In analyses Nos. 2, 5, 9 and 10, very slight residues[1] were left on the filter after treatment of the precipitated sulfides with KOH, but in no case was the size of the residue such as to indicate the presence of significant amounts of metals of the Cu groups.

Summary.

1. The well-known objectionable features of the ammonium polysulfide method for the separation of the copper and tin groups have led to many attempts to replace it by a more suitable process; of these the sodium carbonate, sodium hydroxide, and potassium hydroxide methods taken alone or in conjunction with hydrogen peroxide are the best known. These have been examined and their shortcomings pointed out.

2. A scheme of analysis has been devised which overcomes the chief difficulties in the analysis of the filtrate of Group 1. The chief features of the method are:

(*a*) The preliminary precipitation of the alkaline earth metals together with some of the lead before precipitation of Group 2 with hydrogen sulfide.

(*b*) Treatment of the filtrate from the precipitation of the alkaline earth metals with sulfur dioxide before passing in hydrogen sulfide, in order to oxidize stannous tin and to reduce pentavalent arsenic.

(*c*) The complete separation of the sulfides of the divisions of Group 2 by means of potassium hydroxide.

3. The results of a number of test analyses show the method to be trustworthy.

NEW YORK, N. Y.

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

BY GEO. B. FRANKFORTER AND LILLIAN COHEN.

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Introduction.

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 of value on the efficiency of these drying agents were made by Siebenrock[2] in the

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[1] See note under Test Experiment 5.

[2] *Monatsh.*, 30, 759–66.

drying of ether; Foote and Scholes[1] in the drying of alcohol; and Frankforter and Frary[2] in the drying of alcohol.

Frankforter and Frary[2] showed that anhydrous potassium fluoride is 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 a sufficient quantity of a salt, such as $CaCl_2$, KF, K_2CO_3 or NaCl, was added. Linebarger,[3] Snell,[4] Bell,[5] McElroy and Krug,[6] Timmermans,[7] and Herz and Knoch[8] made investigations on the influence of various salts causing the formation of layers in aqueous solutions of acetone. 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 made of the systems containing potassium carbonate, water and acetone; calcium chloride, water and acetone; and sodium chloride, water and acetone.

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. Schreinemakers.[9] 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

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[1] This Journal, **33**, 1309.

[2] *J. Phys. Chem.*, **17**, 402.

[3] *Am. Chem. J.*, **14**, 380.

[4] *J. Phys. Chem.*, **2**, 458.

[5] *Ibid.*, **9**, 531.

[6] *J. Anal. and App. Chem.*, **6**, 153.

[7] *Z. physik. Chem.*, **58**, 129–213.

[8] *Z. anorg. Chem.*, **41**, 318.

[9] *Z. physik. Chem.*, **22**, 93, 515; **23**, 417, 649; **59**, 647.

phase. In case the hydrate is formed (4) represents two solid phases and one liquid phase. The graphic representation of these systems is the same as that given by Schreinemakers[1] and Frankforter and Frary.[2]

Experimental.

The following determinations were made in all the systems studied:

1. Solubility of the salts in various concentrations of aqueous acetone, ranging from 95 to 100% acetone.
2. The binodal curve.
3. Tie lines.
4. Approximate positions of the plait 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% 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 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 to dryness over water baths or on the radiator. The residue was weighable only in the case of calcium chloride; 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 g. of potassium fluoride are soluble in 100 g. of water; but this is an inconvenient form, the percentage of the an-

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[1] *Z. physik. Chem.*, **59**, 647.

[2] *J. Phys. Chem.*, **17**, 402.

hydrous salt in 100 g. of the saturated solution being more convenient to work with. This is equivalent to 48% of anhydrous salt.[1] The solubility of potassium carbonate is 112 g. of the anhydrous salt in 100 g. of water at 20°, or 53.06% carbonate. For calcium chloride the solubility used is that given by Roozeboom[2] (74.5 g. of $CaCl_2$ in 100 g. of water, which is equal to 42.69 g. of $CaCl_2$ in 100 g. of the solution). The solubility of NaCl used was 35.79 g. in 100 g. of water or 26.35% of the solution as sodium chloride. The following method was employed in determining the binodal curve: An Erlenmeyer flask of about 400 cc. 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 buret 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.

