rected values for the atomic volumes, which should take the place of the old values taken from Ostwald, are as follows: Magnesium, 14.0; silicon, 11.7; white phosphorus, 17.0; calcium, 26.2; chromium, 7.4; iron, 7.5; zinc, 9.2; arsenic, 13.1; bromine, 25.7; molybdenum, 9.4; palladium, 8.7.

Furthermore, the value for the density of arsenic should be given as 5.73, and the true density of aluminum is probably nearer to 2.7 than 2.6, although the latter was Mallet's value.

I am indebted to Professor W. D. Harkins and Dr. R. E. Hall for the discovery of some of these errors.

Fortunately, none of the changes is large enough to effect essentially the curve given on page 1649, or in any way to invalidate the conclusions of the paper in question. Indeed, almost every one of these changes rather improves the agreement of the observed values and those calculated from the equation on page 1652. THEODORE W. RICHARDS.

CAMBRIDGE, MASS., Nov. 4, 1915.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

EQUILIBRIA IN THE SYSTEMS OF THE HIGHER ALCOHOLS, WATER AND SALTS.

BY G. B. FRANKFORTER AND STERLING TEMPLE.

Received September 16, 1915.

The dehydration of alcohols is such a common process that it has been studied by many chemists.[1] Foote and Sholes[2] have studied the general theory of the drying action of a salt on a liquid and the importance of the amount of water which can be taken up by the salt. Frankforter and Frary[3] discovered the efficiency of KF as a salting-out agent for ethyl alcohol, worked out a means of testing the strength of alcoholic liquors by means of the action of KF and investigated the equilibria of the following systems: Potassium fluoride–water–ethyl alcohol; potassium fluoride–water–normal propyl alcohol; potassium carbonate–water–methyl alcohol; potassium carbonate–water–ethyl alcohol; potassium carbonate–water–normal propyl alcohol and sodium chloride–water–normal propyl alcohol. It was thought advisable to continue the work of Frankforter and Frary with some of the other alcohols and with some other salts.

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[1] Soubeiran, *Ann.*, 30, 356 (1839); Mendeléef, *Z. Chem.*, 1865, 260; Erlenmeyer, *Ann.*, 160, 249 (1871); Smith, *Chem. News*, 30, 235 (1874); Lescoeur, *Bull. soc. chim.*, [3] 17, 18 (1897); Yvon, *Compt. rend.*, 125, 1181 (1897); Ostermeyer, *Pharm. Zeit.*, 43, 99 (——); *Z. anal. Chem.*, 39, 46 (1900); Vitali, *Boll. chim. farm.*, 37, 257 (——); *Z. anal. Chem.*, 39, 46 (1900); *Bull. Chem. Zeit.*, 24, 814, 845 (1900); Young, *J. Chem. Soc.*, 81, 707 (1902); Evans and Fetsch, THIS JOURNAL, 26, 1158 (1904); Winkler, *Ber.*, 38, 3612 (1905); Kailan, *Monatsh.*, 28, 927 (1907); Frankforter and Frary, *J. Phys. Chem.*, 17, 402–473 (1913).

[2] THIS JOURNAL, 33, 1309 (1911).

[3] *J. Phys. Chem.*, 17, 402–473 (1913).

It has been shown,[1] the salting out of an alcohol belongs to the class of equilibria in ternary mixtures where two liquid phases are possible. Each component, mixed with either of the others, gives a system of only one liquid phase, that of a solution of one in the other. Only when all three components are present can two liquid phases exist. In representing such systems, use is generally made of the system of coördinates founded on the equilateral triangle, either with unit altitude or with the side of unit length.[2] In the first case, use is made of the fact that the sum of the lengths of the three perpendiculars drawn from a point within the triangle to the three sides is equal to the altitude. The three components of the system are represented by the three vertices, A, B and C; the sides opposite these vertices are lettered *a*, *b* and *c*. Any point O within the triangle represents a mixture of A, B and C in the proportions of and numerically equal to the lines O*a*, O*b* and O*c*, these lines being drawn perpendicular to the sides. In the second case, where the length of a side is taken as unity, the case is the same except that the lines drawn to the sides meet those sides at an angle of 120°. That is, they are drawn to any side in a direction parallel to either of the other two sides.

Some use has also been made of a right-angle isosceles triangle in representing equilibria in ternary mixtures,[3] but this is not at all general. In this paper the triangle with sides of unit length will be employed except where rectangular coördinates are used.

Schreinemakers[4] and others have discussed the general theory of such systems and the application to them of the coördinates based on the equilateral triangle.

Fig. 1 is a general form of the diagram for a ternary system of this class. The three vertices represent the three pure compounds involved; any point within the triangle represents a mixture of all three, while any point on a side represents a mixture of the two components represented by the vertices including that side. In Fig. 1 H represents the composition of a solid hydrate of the salt A, D represents the composition of the saturated solution of the salt in pure water, while G represents the

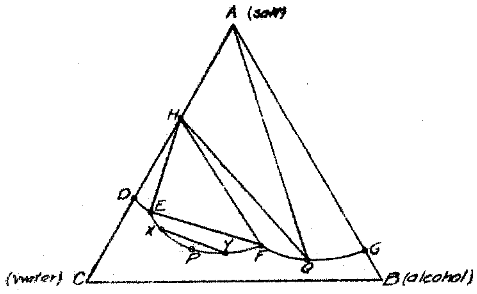

Fig. 1.

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[1] Schreinemakers, *Z. phys. Chem.*, **22**, 93, 515 (1897); **23**, 649 (1897); Frankforter and Frary, *Loc. cit.*

[2] G. G. Stokes, *Proc. Roy. Soc.*, **49**, 174 (1891); Gibbs, *Trans. Conn. Acad.*, **1876**, 3176; Roozeboom, *Z. physik. Chem.*, **15**, 147 (1894).

[3] Roozeboom, *Ibid.*, 12, 369 (1893).

[4] Schreinemakers, *Loc. cit.;* Frankforter and Frary, *Loc. cit.*

composition of the saturated solution of the salt in pure alcohol. The line D E P F Q G is the locus of all homogeneous mixtures which would be separated into two phases by the addition of an infinitesimal quantity of the salt.

This line D E P F Q G, which is the boundary between the homogeneous and heterogeneous systems, may be fairly regular throughout its length, but there are three portions which call for separate consideration. The point E represents the solution which is obtained by adding alcohol to a saturated solution of the salt in water until no more alcohol is taken up. This absorption of alcohol by a solution of a salt in water is usually accompanied by a precipitation of some of the dissolved salt. In case the salt forms a hydrate at the temperature used, the point E represents the lower layer of a system of two liquid phases which is in equilibrium with the solid hydrate. The portion D E of the line D E P F Q G is thus the locus of all solutions which are saturated with respect to the salt, which contain alcohol in amounts varying from none to the amount in the solution at E and which are in equilibrium with the solid hydrate.

