TABLE III.

Bottle.	% PbO found.	Variation from theoretical PbO content of lead hydrogen arsenate.
3	65.49	+1.21%
5	64.45	+0.17%
8	64.66	+0.38%
12	64.44	+0.16%

Conclusion.—In the system disodium hydrogen arsenate, lead nitrate and water there exists at 25° only one compound, lead hydrogen arsenate.

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THE SOLUBILITY CURVES OF SALT HYDRATES: CALCIUM NITRATE.

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Systems formed of two components have attracted considerable attention from phase rule investigators. The phase relationships of systems composed of mixtures of salts and water have been the chief object of experimental study. They may broadly be classified according as the components separate from solution in the pure state or as combination occurs between them with the formation of definite compounds. To the latter class belong the salt hydrates. They form a class of extreme importance, owing to their frequent occurrence in the field of inorganic chemistry. Study of such systems leads to a subdivision of hydrates into two classes, those possessing a definite melting point forming a liquid phase of the same composition as the solid hydrate and those which do not so behave.

Of the latter class of crystalline hydrates, which show no true melting point, but on the other hand a transition point, the classical example is sodium sulfate decahydrate, $Na_2SO_4.10H_2O$. Below 32.4° the saturated solution exists in stable equilibrium with the salt hydrate. Above that temperature, solutions are in stable equilibrium with the anhydrous salt and the solubility curve shows a sharp break at the transition temperature. At this temperature partial fusion occurs, during which the temperature remains constant. This is no true melting point, however, for the composition of the liquid phase is not the same as that of the original solid. The system also shows unstable solubility curves. For example, the curves of the decahydrate and the anhydrous salt may be continued some distance into the unstable region. That of the anhydrous salt, if sufficiently prolonged, meets the solubility curve of the unstable heptahydrate, which exists in equilibrium with solutions of higher concentrations than those in equilibrium with the decahydrate at the same temperature. This phenomenon is characteristic. The solid phase which is stable at the given temperature has the least solubility at that temperature.

The hydrates of ferric chloride[1] illustrate effectively the case of hydrates possessing definite melting points. A succession of hydrates with 12, 7, 5 and 4 molecules of water possess definite melting points corresponding to the point of maximum solubility, in composition the same as that of the solid hydrate, at 37°, 32.5°, 56° and 73.5°, respectively, and solubility curves with retroflex portions. Definite transition temperatures exist at 27.4°, 30°, 55° and 66°, at which the stable existence of the next lower hydrate begins, the solubility curves showing change of direction. The solubility curves may be prolonged into the unstable regions.

The case of calcium chloride hydrates[2] illustrates another point in the study of such hydrates. The highest hydrate of calcium chloride, the hexahydrate, shows a definite melting point similar to those of the ferric chloride hydrates at 30.2°, and also a retroflex portion of the curve. As, however, at a temperature of 29.8° the tetrahydrate, $CaCl_2.4H_2O\alpha$, becomes the stable solid phase in equilibrium, it is obvious that the solubility curve of the hexahydrate above this temperature represents metastable equilibrium and the melting point of the hexahydrate is a metastable melting point due to suspended transformation.

It will be seen, therefore, that true melting points may be met with both in the stable and unstable regions. Now certain hydrates have been found existing in two or more crystalline modifications, the one stable, the other unstable, over a given range of temperatures. The tetrahydrate of calcium chloride shows too such modifications, an α- and a β-form, the former stable, the latter always unstable. Neither of these forms shows a melting point, since they pass through a transition point to the next lower hydrate before the melting point is attained. It is conceivable, however, that hydrates should exist in two crystalline forms each possessing a definite melting point. In two-component systems other than salt hydrates such cases are known. Two such cases may here be cited. The system iodine–chlorine[3] forms a compound ICl, existing in two crystalline modifications each possessing a definite melting point. Further, as has been shown by Philip,[4] phenol can combine with *p*-toluidine, forming an equimolecular compound existing in two crystalline forms melting at 28.5° and 30°, respectively.

Recent investigations of the two-component system calcium nitrate–water have tended to show that this phenomenon may also be established

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[1] Roozeboom, *Z. physik. Chem.*, **10**, 477 (1892).