Bonner[3] 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 buret 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

[1] *Ber.*, 39, 1716.

[2] *Z. physik. Chem.*, 4, 31.

[3] *J. Phys. Chem.*, 14, 738.

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 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° in the latter system, no particular effect was noticed in determining points on the binodal curve. This can also be seen in Fig. 3, where the points determined by Bell[1] 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 Ostwald 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.—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

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[1] *J. Phys. Chem.*, **9**, 537.

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 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 evaporation of the acetone. The contents of the distilling flask were distilled to dryness. The specific gravity of the acetone is then determined, and from the table given by McElroy and Krug[1] 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. In determining the acetone content, 200–400 g. 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.

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[1] *J. Anal. and App. Chem.*, 6, 187, (1892).

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 % 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 at 20°. 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 solutions temperature 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 5°, 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 5° was noted. The process was repeated until temperatures of 40° were reached.

Materials.

Calcium Chloride.—The calcium chloride used was Merck's purified especially for analytical purposes. Five grams of the calcium chloride dissolved in 25 cc. 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. The salt was found to be pure according to tests given by Krauch.[1] 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.[2] To prevent the formation

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[1] Testing of Chemical Reagents.

[2] M. Dennstedt, *Ber.*, 1, 602.

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 by this method. It was therefore 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 sulfuric 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 250–300 g. were placed in the flask, the temperature of the air bath ranging from 160 to 220°. The hydrochloric acid gas was passed into the heated chloride, which 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 removed and the generation of the gas was stopped. When the contents of the flask were cooled to 100°, 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 2 g. 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 Honigschmid[1] in their atomic weight determination of calcium.

Potassium Fluoride.—This salt was labeled "Merck's chemically pure potassium fluoride." If 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 of carbon dioxide and

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[1] This Journal, 33, 28.

water had passed off. The temperature was kept below fusion to prevent the formation of potassium hydroxide and the loss of carbon dioxide.[1] 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 g. of salt in 100 g. 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% pure, was used, specific gravity 0.79576, at 15.55°/4°, b. p. 64.6°.

Acetone and Its Purification.—The acetone was Kahlbaum's purest quality from the bisulfite compound. 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 of purification was yellow, which may have been due to decomposition, as it was found that acetone that had stood in the sunlight gradually turned yellow. This method of treatment gave strictly pure acetone even from the commercial product, hence practically all the material used in this work was prepared from the crude product by the above method.

R. Bacon and P. Freer[2] 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 Taylor.[3]

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[1] Roscoe and Schorlemmer, 2, 351 (1907).

[2] *Philipp. J. Sci.*, 267, 76; through *C. A.*, 1, 1694.

[3] *J. Chem. Soc.*, 89, 1257.

PHYSICAL CONSTANTS.

Index of Refraction. Pulfrich refractometer (latest model). Temperature 20°.

Commercial acetone.........	H α 1.36309	H β 1.34882	H γ 1.33999
Purified acetone.............	H α 1.36213	H β 1.34834	H γ 1.339506
Kahlbaum's acetone, purified.	H α 1.36219	H β 1.34823	H γ 1.33943

Brühl[1] obtained the following results:

Acetone, sp. gr. 20°/4°......	0.7920		
	H α 1.35715	H β 1.36393	H γ 1.36780

The data given for the specific gravity and the boiling point of acetone by different investigators do not generally agree. The acetone used in this work had a boiling point of 56.3–4°.

Systems.