The point F represents the upper layer, *i. e.*, the alcoholic solution of salt and water which is in equilibrium both with the solution at E and with the solid hydrate if one exists, otherwise with the anhydrous salt. Whenever we have the condition of two liquid phases, the lower layer has a composition represented by x, and the upper layer that represented by y. With increasing salt content x approaches the point E, while y approaches F. With decreasing salt content x and y approach the limiting position P and with less than this amount of salt the solution becomes homogeneous. The line E P F is the locus of all values of x and y and is called the binodal curve, the point P is called the plait point and the straight lines connecting x and y are called tie lines. The tie lines may be parallel but are not so necessarily.

The line F Q G is the boundary between homogeneous solutions with alcoholic content higher than F and heterogeneous mixtures of such solutions with either the hydrate or the anhydrous salt. The point Q is the limiting value of four areas and by an infinitesimal change in composition may become any one of the following: a homogeneous system below F Q G, a mixture of the anhydrous salt with the solution Q G, a mixture of the solid hydrate and the solution F Q or a mixture of solution Q with both the anhydrate and the anhydrous salt.

The area C D E P F Q G B is the locus of all homogeneous systems. The remaining areas are all heterogeneous and contain either a solid phase or two liquid phases. Area H D E is a mixture of the solid hydrate in equilibrium with a solution represented by some portion of D E. Area E P F consists of two liquid phases only. Area H F Q contains the solid hydrate in equilibrium with the solution F Q. Area H E F contains the solid hydrate in equilibrium with two liquid phases. Area A Q G represents a mixture of the anhydrous salt with a solution represented by some point on Q G, while the area A H Q represents all of the solid hydrate and the anhydrous salt which are in equilibrium with the alcoholic solution of the salt.

In case the salt does not form a hydrate, or in case the hydrate does not exist at the temperature involved, the point H may be considered as having moved along C A until it coincides with A, while Q moves to the left and becomes identical with F. Thus the three lines, H F, H Q and A Q become the single line A F, areas H F Q and A H Q disappear entirely, and we have the diagram shown in Fig. 2. Area E P F is unchanged, A F G in 2 is represented by A Q G in 1. Area A D E is a mixture of the anhydrous salt with a solution on D E and area A E F is the anhydrous salt in equilibrium with two liquid phases.

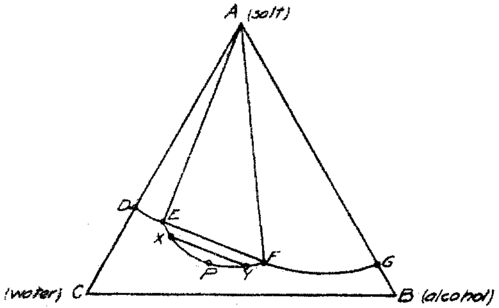

Fig. 2.

For most purposes the chief interest is in simply locating the line D E P F Q G and especially the portion E P F. As the interpretation of a curve is more automatic in the case of rectangular coördinates, it is advisable to put some of the value in the form for comparison. In general, when it is desired to represent the composition of a three-component system in terms of rectangular coördinates, the values used are the ratios of the two most similar components to the third component. Thus in the case of two soluble salts and water, the two sets of values obtained by dividing the weights of the salts by the weight of the water present might be used. This method, however, does not well represent the relations existing between three such components as a salt, water and an alcohol. If only two of the three components are represented, the third can always be found by difference and some important inferences may at once be apparent, no matter which pair of components is used.

To illustrate the foregoing, the values obtained by Frankforter and Frary in their study of the system, potassium fluoride–water–ethyl alcohol may be used in the following ways: If we plot the percentage of water against the percentage of alcohol, we obtain Fig. 3, which shows clearly that as the alcoholic content varies, the percentage of water, which is possible in a heterogeneous mixture of these two with the salt, reaches a maximum at about 8% alcohol and becomes less with any change in the alcoholic content. If we plot the percentage of K F against the percentage of water, we obtain Fig. 4, which tells us that the heterogeneous mixture of the three components which contains the maximum amount of water contains neither more nor less than about 22% K F. If we plot the percentage of K F against the percentage of alcohol we obtain Fig. 5, which shows that the K F and the alcohol are able to replace each other to some extent in the solution and that the influence of the K F in producing saturation in a homogeneous system is greater than that of the alcohol for equal weights.

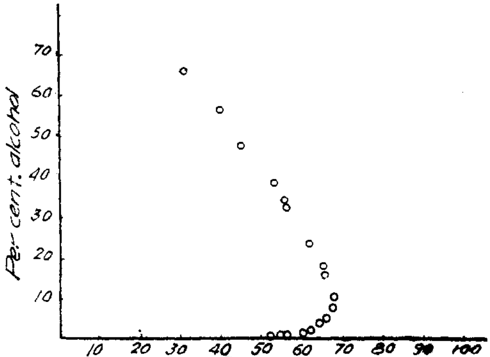

Fig. 3.

For analytical purposes, the best method of representing the binodal curve in ternary systems of this class seems to be that chosen by Frankforter and Frary, which consists in plotting all alcohol water mixtures on the vertical axis and the number of grams salt per hundred grams solvent on the horizontal axis. In this method the first set of values are obtained by dividing the weight of alcohol by the combined weight of the alcohol and water and the second set are obtained by dividing the weight of salt by the combined weight of water and alcohol. Thus the solubility of the salt in alcohol of all strengths is shown at a glance and when the solubility of the salt in any alcohol water mixture is known, the strength of the alcohol is read off at once from the curve. Fig. 6 shows this system of plotting, using the same values as those used in Figs. 3, 4 and 5.

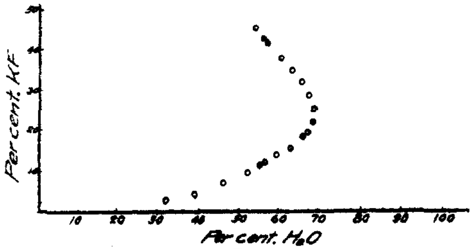

Fig. 4.

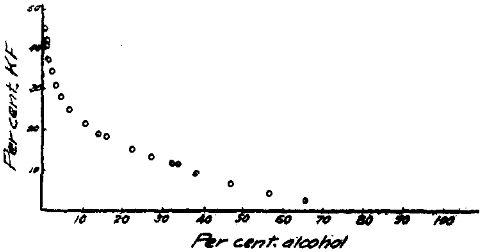

Fig. 5.

Experimental Methods.