[2] Roozeboom, *Ibid.*, **4**, 31 (1889).

[3] Stortenbeker, *Ibid.*, **3**, 11 (1889).

[4] *J. Chem. Soc.*, **83**, 821 (1903).

in the case of salt hydrates. The phase relationships at various temperatures from —28° to 151° were investigated by one of the authors under the direction of Bassett, whereby it was shown[1] that in addition to ice and the anhydrous salt, three hydrates could exist in stable equilibrium with the saturated solutions, *viz.*, with 4, 3, and 2 molecules of water. The first two hydrates showed true melting points at 42.7° and 51.1°, respectively, the last a transition point. Later it was shown by Hasselblatt,[2] in investigations of the velocity of crystallization, that cadmium nitrate tetrahydrate cannot be inoculated with calcium nitrate tetrahydrate, but that the cadmium salt readily inoculates the melted calcium salt. It was therefore concluded that two forms of the tetrahydrate of calcium nitrate exist, the unstable form isomorphous with the tetrahydrate of cadmium nitrate. The melting points of the two forms were determined, and gave 42.6° and 39.7°, the former in agreement with the value of Bassett and Taylor. Obviously, therefore, to the phase diagram previously established there could be added the solubility curve of unstable calcium nitrate tetrahydrate. This should show a maximum solubility corresponding to the composition of the solid phase at the temperature of 39.7°, the melting point of the substance as well as a retroflex portion of the curve. To establish these points the experimental investigation of the solubility curve has been undertaken.

Immediately subsequent to the publication by Bassett and Taylor of the results of the investigation of the two-component system calcium nitrate–water, there appeared a communication by D'Ans[3] on the solubility isothermals of the alkali-earth nitrates in alcohol-water mixtures. It was shown, *inter alia*, that calcium nitrate existed at 25°, in stable equilibrium with the various solutions as tetrahydrate, anhydrous salt and alcoholate, $Ca(NO_3)_2.2C_2H_5OH$. It is remarkable that neither of the two lower hydrates were discovered, as it is generally found that the dehydrating action of the alcohol passes successively through the stages of hydrates found in the two-component system. Further, the metastable solubilities of the anhydrous salt in various alcohol-water mixtures and in pure water were given. For the latter a value of 82.5 g. $Ca(NO_3)_2$ per 100 g. solution was given. The work of Bassett and Taylor had shown that between 50° and 151° the boiling point of the saturated solution, the solubility curve of the anhydrous salt ran practically parallel to the axis of temperature and that at the highest temperature the solubility amounted to 79.0 g. per 100 g. solution. If the figure of D'Ans be correct the curve of the anhydrous salt in the unstable region must show a very sharp change of direction below 50°, or in other words the heat of solution in the almost

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[1] *J. Chem. Soc.*, **101**, 576 (1912).

[2] *Z. physik. Chem.*, **83**, 1 (1913).

[3] *Ibid.*, **82**, 35 (1913).

saturated solution must undergo a very sudden change in the region 25–50°, which seems, however, little likely. To test this point, a determination of the solubility of the anhydrous salt at 25°, was made.

Experimental.

The saturated solutions analyzed in the experiments on the unstable tetrahydrate solubility curve were all prepared from supersaturated solutions from which all germs of the stable hydrate were removed by maintenance at a temperature of 50–60°, for a period of time. Crystallization was induced in the solutions by inoculation with a small crystal of cadmium nitrate tetrahydrate and the solution allowed to come into equilibrium with the solid phase by standing in the thermostat at the desired temperature, which could be controlled to 0.05°. This procedure was adopted owing to the instability of the β-tetrahydrate and the readiness with which it changed to the α-form when attempt was made to isolate it. In all cases separate concordant determination of the various points were obtained.

From the temperature of 30° upwards the attainment of equilibrium was comparatively easy and reproducible figures readily obtainable. Below this temperature the values obtained show great uncertainty, this being due to the readiness with which the unstable modification changes to the stable form. Before equilibrium between saturated solution and unstable hydrate could be attained, the change in the solid phase consistently occurred and the solution underwent the corresponding change in concentration. The stable solubility curve of Bassett and Taylor has been re-checked, and in one or two cases minor changes in the values of the solubilities have been made.