Potassium Fluoride Water and Acetone.—This system is one that has never been studied, because the usefulness of potassium fluoride has but recently been shown by Frankforter and Frary.[2] 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 salted out the alcohol. 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. 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, and 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 subsequent evaporation. 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. The acetone layers in no case gave any perceptible amount of potassium fluoride in the solution, and, in general, 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

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[1] *Z. physik. Chem.*, **22**, 189, 409.

[2] *J. Phys. Chem.*, **17**, 402.

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 Fig. 1. 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 20–30 g. 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 cc. 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 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, a very slight brown resin, which decomposes at a high temperature, is left behind.

The specific gravity of this distillate was then determined. McElroy and Krug[1] have determined the data for a table of specific gravities for acetone at 20°/4°. In this table the specific gravities of 20 mixtures of acetone and water, ranging from zero to 100% of acetone, are given. In order to determine intermediate points, this table was plotted, the rectangular coördinates giving percentages and specific gravities. From the diagram the percentage 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% acetone. A saturated solution of potassium fluoride will, then, dehydrate acetone to the extent of 98%. The amount of potassium fluoride in the lower layer was next determined. 32.679 g. 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 hydro-

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[1] *J. Anal. and App. Chem.*, 6, 187.

fluoric acid, as the salt hydrolyzes. 19.625 g. of potassium chloride were obtained, which is equivalent to 46.3 g. of potassium fluoride in 100 g. 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 g. 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 $KF.2H_2O$, 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 99.9% 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% 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 g. of solution.
I.	Upper layer	45.98	0.0295	0.05
	Upper layer	39.37	0.03	0.059
	Lower layer	53.936	16.006	23.12
	Lower layer	55.81	16.64	13.23
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 $CaCl_2.H_2O$ and acetone, it was noticed that the solution, just homogeneous 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.—FOR THE BINODAL CURVE OF POTASSIUM FLUORIDE WATER AND ACETONE AT 20°.

Solvent added.		Total wt. of subst. present.			Wt. of subst. present in 100 g. of soln.		
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	56.28	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	9.72
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	33.86	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

Fig. 1 gives a graphic representation of this system.

Potassium Carbonate, Water and Acetone.—That potassium carbonate forms two layers when added to an aqueous solution of acetone has been shown by Linebarger,[1] Snell[2] and Bell.[3]

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[1] *Ann. Chem. J.*, 14, 380.

[2] *J. Phys. Chem.*, 2, 457.

[3] *Ibid.*, 9, 531.

Linebarger's work, although classed as quantitative by Timmermans,[1] is 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 buret to a titrated solution of the carbonate, until just a drop of water would clear up the milkiness caused by a drop of acetone. The data obtained by Linebarger have been recalculated and tabulated in parts per 100 g. of the solution. These are given in Table II, while in Fig. 3 the points on the curve indicated by ° are those obtained by Linebarger. His results were obtained at 20°.

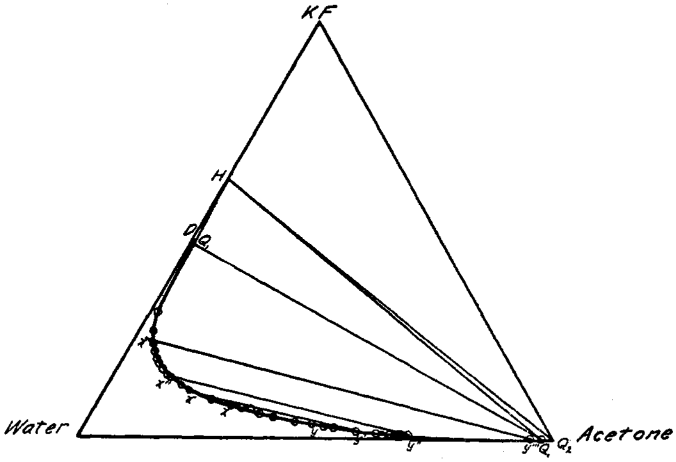

Fig. 1.—Equilibrium in the system: potassium fluoride, water and acetone.

TABLE II.

Temperature 20°.