An Erlenmeyer flask with a tightly fitting ground glass stopper and a side tube carrying a short thermometer, so placed that the bulb of the thermometer was just above the center of the bottom of the flask, was used throughout the work. The flask was cleaned, dried and weighed. The salt to be used was transferred directly from the desiccator to this flask, using a wide funnel to prevent any of the salt from adhering to the neck or sides of the flask. The flask was again weighed, the weight of the salt being obtained by difference. Water was then added from a buret in amount sufficient to just dissolve the salt and the flask and contents were weighed. Alcohol in sufficient quantity to cause a separation into two layers was then added and another weighing made. Water was now added one drop at a time until the mixture just became homogeneous. After this was weighed all the data for the calculation of the first point on the binodal curve had been obtained.

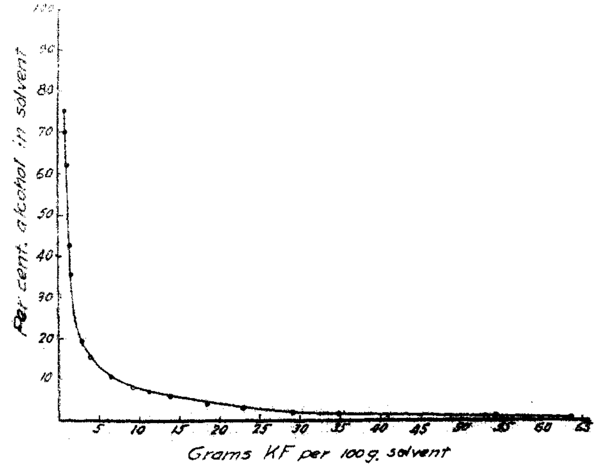

Fig 6.

Successive points on the curve were obtained by adding to this solution, first enough alcohol to cause the appearance of two layers or of a distinct turbidity after shaking and then just enough water to again clear the solution. The flask was kept stoppered, except for the moment when one of the components was being added, and as neither the alcohol nor the water were allowed to come in contact with the neck or upper portion of the inside of the flask, the loss from evaporation was very small.

As the end point was always obtained by adding water from a buret, it is probable that the accuracy in individual tests was frequently not greater than 100 mg. However, these errors, instead of being cumulative, tended to neutralize each other, since after every addition the true amount of water present was determined by weighing the flask and its contents.

All weighings were made on a large Troemner balance, which was easily sensitive to 0.2 mg. under a load of 200 g., but most of the weighings were made to milligrams only. The room in which the work was done was easily kept within 0.5° of 20° during the progress of all the measurements. The temperature of the solution itself at the time of the disappearance of the two layers was never allowed to differ by more than 0.2°

from 20°. As the heat of dilution of the concentrated solutions always tended to produce a rise in temperature on the addition of water, only a little water was added at a time, preventing even a temporary rise of more than 2.0°, and the mixture was always cooled to 20.0° before the final addition of water for clearing the solution, by gentle shaking in an adjoining room where the temperature was kept at about 18°.

As losses by evaporation would cause cumulative errors in case the solvent did not vaporize in the proportions present, several series of determinations were made starting with different points along the binodal curve. For example, the first series might be made by starting with a saturated solution of the salt in water as has been described. The first points in this series would be taken fairly close together, but the later ones farther apart by making successive addition of water and alcohol larger in proportion to the total weight of the contents of the flask as the solution became more dilute. The second series might be begun by making a solution containing only 60% of the amount of salt required for a saturated solution and a third series might start with 40% of the amount of salt needed for saturation. This not only tended to eliminate the cumulative effect of evaporation on the middle and right end of the binodal curve, but also did away with the objection that the decreased sensibility of all the measurements made as the solution became more dilute and larger in amount, rendered the determinations less accurate.

In those experiments where potassium fluoride and sodium chloride were used, spirit blue was chosen as an indicator, barely enough being added to give a clear color to the alcoholic layer. With potassium and sodium carbonates phenolphthalein was used, since these salts destroy the color of the spirit blue.

With increasing percentage of alcohol the consequent decrease in concentration of salt caused a continually decreasing difference in density of the two liquid layers. With solutions containing more than 60% of alcohol the separation into two distinct layers often required 20 minutes or more. However, the end point was more easily determined in these solutions by noting the time when the solution just ceased to be turbid after shaking. In the case of some of the mixtures obtained, a single drop of water would clear a solution which was so turbid that the outline of the thermometer bulb in the solution was only faintly seen.

In handling the flask, the hands were never allowed to come in contact with the sides or bottom of the flask. The flask was lifted by the flange at the top of the neck and when not in the balance was always placed on a sheet of filter paper.

The Purification of Propyl Alcohol.—The alcohol used in the following experiments came from C. F. A. Kahlbaum's factory of Berlin. It was obtained especially for the work tabulated below and represents Kahlbaum's highest purity. Test indicated, however, that it was not pure. Its boiling point was not constant and its specific gravity did not agree with results obtained by others, who had studied it. On examining the literature, a fairly wide range of variation in the physical constants was found. The variation was due, without doubt, to the extreme difficulty in obtaining the alcohol in perfectly pure form as was indicated in the final purification of the samples in hand. The sample, just as it came from the factory, began to boil at 94.5° under 750 mm. pressure, gradually increasing to 97° as the process continued. The specific gravity changed but little, increasing from 0.7954 to 0.8015. That there was water present as one of the impurities there can be but little doubt; that there was some little ethyl or possibly isopropyl alcohol present seems also quite likely. Work was therefore begun for the purpose of removing the above-mentioned impurities and any others which perchance might be present.

The first attempt to purify the alcohol was made by treatment with the dehydrating substance, potassium fluoride. While the process[1] evidently removed some of the impurities, as water, the sample was by no means pure, after such treatment. After this it was boiled for some hours with powdered quicklime under a reflux condenser, and again redistilled. This treatment again removed some of the impurities, as indicated by the more constant boiling point. It began to boil at 96° and gradually increased to 97.2 at 754 mm. Anhydrous copper sulfate was next tried, but without changing either the boiling point or the specific gravity. Magnesium amalgam was then tried. After standing 24 hours in contact with the amalgam, the alcohol was decanted off and again redistilled. Both the boiling point and the specific gravity approached a constant value, although not entirely so. The sample was finally boiled for several hours with sodium amalgam, again decanted off and redistilled over quicklime. The boiling point was practically constant at 97.5° and 753 mm. pressure. As further treatment failed to change the boiling point, the alcohol was regarded as pure. No attempts were made to determine the nature of the impurities present. There seems to have been an appreciable quantity of water and possibly, as already stated, ethyl alcohol.

The physical constants were then taken with the following results:

B. p. 97.3–5° at 752 mm.

Sp. gr. (20°) mean of three determinations 0.8032.

The refractive index was taken with the latest type of Pulfrich refractometer at 20° using the hydrogen spectrum tube as the source of light. Three different sets of readings gave the following average values: Hα 1.39023, Hβ 1.37651, Hγ 1.36786.

