uses a similar plan with solutions containing acetone in water. The salt used in his case was potassium chloride. Instead of adding more salt or water to obtain homogeneity he increases^{or}decreases the temperature until the solution just gives two layers. The temperatures and the aqueous acetone solutions are plotted as coordinates, and a curve is drawn through the points obtained experimentally. This method can be used only with mixtures containing 20 to 85 per cent. of acetone and would not be accurate for mixtures containing 50 or 60 per cent. acetone because of the flatness of the curve. The results are not satisfactory if a third substance is present. The temperatures range from 32° to 46°. Potassium chloride is not a very satisfactory agent for the salting out of acetone. The value of potassium fluoride in this respect has already been shown.

In the determination of the binodal curve, there is only one concentration for any given quantity of potassium fluoride in 100 grams of the just homogeneous mixture, since the acetone, water and salt solution conducts itself in the same manner as the alcohol, water and salt solution, the per cent. of acetone in any aqueous solution can be determined in exactly the same manner as Frankforter and Prary determined alcohol. In Table I, it will be necessary to recalculate all values given so that the sum of the acetone and water will always

be represented by 100 grams of the salt. The amounts of potassium fluoride will be changed. By plotting the aqueous acetone solution and the potassium fluoride as rectangular co-ordinates, a curve is obtained. When a solution contains an unknown quantity of acetone, a definite amount of the liquid is weighed out, and the salt is added until two liquid phases just appear, then additional water is added until the two layers just disappear, and the additional water is weighed. The total volume of the solvent and the amount of the potassium fluoride used are known. These are calculated in the form, x grams of potassium fluoride to 100 grams of solvent. There is only one point on the curve which corresponds to x grams of potassium fluoride. From this point the other coordinate or the per cent. of aqueous acetone can be directly determined. When the per cent. of acetone is higher than 60, it is advisable to dilute the solution, as this method gives more accurate results for solutions containing between 1 and 60 per cent. of acetone. While the carbonate of potassium and the chloride of sodium and calcium could be used, they would not be as satisfactory. The end points with potassium carbonate are not sharp. Calcium and sodium chloride do not give results with solutions containing less than 21 percent. of the acetone.

While this is a neat and rapid method for the determination of acetone in just aqueous solutions, its value would be far greater if it could be used in the presence of a third substance, such as methyl or ethyl alcohol or the higher ketones. None of the higher ketones were available, so the efficiency of the method in the presence of these could not be tried. The method is not efficient in the presence of ethyl alcohol because ethyl alcohol is salted out by potassium fluoride. With methyl alcohol, absolutely satisfactory results were not

obtained. When a solution of methyl alcohol containing small quantities of acetone was tested by this method, no results were obtained. So the presence of small amounts of acetone in methyl alcohol cannot be determined quantitatively. More satisfactory results were obtained in testing the effects of small quantities of methyl alcohol in the presence of large quantities of acetone, as indicated in tables XII and XIII.

A definite mixture of ^{methyl} alcohol and acetone was made up by weight. The method for the determination of the binodal curve was used, only the mixture of acetone and methyl alcohol was used in place of the pure acetone. Fairly good results are given in this determination. Acetone can be determined in the presence of methyl alcohol, provided the acetone is in excess and not the methyl alcohol.

T A B L E X I I .
- - - - -
Temperature 20°.

1	2 Potassium Fluoride, Methyl Alcohol, Acetone and Water.								10
K F	Water	Mixture Alcohol Acetone	Alcohol	Acetone	Per cent. K F	Per cent. Water	Per cent. Alcohol	Per cent. Acetone	Percent. Mixture water and Alcohol
16.949	34.46	0.636	0.0727	0.5633	32.58	66.20	0.14	1.08	66.34
16.949	62.030	0.4977	0.5691	4.408	20.19	73.88	0.68	5.25	74.56
16.949	83.571	14.825	1.694	13.130	14.69	72.45	1.46	11.40	73.91
16.949	102.809	28.486	3.256	25.230	11.43	69.35	2.19	17.02	71.54
16.949	117.712	43.455	4.966	38.489	9.52	66.09	2.79	21.60	68.88
16.949	137.936	68.43	7.82	60.609	7.59	61.77	3.50	27.14	65.27
19.2975	86.797	13.514			16.13	72.57	1.40	9.90	73.97
19.2975	119.047	34.075			11.19	69.05	2.45	17.31	71.50
19.2975	141.237	63.423			8.62	63.07	3.51	24.80	66.58
19.2975	155.695	83.221			7.47	60.30	4.00	28.73	64.30

T A B L E XIII.

By referring to Figure III, the weights of water and acetone corresponding to the above quantities of potassium fluoride are found, and are the following:

1	2	3	(Column 10, table XII.)
K F	Acetone	Water	
32.58	1.42	66	66.34
20.19	5.81	74	74.56
14.69	11.81	73.5	73.91
11.43	17.57	71.	71.54
9.52	22.48	68	68.88
7.59	28.41	64	65.27
16.13	9.87	74	73.97
11.19	17.81	71	71.5
8.62	25.38	66	66.58
7.47	28.53	64	64.30

If the weights in column 10 table XII are compared with the weights given in column 3, table XIII it will be seen that the methyl alcohol does not interfere to any marked extent in the determination of acetone by this method. This holds true if the amount of methyl alcohol is not too high. In the first six determinations a solution containing 92.87 grams of acetone and 11.99 grams of methyl alcohol was used, ^{and} in the last four determinations 139.895 grams of acetone and 19.775 grams of methyl alcohol.

S U M M A R Y.

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In the study of the four systems, it has been shown that potassium fluoride and potassium carbonate in the anhydrous form are equally efficient in dehydrating acetone. Potassium fluoride is the more rapid agent of the two, and gives cleaner out separations. If a large excess of anhydrous calcium chloride is used the acetone is completely dehydrated. Sodium chloride dehydrates to 85.8 per cent of acetone.

The saturated solution of potassium fluoride will dehydrate to the extent of 98 per cent., while the saturated potassium carbonate dehydrates only to 96.5 per cent, of acetone. 98.4 per cent. acetone can be obtained with a saturated calcium chloride solution.

Neither the fluoride nor the carbonate solutions entail much loss of acetone, practically no acetone being soluble in these saturated solutions, while calcium chloride retains 23 per cent. of acetone in the aqueous solution of the chloride. Sodium chloride is the least satisfactory of the four, as it retains over 21 per cent. of acetone, and in addition dehydrates only to 85.8 per cent. The viscid nature of the calcium chloride solution is objectionable. The fluoride gives the cleanest and most rapid separation and seems to be the most satisfactory, salting out or dehydrating agent for acetone.

In this thesis investigation covers the following lines:

(1) The isotherms at 20° for the systems water, acetone, and potassium fluoride; water, acetone and potassium carbonate, water, acetone and calcium chloride and water, acetone and sodium chloride are given and thoroughly investigated.

(2) Temperature effects in the systems are noted, and while no upper critical solution temperatures were found, the lower critical solution temperatures of a series of solutions are given.

(3) A quantitative method is given for the determination of acetone in an aqueous solution, provided a third substance is not present. The effect of the presence of methyl alcohol, when this method is used, is discussed.

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