K_2CO_3.	Acetone.	Water.	Total.	Per cent. K_2CO_3.	Per cent. acetone.	Per cent. water.
1	4.8	9.2	15.0	6.67	32.0	61.33
1	11.4	16.1	28.5	3.51	40.0	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	50.0	38.7	89.8	1.11	55.67	43.23
1	89.7	49.9	141.6	0.7	64.0	35.20

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[1] *Z. physik. Chem.*, **58**, 123.

These points fit in fairly well with the binodal curve, but when one considers the fact that the maximun amount of the carbonate used by Linebarger was 6.67 g. in 100 g. of the solution, and that a saturated solution contains over 53% of carbonate, the results cannot be considered very satisfactory, especially if one takes into consideration the dehydrating effect of potassium carbonate on acetone.

Bell determined points on the binodal curve over a much wider range, his concentrations of the carbonate varying from 2.34 g. in 100 g. of solution to 30.58 g. in 100, while the percentage of acetone decreased from 42.56 to 1.27. His particular object was not so much the determination of the points on the curve as to prove that the exponential expression of Bancroft,[1] $X^{\alpha}.y^{\beta}/z^{\alpha+\beta} = K$ would describe the equilibrium in the system, acetone, potassium carbonate and water. By simplification the above equation becomes $Z^{n}/_{y} = K$. Z denotes the grams of water, and y the grams of acetone per gram of salt. Bell tried to apply this equation to Linebarger's data, as well as to his own, and found that it could be applied neither to this system not to any system containing two consolute liquids and an electrolyte. Bell's data are obtained at 25° and are given in Table III and plotted in Fig. 3. The points are indicated by X. It is noticed

TABLE III.

Bell's data.			Recalculated in parts per 100 g.		
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	23.64	3.14	58.26	38.61
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	31.0
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	45.0	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	49.99	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	25.28	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

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[1] *J. Phys. Chem.*, 1 34, 760.

that Linebarger's and Bell's data combined give a fair idea of the general character of this curve. Though Bell's data were obtained at 25°, they are compared 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. With extreme concentrations of carbonate in the water, where only 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% acetone and less than 0.5% potassium carbonate, the cloudiness was difficult to perceive, but by holding the flask to the sunlight the cloudiness was detected by transmitted light.

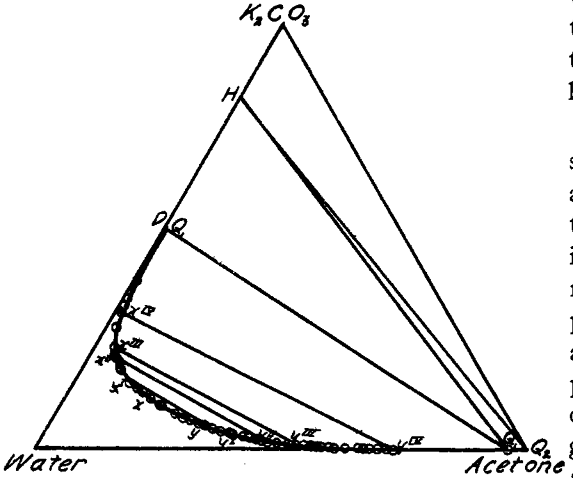

Fig. 2.—Equilibrium in the system: water, acetone and potassium carbonate.

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 Fig. 2. Potassium carbonate was found to be practically insoluble in acetone, and was also found to be practically insoluble in solutions of 95–100% acetone. The determinations of the solubilities up to 92% 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_2CO_3 found.	Total K_2CO_3 in 100 g.
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 Fig. 2 will show the position of the last 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°/4°. Reference to the tables in use give an acetone content of 96.4%. 29.09 g. of the original solution of the upper layer gave a carbonate content of only 0.0007 g., or 0.0024 g. in 100 g. of solution. No attention is given to this result, as it practically coincides with the point of 100% acetone on the triangle.