	Brühl.	**Landoldt and Jahn.**	**Zander.**	**Frankforter and Temple.**
Sp. gr........	0.8044 (20°)	0.8074 (19°)	0.8069 (17°)	0.8032 (20°)
B. p.........	97.2	97.0	97.4	97.3–5

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The purified alcohol was kept in a double stoppered bottle until it was to be used. All the experiments tabulated below were made with this purified alcohol.

Purification of Isopropyl Alcohol.—The alcohol used in the following experiments came from Kahlbaum's factory of Berlin. It was bought for pure alcohol, although, as in the case of propyl alcohol, this sample was by no means pure. It evidently contained, as was the case with propyl alcohol, some water, and the careful observation of the boiling point indicated that there was some ethyl alcohol present.

The purification was carried out as in the case of propyl alcohol. The original sample began to boil at 79.5°, after which the boiling point slowly rose to 82°, over half passed over, however, below 82°. Repeated distillation failed to yield more than 40% of the original sample with a boiling point of 82°.

The first purification was made by potassium fluoride. The fluoride raised the boiling point but it was nevertheless not constant. The sample was next boiled under a reflux condenser for several hours with powdered quicklime and again redistilled. The boiling point again indicated further purification. Finally, the partially purified sample was treated with sodium amalgam, the alcohol decanted off, dried thoroughly, again treated with powdered quicklime and redistilled. The boiling point rose to 82° and remained practically constant, rising less than one degree during distillation. The sample thus treated was used in the experiments given below.

The physical constants were then taken and compared with those obtained by others. The following tabulation gives the constants as compared with those given by others:

	Brühl.	Zander.	F. and T.
Sp. gr.	0.7887 (20°)	0.7861 (17°)	0.7881 (20°)
B. P.	82.3	82.3	82.5

Refractive index (20°). Hα 1.37960, Hβ 1.36550, Hγ 1.35584.

System: Normal Propyl Alcohol–Sodium Carbonate–Water.—This was the only system containing propyl alcohol which was studied as the systems: propyl alcohol–potassium fluoride–water, propyl alcohol–potassium carbonate–water, propyl alcohol–sodium chloride–water had been thoroughly investigated by Frankforter and Frary. For purposes of comparison, data were sought on the behavior of a single salt with four different alcohols and also on the behavior of single alcohols with four different salts. To make certain that the values obtained were strictly comparable with those obtained by Frankforter and Frary, preliminary sets of readings were made with propyl alcohol, using potassium fluoride and potassium carbonate as the dehydrating salts. All of these results checked well and could be plotted in on the same curves as those obtained by them.

The system: normal propyl alcohol–sodium carbonate–water has a long binodal curve and is an easy one to measure, as the separation into two layers takes place easily and quickly and the end point with phenolphthalein was easily determined even in mixtures where the solvent consisted of 60% or more of alcohol. Eight sets of measurements were made on this system and three individual measurements in addition. These determinations extended over about a week and the extent of the agreement between successive series, as shown by the curve in Fig. 7, indicates that the method used was at least free from any large variable error. All measurements were made as described under Experimental Methods and the results are shown in Table I, Table II, and Fig. 7.

TABLE I.

System: Normal Propyl Alcohol–Sodium Carbonate–Water at 20.0°.

Solvent added.		Total weight present.			Total contents.	Total solvent.
Water.	Alcohol.	Na_2CO_3.	Water.	Alcohol.		
12.310	1.771	0.891	12.310	1.771	14.972	14.081
4.102	1.482	0.891	16.412	3.253	20.556	19.665
5.135	3.133	0.891	21.547	6.386	28.824	27.933
11.714	7.555	0.284	11.714	7.555	19.553	19.269
2.394	3.527	0.284	14.103	11.082	25.474	25.190
6.818	11.181	0.284	20.926	23.263	44.473	44.189
14.794	0.756	2.354	14.794	0.756	17.904	15.550
15.413	0.756	2.461	15.413	0.756	18.630	16.169

TABLE II.

System: Normal Propyl Alcohol–Sodium Carbonate–Water.

Grams per 100 g. solvent.

Na_2CO_3.	Water.	Alcohol.	Na_2CO_3.	Water.	Alcohol.
6.328	87.423	12.577	2.863	78.020	21.980
4.531	83.458	16.542	2.320	72.580	27.420
3.190	77.138	22.862	1.990	68.463	31.537
1.474	60.972	39.208	1.650	63.519	36.481
1.127	56.006	43.994	1.338	59.204	40.796
0.643	47.356	52.644	1.084	55.438	44.562
15.138	95.138	4.862	1.119	57.292	42.708
15.220	95.324	4.676	0.930	53.067	46.933
11.540	93.458	6.542	0.733	49.449	50.551
8.415	90.824	9.176	0.567	46.125	53.875
6.669	88.779	11.221	0.394	42.413	57.587
5.123	86.396	13.604	0.298	40.493	59.507
4.138	84.215	15.785	0.243	38.913	61.087
3.609	82.823	17.177	0.160	36.432	63.568
2.878	78.901	21.099	0.109	24.841	75.159
			15.363	95.528	4.472
			11.696	93.405	6.595
			16.568	96.591	3.409

System: Isopropyl Alcohol–Potassium Fluoride–Water.—Two series of measurements of this system were made, one starting with 23.474% salt and running to 15.119%, the other between 34.134 and 11.020% by weight of KF. As it was quite difficult to get good end points in the titration of solutions of isopropyl alcohol containing over 20% of the alcohol, *i. e.*, with less than 10% of KF, five separate determinations were made by adding to a solution of KF and water just enough of the alcohol to cause the separation into two layers, weighing each of the components as it was introduced. The temperature was carefully controlled and kept within ±0.2° of 20.0°.

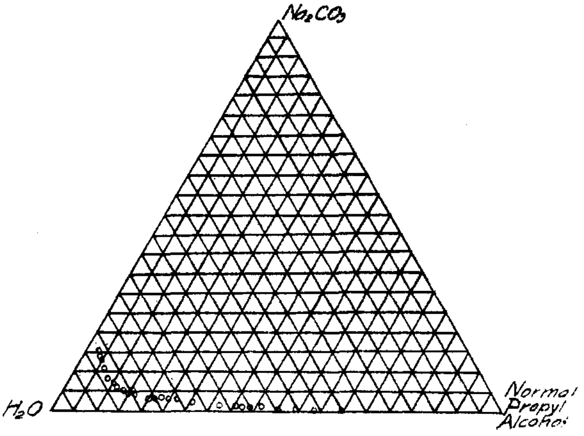

Fig. 7

It was expected that the results for isopropyl alcohol would somewhat resemble those obtained by Frankforter and Frary with normal propyl alcohol, using the same salt. However, on plotting the values obtained, the differences were so great that it was thought possible that difference in the conditions or in the condition of the salt were responsible and a portion of their work was repeated. As the results all checked with those of the earlier work it was plain that the difference was due to difference in the alcohols alone. and later work, as will be shown, corroborates this view.