The solution in equilibrium with the anhydrous salt at 25°, was prepared by evaporating a solution of the salt until salt just began to separate at the boiling point (151°). The mixture thus obtained was cooled to 25°, stirred for several days and the solid phase finally allowed to settle. The clear, viscous liquid thus obtained was then analyzed.

In all cases the analysis was made by weighing as oxide after precipitation as oxalate.

Precautions were taken to ensure purity of material similar to those previously employed. The solution of a high-grade calcium nitrate was treated with a considerable excess of pure and freshly ignited calcium oxide. The mixture was shaken frequently for several days and then filtered. In this way magnesium salts were removed as hydroxide. The solution was then neutralized with nitric acid and evaporated to the crystallization point.

The data obtained from the analyses of the various solutions at the various temperatures are compiled in Table I.

The point on the reflex portion of the unstable solubility curve entailed considerable trouble in attainment. After repeated trials a solution was obtained, of the composition analyzed, in equilibrium with the unstable hydrate. That the solid phase was the unstable form was shown by bringing to the equilibrium mixture a crystal of the stable hydrate. This resulted in a rapid change of the equilibrium with separation of a considerable bulk of solid phase. It will be noted how considerable the change in concentration on the retroflex portion of the curve for small variation of the temperature, in other words, how flat the curve is around the maximum, corresponding to considerable dissociation into the components.

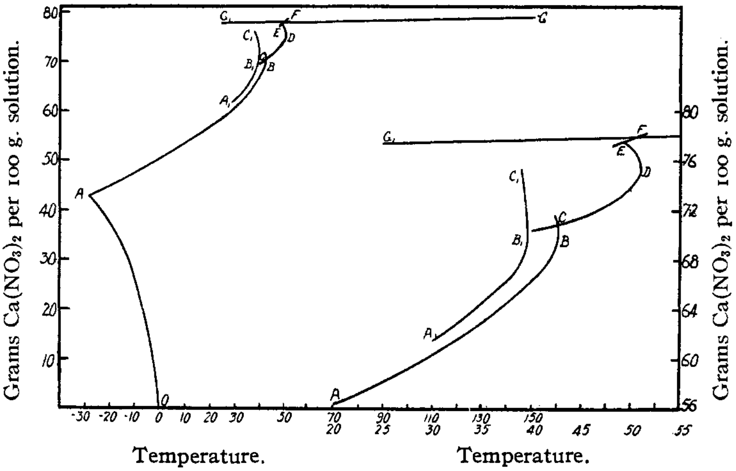
TABLE I.

Temperature.	G. $Ca(NO_3)_2$ per 100 g. of solution.	Composition of the solid phase.	Observer.
0	50.17	$\alpha Ca(NO_3)_2.4H_2O$	T. & H.
22.2	56.88	$\alpha Ca(NO_3)_2.4H_2O$	T. & H.
25.0	57.90	$\alpha Ca(NO_3)_2.4H_2O$	T. & H.
30.0	60.16	$\alpha Ca(NO_3)_2.4H_2O$	T. & H.
30.0	61.57	$\beta Ca(NO_3)_2.4H_2O$	T. & H.
34.0	63.66	$\beta Ca(NO_3)_2.4H_2O$	T. & H.
35.0	62.88	$\alpha Ca(NO_3)_2.4H_2O$	B. & T.
38.0	64.34	$\alpha Ca(NO_3)_2.4H_2O$	T. & H.
38.0	66.65	$\beta Ca(NO_3)_2.4H_2O$	T. & H.
39.0	67.93	$\beta Ca(NO_3)_2.4H_2O$	T. & H.
39.6 (m. p. of hydrate)	69.50	$\beta Ca(NO_3)_2.4H_2O$	T. & H.
39.0 (reflex pt.)	75.34	$\beta Ca(NO_3)_2.4H_2O$	T. & H.
40.0	66.21	$\alpha Ca(NO_3)_2.4H_2O$	B. & T.
42.7 (m. p. of hydrate)	69.50	$\alpha Ca(NO_3)_2.4H_2O$	B. & T.
42.4 (reflex pt.)	71.70	$\alpha Ca(NO_3)_2.4H_2O$	B. & T.
25.0	77.30	$Ca(NO_3)_2$	T. & H.