Four hundred 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, ap-

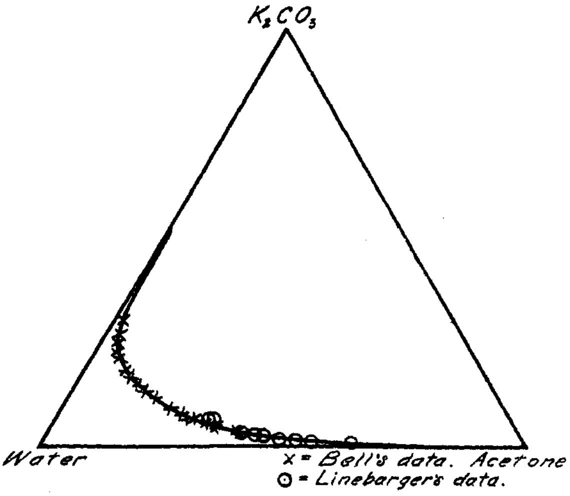

Fig. 3.

parently, possible to obtain enough acetone to determine the amount in the solution. The specific gravity of the weighed distillate from 400 g. of the solution was 0.9994, although acetone was present. In the reference tables, 0.9994 gives zero, or negligible quantities of acetone. In this solution, evaporation of 29.503 g. gave 15.4567 g. of K_2CO_3, which is equivalent to 52.38 g. of K_2CO_3 in 100 g. 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 g. in 100 g. of the 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 $2K_2CO_3.3H_2O$. 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%. This acetone was again kept in contact with more of the anhydrous salt, and the hydrate and the solution were 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% acetone, thus 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 g. potassium carbonate, 29.701 g. water and 12.95 g. 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.

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. Snell[1] and Linebarger[1] 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. McElroy and Krug[1] classify calcium chloride among the salts that are very sparingly soluble. It was found that the average results of a series of determinations at 20° gave 0.02 g. of calcium chloride in 100 g. of

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[1] *Loc. cit.*

TABLE IV.

System Potassium Carbonate, Water and Acetone.

Solvent added.		Total wt. of subst. present.			Per cent. in 100 g. solution.		
Water.	Acetone.	K_2CO_3.	H_2O.	$(CH_3)_2CO$.	K_2CO_3.	H_2O.	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	71.98	4.08
13.974	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	55.36	42.21
38.055	2.56	11.652	38.055	2.56	22.29	72.81	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	28.231	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	40.48	60.06

acetone. The method used has already been described. The solubility of calcium chloride in acetone ranging in concentration from 95–100% acetone gave negligible results at 20°. Not very satisfactory results were obtained in determining the solubility of the calcium chloride in aqueous solutions containing 1–10% of acetone. 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% water and 9% acetone was found to be 40.5 g. $CaCl_2$ in 100 g. of the solution. This gives one point in the line D Q, Fig. 4. The point D represents the solubility of the salt in water, or 74.5 g. of calcium chloride in 100 g. of water, or 42.70 g. in 100 g. of the solution. 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% 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 separation. 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 to 20° there is no appreciable clouding, but when the solution is heated from 20 to 21°, immediate cloudiness is noted.

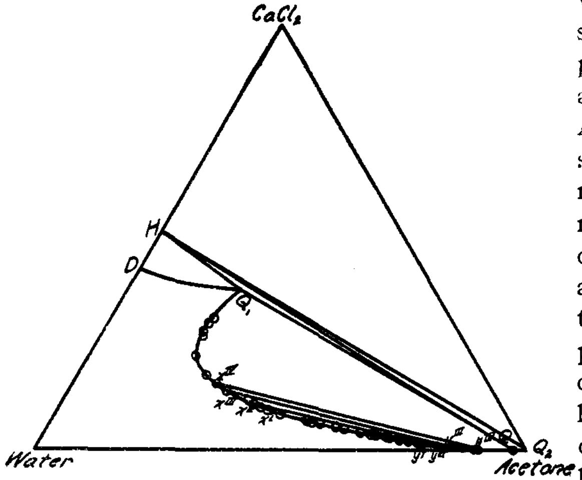

Fig. 4.—Equilibrium in the system; calcium chloride, water and acetone.