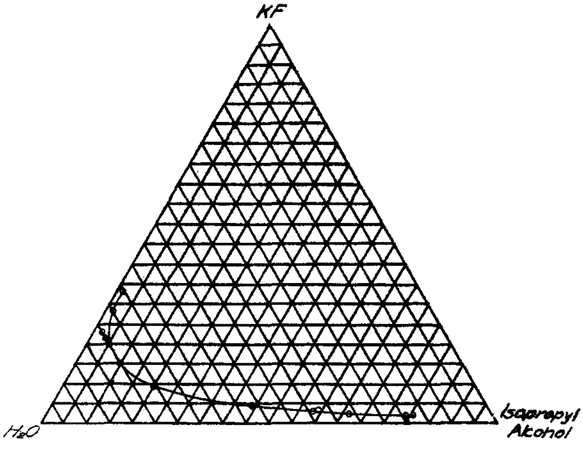

Fig. 8.

The percentage of alcohol present in the solvent ranges from 1.555 to 82.750 and the agreement between the successive values was especially good. The measurements and calculated results are shown in Table III and are plotted in Fig. 8.

TABLE III.

System: Isopropyl Alcohol–Potassium Fluoride–Water.

Grams per 100 g. solvent.

KF.	Water.	Alcohol.	KF.	Water.	Alcohol.
30.675	97.334	2.666	1.864	19.082	80.918
29.092	95.316	4.684	1.705	17.250	82.750
26.039	93.475	6.525	5.071	40.661	59.339
21.755	91.400	8.600	4.738	52.957	47.043
17.812	87.785	12.215	3.973	34.545	65.455
51.826	98.445	1.555	..	..	..
38.748	97.035	2.965	..	..	..
21.939	91.006	2.994	..	..	..
12.385	78.562	21.438	..	..	..

System: Isopropyl Alcohol–Potassium Carbonate–Water.—A few measurements were made in the systems isopropyl alcohol–NaCl–water and isopropyl alcohol–sodium carbonate–water, but as the addition of alcohol caused a separation of the solid salt, instead of a separation into two layers, over quite a wide range and as end points were very slow, complete curves have not as yet been worked out.

In the system isopropyl alcohol–potassium carbonate–water, four series of measurements were made, the alcohol varying from 2.009 to 55.650% of the mixture and the salt content from 2.869 to 30.979%. The maximum amount of water was found when the solution contained about 19% of salt and 7% of alcohol.

In this system, as in that of isopropyl alcohol–potassium fluoride–water, the values were found to differ greatly from those obtained with normal propyl alcohol and the differences found were entirely similar in the two cases. When plotted in rectangular coördinates the curve for this system more nearly approached a straight line than in any other system of alcohols and water in which potassium carbonate was used. That is, the isopropyl alcohol and the potassium carbonate were able to replace each other in solutions just in equilibrium in almost constant proportions throughout.

The measurements for this system are shown in Table IV, and the percentages of the three components present are plotted in Fig. 9.

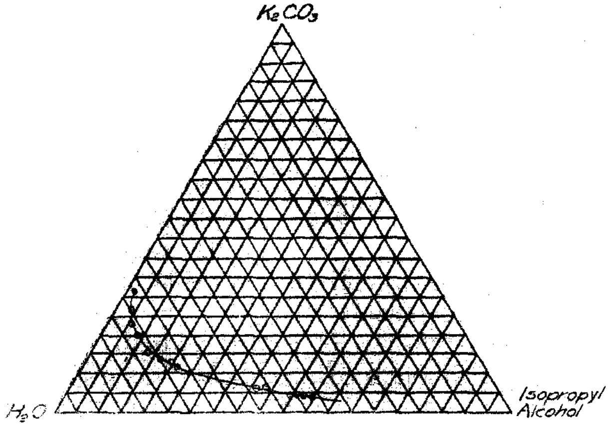

Fig. 9

TABLE IV.

System: Isopropyl Alcohol–Potassium Carbonate–Water.

Grams per 100 g. solvent.

K_2CO_3.	Water.	Alcohol.	K_2CO_3.	Water.	Alcohol.
13.963	77.633	22.367	17.665	85.605	14.395
13.560	76.901	23.099	15.021	80.555	19.445
13.244	76.081	23.919	3.933	46.735	53.265
44.844	97.089	2.911	3.726	46.188	53.812
36.137	95.217	4.783	3.391	44.797	55.203
28.879	92.651	7.349	2.954	42.706	57.294
24.152	90.841	9.159	6.065	54.603	45.397
..	..	..	5.841	53.965	46.035

System: Allyl Alcohol–Potassium Fluoride–Water.—Three sets of measurements were made in this system. The first series was made with a solution containing 2.251 g. of potassium fluoride and the first measurement was made with 7.129% alcohol in the solvent. Alcohol and water were added in succession through ten measurements, bringing the alcohol up to 54.211% of the solvent. A separate determination was made on a solution containing 65.221% of alcohol in the solvent, then a series running from 59.948 to 75.377% alcohol in the solvent and to obtain points at the other end of the curve 10.190 g. of potassium fluoride were dissolved in 20 cc. of water, 0.506 g. of alcohol was added

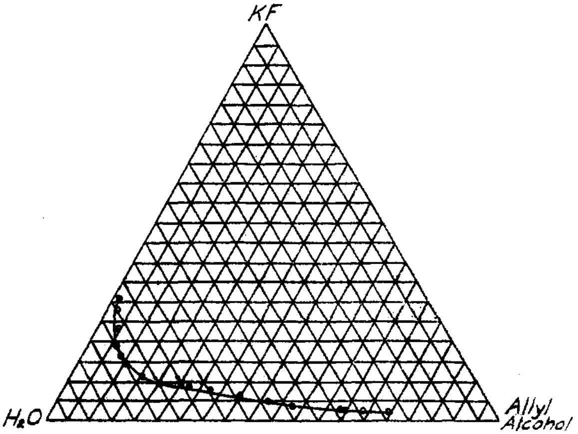

Fig. 10.

TABLE V.

System: Allyl Alcohol–Potassium Fluoride–Water.

Grams per 100 g. solvent.