Determination of Quadruple Points.—Acetone was added to an almost saturated solution of the hexahydrate of calcium chloride in water. The bottle containing the mixture was placed in a thermostat, with a constant temperature of 20°. Every addition of the hydrate increased the amount of water present, making it necessary to add more acetone to produce equilibrium. Finally anhydrous calcium chloride was added and the temperature of the system was allowed to reach 28°. All the calcium chloride went into solution. The flask was again placed in the thermostat, and the contents of the flask were thoroughly agitated and mixed for a day by means of a rotating fan. The contents of the flask were allowed to settle, when the following layers appeared: An upper layer containing acetone and a little water and traces of calcium chloride, then crystals of the hydrate of calcium chloride, a lower layer of a saturated solution of calcium chloride, water and acetone. The lower layer was siphoned off and its acetone and calcium chloride content determined in exactly the same manner as the one previously described. 341.5 g. of the solution, when distilled, gave a mixture of 126.905 g. of acetone and water. The specific gravity found at 20°/4° was 0.8936, at 20°/20° 0.8969. On the tables this corresponds to 61% acetone, or there was 77.41 g. acetone in 126.905 g. of the mixture as well as in the 341.5 g. originally taken. This gives 22.66% of acetone. 33.88 g. of the solution, dehydrated, gave 12.927 g., or 38.16% $CaCl_2$. The crystals were filtered off and dried by suction. They were pressed between several thicknesses of filter paper and rapidly transferred to a weighed bottle. 6.303 g. of the crystals, when heated above 300°, gave a residue weighing 3.18 g. This shows that the crystals were $CaCl_2.6H_2O$.

Analyses of the upper layer gave no weighable amount of calcium chloride. The acetone content was determined in the usual manner, and was found to be 98.4%. A saturated solution of calcium chloride will not remove all the water from acetone. It is wasteful, as it retains over 20% of the acetone.

The second quadruple point was determined by using the 98% 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, no liquid seemed to be present, and the contents of the flask appeared as 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. In 1850, Hlasiwetz[1] 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 20°/4° was 0.7915, which corresponds to 100% 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 points accurately, but separation into distinct upper and lower layers were rather difficult to obtain.

The following results were obtained:

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[1] *Jahr. Ber.*, 3, 394; *J. prakt. Chem.*, 51, 355.

TABLE V.

		Amount of solution.	Grams $CaCl_2$.	Grams of $CaCl_2$ in 100 g. 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.

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. Linebarger[1] and Snell have shown that two liquids 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. Knoch[2] 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 cc. of the solution which contains the salt, water and acetone. The solubility is plotted on a diagram and the rectangular coördinates are volumes of acetone and millimols of sodium chloride in 100 cc. 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 cc. of the solution, which corresponds to 31.44 g. in 100 cc. of the solution. The only data which corresponds to this are those given by Bödlander,[3] who gives 31.6 g. of sodium chloride in 100 g. 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 the quadruple points, as follows: water

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[1] *Loc. cit.*

[2] *Z. anorg. Chem.*, 41, 319.

[3] *Z. physik. Chem.*, 7, 316.

TABLE VI.

Solvent added at one time.		Total amount of components present.			No. of g. of each component in 100 g. 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	58.70
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	74.63
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

68, acetone 32 and salt 18.03 in the lower layer, and water 13, acetone 87 and salt 0.45 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 cc. of the salt solution so made will contain 18.03 g. of salt. No attempt was made to check these results.

The salt used was Kahlbaum's "Zur Analyse mit Garantieschein." 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 g. in 100 g. of water, or 26.3+ g. in 100 g. of solution. This is given by point D in Fig. 5. 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 to 91% of acetone was determined. These determinations are given in Table VII. The solubilities from 91 to 100 are interpolated. The solubility of NaCl at 100 is zero.