KF.	Water.	Alcohol.	KF.	Water.	Alcohol.
24.341	92.871	7.129	1.895	34.779	65.221
20.580	90.309	9.691	2.233	36.443	59.948
17.371	88.509	11.491	1.931	34.370	65.630
13.184	82.236	17.764	1.635	31.155	68.845
10.880	77.463	22.537	1.368	28.605	71.395
8.873	70.471	29.529	1.066	24.223	75.377
7.508	64.610	35.390	45.707	97.730	2.270
6.024	57.989	42.011	38.076	96.017	3.983
4.813	52.450	47.550	30.675	94.121	5.879
3.631	45.789	54.211	..	..	..

and water added to just clear the solution which now contained 21.788 g. of water. This solution contained only 2.27% of alcohol in the solvent and two more additions of both alcohol and water were made, bringing the alcohol content up to 3.879% of the solvent.

When plotted in rectangular coördinates the curve for allyl alcohol–potassium fluoride–water closely approaches that of isopropyl alcohol, which it most nearly resembled in slope throughout. The measurements are recorded in Table V, and the curve is shown in Fig. 10.

System: Allyl Alcohol-Potassium Carbonate-Water.—This system was studied in the same manner as those first mentioned, nineteen readings being taken. The alcohol ranged from 1.424 to 81.159% of the mixture. The results are shown in Table VI and in Fig. 11.

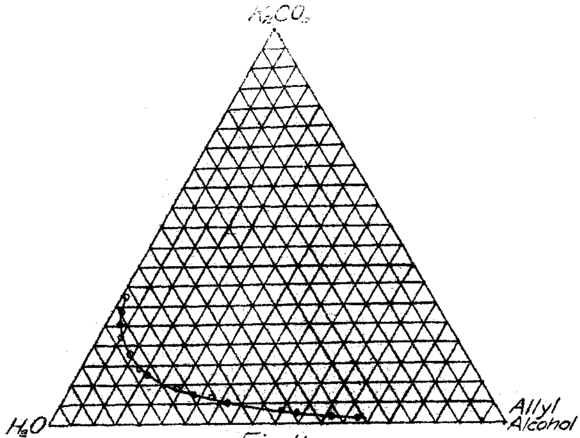

Fig. 11.

System: Allyl Alcohol–Sodium Carbonate–Water.—Values were obtained for mixtures ranging from 16.722% to 60.835% alcohol, only eleven readings being taken. End points at both ends of the binodal curve were hard to obtain. Results are shown in Table VII and in Fig. 12.

System: Allyl Alcohol–Sodium Chloride–Water.—As in the previous system, the end points were rather uncertain with less than 20 or more than 70% of alcohol in the solvent, so record is made only of such readings as seemed most trustworthy, as they suffice to give a very good idea of the general form and slope of the binodal curve.

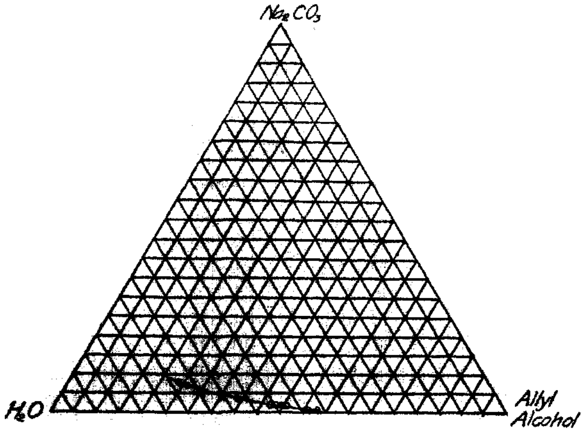

Fig. 12.

With allyl alcohol the position of the curves obtained with the different salts used is much greater than with the propyl or isopropyl alcohol and in consequence any inferences which might be drawn as to the effect of the presence of various ions in the solution should be more evident in the systems containing allyl alcohol as one component.

Results for this system are shown in Table VIII and in Fig. 13.

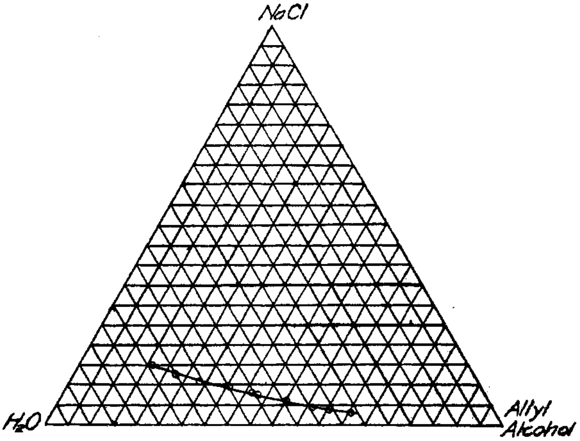

Fig. 13.

TABLE VI.

System: Allyl Alcohol–K_2CO_3–Water Measured at 20.0°.

Grams per 100 g. solvent.

K_2CO_3.	Water.	Alcohol.	K_2CO_3.	Water.	Alcohol.
47.746	97.897	2.103	9.653	73.553	26.447
38.298	96.181	3.819	8.239	69.323	30.677
33.200	94.733	5.267	6.729	64.569	35.431
28.163	93.039	6.961	5.521	60.663	39.337
23.486	90.691	9.309	2.457	48.402	51.598
20.037	88.323	11.677	2.020	45.513	54.487
16.354	84.963	15.037	1.464	41.749	58.251
13.696	81.733	18.267	1.015	37.390	62.610
11.331	77.546	22.454	0.526	31.413	68.587
..	..	..	0.0853	18.772	81.228

TABLE VII.

System: Allyl Alcohol–Sodium Carbonate–Water (20°).

Grams per 100 g. solvent.

Na_2CO_3.	Water.	Alcohol.
10.079	81.593	18.407
7.774	76.247	23.753
6.084	71.584	28.416
4.739	67.834	32.166
3.414	62.874	37.126
2.580	58.948	41.052
1.468	51.891	48.109
1.282	51.026	48.974
1.011	48.070	51.930
0.708	43.666	56.334
0.456	38.888	61.112

TABLE VIII.

Allyl Alcohol–Sodium Chloride–Water (20°).

Grams per 100 g. solvent.

NaCl.	Water.	Alcohol.
5.079	39.179	60.821
4.452	33.142	64.858
3.509	30.133	69.867
18.557	80.295	19.705
14.925	72.739	27.261
12.535	66.776	33.224
10.650	59.608	40.392
8.776	52.868	47.132
6.712	45.317	54.683
..	..	..
..	..	..

In order to get an idea as to the relative efficiency in salting out power of the various salts employed and also as to the varying effect of individual salts on different alcohols, four diagrams have been made. Fig. 14 is a comparison of the values obtained with sodium chloride, sodium carbonate, potassium fluoride and potassium carbonate with mixtures of propyl alcohol and water. Fig. 15 is a comparison of the same four salts, using allyl alcohol and water as the solvent. In addition, Fig. 15 contains two values for sodium fluoride and four for potassium chloride. These will be discussed later. Fig. 16 is a comparison of solvents from four different alcohols, ethyl, allyl, normal propyl and isopropyl alcohol using a single salt, potassium fluoride. Fig. 17 shows the results with the same four alcohols using potassium carbonate.