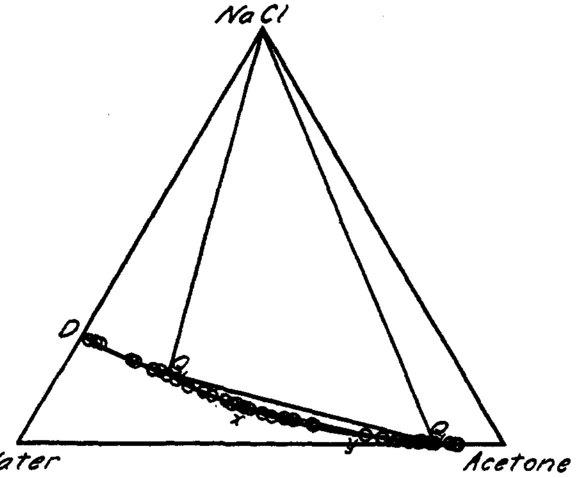

Fig. 5.—Equilibrium in the system: sodium chloride, water and acetone.

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 layers was determined in the usual manner. 23.543 g. and 23.65 g. of the upper layer gave 0.110 and 0.103 g. of salt, equal to 0.44 and 0.48 g. of salt in 100 g. of solution, and 22.530 g. of the lower solution gave 3.729 g. of salt or 16.55 g. 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 specific gravity of the solution obtained by complete distillation of the upper layer was 0.8338, which gives an acetone content of 85.8%. Salt dehydrates only to this percentage, showing that it would be of no value in removing water from acetone.

TABLE VII.—SOLUBILITY OF SALT IN ACETONE AND WATER.
Temperature 20°.

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

TABLE VIII.—BINODAL CURVE OF SALT, WATER AND ACETONE.
Temperature 20°.

Solvent added.		Total amount of components present.			Per cent. components present in 100 g. of soln.		
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

259.79 g. of the lower solution, which was distilled until the temperature remained at 100° over five minutes, gave 83.645 g. of a distillate which had a specific gravity of 0.8810. This corresponds, on the McElroy and Krug tables, to 67.9% acetone; or, in 83.645 g. there are 56.80 g. of acetone, which is equivalent to 21.86%. Then the upper layer contained 85.8% acetone and 0.45% of sodium chloride, while the lower layer contained 21.86% acetone and 16.55% 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 plait 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 Fig. 5.

In determining points on the line D Q, 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 parts 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 15.9 g. salt were present in 100 g. of the salt solution. In a similar manner the solubilities of salt in a 96.10 and a 93.9% water acetone solution were determined. 24.19 g. of salt were present in 100 g. of a 93.9% water acetone solution and 25.06 g. of salt were present in a 96.10% solution. These points are given in Table VII, which gives the solubility of salts without appearance of layers.

Temperature Effects.—Acetone and water are two liquids miscible in all proportions. 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 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 phenomenon 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 addi-

TABLE IX.—BINODAL CURVE POINTS AT VARYING TEMPERTAUES 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	1.80	11.51	70.89	17.60

TABLE X.—TEMPERATURE EFFECT IN THE SYSTEM SODIUM CHLORIDE, WATER AND ACETONE.

Temperature.	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°[1]	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	58.74	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	36.45
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

[1] NOTE.—The reading at 20° is too high and at 25° too low, too much water was added at 20°. 3.62 g. 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°.

tional 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.

TABLE XI.—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	56.31	21.44
30°	15.430	40.505	14.86	70.795	1.460	21.79	57.22	20.99
35°	15.430	43.485	14.86	73.775	2.980	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°[1]	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

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.[2]

W. Dolgolenko[3] 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. Rotmund[4] 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,[5] 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 sulfate, sodium carbonate, disodium phosphate and sodium ammonium phosphate) clouded when they were warmed. Linebarger[5] stated that the lower the temperature the

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[1] NOTE.—The change occurred at 18°.

[2] *Z. physik. Chem.*, **58**, 129–213; *Z. Electrochem.*, **12**, 644.

[3] *Z. physik. Chem.*, **62**, 499.

[4] *Ibid.*, **63**, 54.

[5] *Loc. cit.*

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 Neuberg[1] show that temperature will affect the composition of the two layers when the two solutions are heated, the lower layer increasing in volume and the upper layer decreasing. Saturated solutions of calcium chloride, sodium chloride, and potassium fluoride, were made and acetone added 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 the 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.

The concentrations of all the solutions were changed and the effect of warming and cooling the different layers was noted. 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.

Determination of 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 solutions just homogeneous. The salt giving the most satisfactory results was potassium fluoride. Snell 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 coördinates, and a curve is drawn through the points obtained experimentally. This method can be used only with mixtures containing 20–85% of acetone and would not be accurate for mixtures containing 50 or 60% 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

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[1] *Z. physik. Chem.*, 1, 510.

not a very satisfactory agent for the salting out of acetone. The value of potassium fluoride in this respect has already been shown.

New Method for Determination of Acetone.—In the determination of the binodal curve, there is only one concentration for any given quantity of potassium fluoride in 100 g. 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 percentage of acetone in any aqueous solution can be determined in exactly the same manner as Frankforter and Frary 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 g. of the solvent. The amounts of potassium fluoride will be changed. By plotting the aqueous acetone solution and the potassium fluoride as rectangular coördinates, 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 g. of potassium fluoride to 100 g. of solvent. There is only one point on the curve which corresponds to x grams of potassium fluoride. From this point the other coördinate or the percentage of aqueous acetone can be directly determined. When this 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% 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% of the acetone.

While this is a neat and rapid method for the determination of acetone in pure 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 obtained in this determination. Acetone can be determined in the presence of methyl alcohol, provided the acetone is in excess and not the methyl alcohol.

TABLE XII.—POTASSIUM FLUORIDE, METHYL ALCOHOL, ACETONE AND WATER.
Temperature 20°.

KF.	Water.	Mixture. Alcohol acetone.	Alcohol.	Acetone.	Per cent. KF.	Per cent. water.	Per cent. alcohol.	Per cent. acetone.	Per cent. 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

By referring to Fig. 1, the weights of water and acetone corresponding to the above quantities of potassium fluoride are found, and are the following:

TABLE XIII.

KF.	Acetone.	Water.	(Last column, Table XII.)
32.58	1.42	66.0	66.34
20.19	5.81	74.00	74.56
14.69	11.81	73.5	73.91
11.43	17.57	71.0	71.54
9.52	22.48	68.0	68.88
7.59	28.41	64.0	65.27
16.13	9.87	74.0	73.97
11.19	17.81	71.0	71.5
8.62	25.38	66.0	66.58
7.47	28.53	64.0	64.30

If the weights in the last column of Table XII are compared with the weights given in the third column of 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 g. of acetone and 11.99 g. of methyl alcohol was used, and in the last four determinations 139.895 g. of acetone and 19.775 g. of methyl alcohol.

Summary.

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 cut separations. If a large excess of anhydrous calcium chloride is used, the acetone is completely dehydrated. Sodium chloride dehydrates to 85.8% of acetone.

The saturated solution of potassium fluoride will dehydrate to 98%, while the saturated potassium carbonate dehydrates only to 96.5% of acetone. 98.4% 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% of acetone in the aqueous solution of the chloride. Sodium chloride is the least satisfactory of the four, as it retains over 21% of acetone, and in addition dehydrates only to 85.8%. 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.

This 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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A NEW METHOD FOR THE DETERMINATION OF THORIUM IN MONAZITE SAND.

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The large amount of work published upon the determination of thorium in monazite sand is an indication of the importance of this problem. Several methods have been devised for this determination. The principal ones, up to the year 1910, were the ammonium oxalate method,[1] the

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[1] Glaser, *Chem. Ztg.*, 20, 612 (1896).