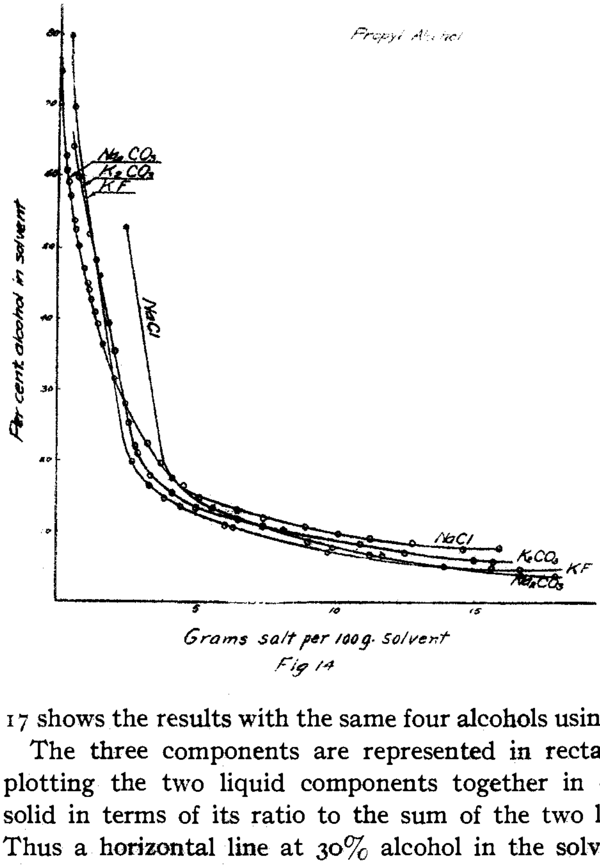

Fig 14

The three components are represented in rectangular coördinates by plotting the two liquid components together in one direction and the solid in terms of its ratio to the sum of the two liquids at right angles. Thus a horizontal line at 30% alcohol in the solvent also represents by difference 70% of water in the solvent. All the points plotted represent what might be called "turbidity points," the line connecting the points in any system being the boundary between the homogeneous and heterogeneous systems. To illustrate: Given any solution with a composition represented by any point on any of the lines shown and if its composition be altered by the addition of an infinitesimal amount of the salt, the solution will separate into two phases. In all cases, except the values for allyl alcohol with potassium chloride and sodium fluoride on Fig. 15, these phases are both liquid. In the portions of the curves shown in Figs. 14, 15, 16 and 17 the addition of an infinitesimal amount of the alcohol will effect the same separation into two phases.

One of the most noticeable things in Figs. 14 and 15 is that the order of efficiency in salting out effect, per gram salt in 100 g. solvent, is the same for propyl alcohol as for allyl alcohol in solutions with high alcoholic content, sodium chloride having the least effect and sodium carbonate the most per weight used.

It has been suggested that the salting out effect of salts on alcohols was largely a matter of the ions present in the solution of the salt. In order to determine whether any such law governed the matter, trials were made using sodium fluoride and potassium chloride with allyl alcohol as these two salts, with the other four used, would give us three potassium salts, three sodium salts, two carbonates, two chlorides and two fluorides—thus completing series which should show any very definite relations if these existed. With both potassium chloride and sodium fluoride results were somewhat undecided, as neither salt gave two liquid phases on addition to an alcohol-water mixture within the limits of composition used in the other curves. However, two phases were easily obtained, one solid and one liquid, which could be made homogeneous by the addition of water and again separated by addition of alcohol or of salt. Thus, while these points measured are real turbidity points, they are not strictly comparable with points on the other curves. However this would not seem to vitiate the conclusions drawn, since the existence of any law correlating solubility and the ions present would apply equally here.

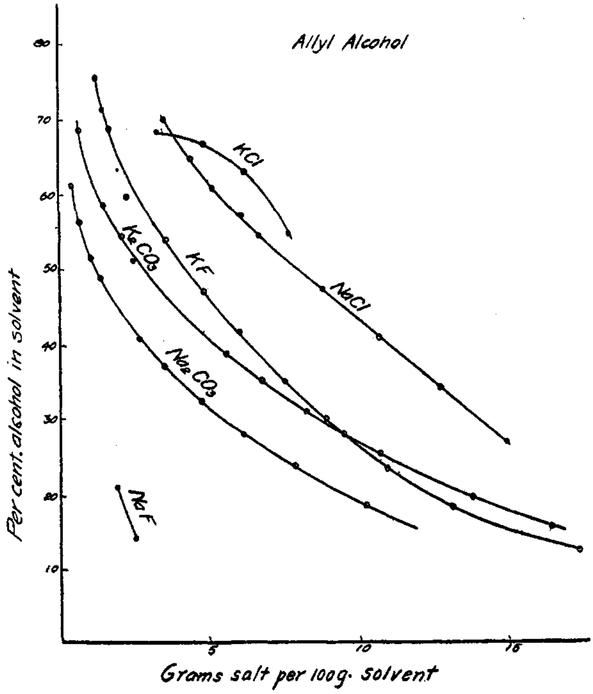

Fig. 15.

If we examine Fig. 15 for such evidence, we find that it takes less of the sodium salt than of the potassium salt to cause a separation into two phases, whether the salt be the carbonate, the chloride or the fluoride. This, however, may be due as much to the greater weight of the molecule of potassium salt as to the individuality of the ion concerned. If we should express the amount of salt used in terms of gram-molecules or in normality, our curves would not show the same regularity and the

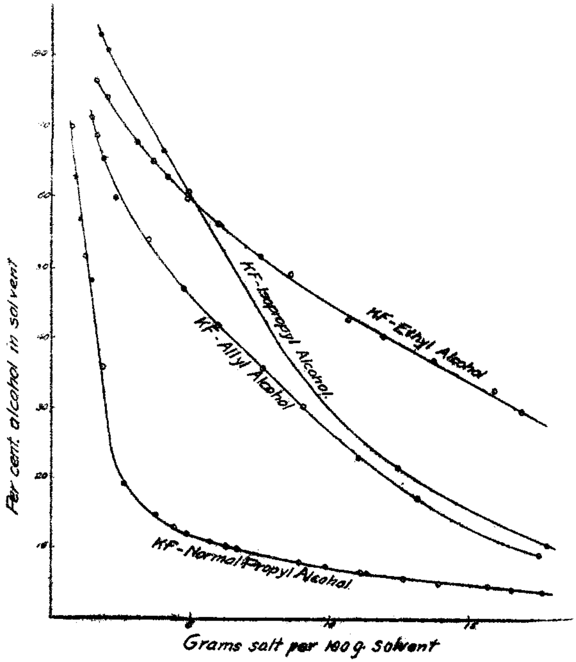

Fig 16.

similarity between the order of the salts in Figs. 14 and 15, would disappear entirely.

If we look for a specific effect of the acid ion, in Fig. 15, we get but little encouragement. It requires less of the fluorides to salt out the alcohol than of the corresponding chlorides,—but when we compare the fluorides with the carbonates, we see that, while it takes less of the sodium fluoride than of the sodium carbonate to cause a separation into two phases, it requires more of the potassium fluoride than of the potassium carbonate.

Attention should be called to the fact that while many of the curves seem to approach as the alcoholic content decreases, in reality they usually diverge, for the difference in salt content of limiting homogeneous solutions containing solvents of like composition is measured by horizontal distances between parallel curves and not by perpendicular distances.

A comparison of Figs. 16 and 17 shows at once a striking similarity. Through a large portion of their length the order is the same for the different alcohols in the case of the dehydration with potassium fluoride as with potassium carbonate. The position and the slope both give the same average values. This makes it clear that the salting our effect of salts on water–alcohol mixtures is dependent largely on the individuality of the alcohol used and that differences are fairly constant with changing salts. When we seek the reason for the differences in the curves of the various alcohols with a single salt, the most noticeable fact is the great difference in the values for the isomeric propyl alcohols. None of the alcohols investigated show great differences than these two and it is at once plain that there is no additive property involved. The two curves showing the most similarity are those for allyl and isopropyl alcohol in both Fig. 16 and Fig. 17. This in spite of the fact that this pair shows the most dissimilarity, chemically, of any of the possible six pairs present. Normal propyl alcohol and ethyl alcohol are most similar chemically, and while there is some slight resemblance between their curves as shown in Figs. 16 and 17, it is not pronounced and the differences in the amounts of salt present necessary to cause a separation into two layers is very great, and becomes increasingly so as we increase the amount of water present in solutions of both. This is especially evident if we note the horizontal distances between the two curves.

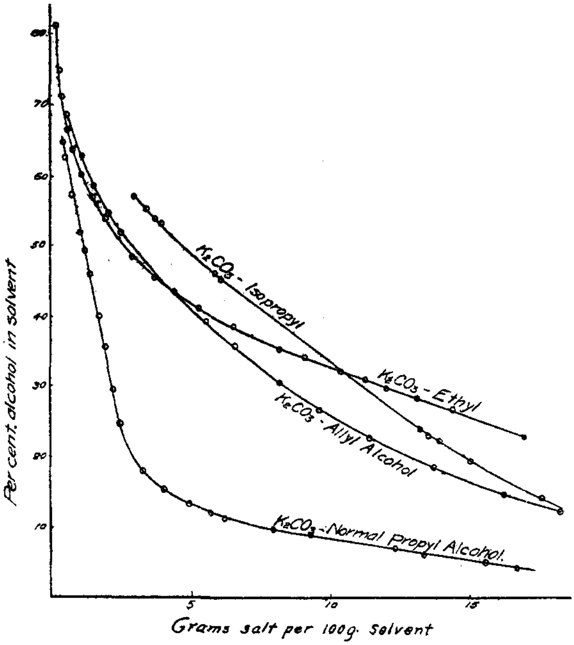

Fig. 17.

Summary.

Seven new systems have been investigated and curves plotted, namely:

Normal propyl alcohol–sodium carbonate–water;

Isopropyl alcohol–potassium fluoride–water;

Isopropyl alcohol–potassium carbonate–water;

Allyl alcohol–potassium fluoride–water;

Allyl alcohol–potassium carbonate–water;

Allyl alcohol–sodium carbonate–water;

Allyl alcohol–sodium chloride–water.

Potassium fluoride was found to be the most satisfactory of the dehydrating agents employed, especially when the object was the determination of the water content of the alcohol, on account of the ease with which the end point could be determined with widely varying composition of solvent, on account of the fact that it caused a separation into two phases only and those both liquid phases over a relatively large range in composition of solvent and on account of the large amount of water with which it combines to form its lowest hydrate. Potassium carbonate was found to work very satisfactorily for all of the alcohols studied.

Curves have been worked out for the determination of the water content of allyl alcohol and of isopropyl alcohol by the method used and recommended by Frankforter and Frary for ethyl and normal propyl alcohols.

No evidence was found relating the salting out effect to the chemical constitution of the salts or of the alcohols. The salting out efficiency of a salt seems rather to be a function of its solubility in the water and in the alcohol, of the amount of water with which it unites to form its lowest hydrate, and of the ability of the alcohol to replace the water of hydration.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

PHENYL ESTERS OF OXALIC ACID.

BY ROGER ADAMS AND H. GILMAN.

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Introduction.

In the course of a research in this laboratory, we desired to use one of the substituted phenyl esters of oxalic acid. In reviewing the methods already available for the preparation of these substances, we found them to be few in number, limited in applicability and not suited to the preparation of the particular compound wanted. Nencki[1] first prepared the phenyl ester of oxalic acid by boiling phosphorus oxychloride with anhydrous oxalic acid and phenol. This method was extended by Bischoff[2] to the preparation of substituted phenyl esters of oxalic acid, and was shown by him to work well with certain types of substituted phenols. With many phenyl derivatives, however, only small yields of esters could be thus produced, and in several cases the esters, if they were formed at all, could not be isolated from the reaction mixtures. Thus, *e. g.*, the cresols, xylenols and carvacrol gave good results, thymol, *p*- and *m*-nitrophenols gave very poor yields, while the desired products from the *o*-nitrophenol, α- and β-naphthols, could not be obtained. Moreover, this method cannot be applied to any phenol containing a substituting group which is sensitive to hot phosphorus oxychloride.

A second method was used by Bischoff[3] for the preparation of this class of compounds. It consisted in heating the phenyl ester of oxalic acid with the substituted phenol, when replacement occurred and the substituted phenyl ester resulted. This gave poor results, but was applicable to a number of esters which could not be made by the first process. The α- and β-naphthyl esters are examples.

In the manufacture of aurin, from phenol, oxalic acid and sulfuric acid, a by-product was obtained which Claparède and Smith believed to be the phenyl ester of ortho-oxalic acid.[4] This they also synthesized by distilling a mixture of oxalic acid and phenol, or by simply dissolving phenol

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[1] *J. prakt. Chem.*, [2] **25**, 283 (1882).

[2] *Ber.*, **35**, 3440 (1902).

[3] *Ibid.*, **35**, 3441, 3448 (1902).

[4] *J. Chem. Soc.*, **43**, 358 (1883).