Discussion of the Results.

The results from the investigation are expressed graphically in Fig. 1. For the sake of completeness and to facilitate the following discussion the whole curve has been drawn employing the data of Bassett and Taylor. The new material communicated in the present paper is also plotted, for the sake of clearness, on a large scale to the right of the complete curve.

It will be seen that the two-component system calcium nitrate–water forms a very interesting example of phase equilibria, in that by use of it alone all the various possible types to be met with in phase relationships of salt hydrates may be illustrated. Curve OA represents the ice curve and point A the cryohydric point. Curves ABC and CDE, representing the solubility curves of the α-tetrahydrate and trihydrate, exemplify the case of hydrates with a true melting point such as are found with the ferric chloride hydrates. Curve $A_1B_1C_1$, that of the β-tetrahydrate, illustrates the solubility curve of a metastable hydrate with a metastable melting point, similar to that obtained with calcium chloride hexahydrate. The dihydrate, represented by Curve EF, illustrates, like sodium sulfate decahydrate, the class of hydrates which show no true melting points but transition points where partial fusion occurs with the formation of anhydrous salt and saturated solution. The whole diagram, therefore, shows a succession of stable hydrates, a metastable hydrate, true melting points, a metastable melting point, stable and metastable retroflex solubility curves.



An interesting point may here be emphasized with regard to the solubility curves of unstable hydrates possessing a melting point and retroflex solubility curves. As is well known, the solid phase most stable at the temperature of the experiment has, at that temperature, the least solubility. This is true even on the retroflex portions of the curves, although, as can be seen from the diagram, the concentration in grams of anhydrous salt per 100 g. of solution is greater in the case of the stable hydrate. Since, however, the calcium nitrate content of the solid hydrate is less than that of the saturated solutions on the retroflex portions of the curve, it follows that the unstable hydrate, having in accordance with the theory the greater solubility, will give rise to saturated solutions less rich in the anhydrous salt than those given by the stable form at the same temperature.

Attention may here be directed to the method described by Foote,[1] for the determination of the hydrates formed by a salt. The method described for sulfuric acid is capable of extension to salts of other acids using the corresponding acid as dehydrating agent. For example, in this connection it was shown by Bassett and Taylor that while in aqueous solutions the calcium nitrate dihydrate was difficult to prepare and stable over a short range of temperature only, still at 25°, it was readily obtained and existed in stable equilibrium over a considerable range of nitric acid

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[1] This Journal, 37, 288 (1915).

concentrations. Similarly, the three-component system $BaCl_2$–HCl–H_2O studied by Schreinemakers at 30°,[1] illustrates the use of hydrochloric acid to the same purpose. Indeed the method can, generally speaking, be recommended before the study of the two-component system whenever there is considerable tendency to formation of concentrated, viscous, aqueous solutions, provided of course that acid salts are not readily formed.

Finally it may be observed that the solubility of the anhydrous salt at 25° corresponds to those obtained by Bassett and Taylor at the higher temperatures and not with that obtained by D'Ans as previously mentioned.

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RADIOMETRIC MEASUREMENTS OF THE IONIZATION CONSTANTS OF INDICATORS.[2]

[SECOND COMMUNICATION.]

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An investigation of the ionization constants of methyl orange and phenolphthalein has already been published in THIS JOURNAL by Shaeffer, Paulus and Jones.[3] In this paper a new method, based upon the absorption of light by solutions of indicators, was developed for the determination of the constants of indicators. It was shown that this method serves as well for a two-colored as for a one-colored indicator. The work recorded herein is to be regarded as a continuation of the original investigation, and the purpose is to test the applicability of the method to the determination of the ionization constant of rosolic acid. A description of the apparatus used has already been given in detail in the original paper.

Theoretical Discussion.—Considering, first of all, that rosolic acid is monobasic,[4] the ionization constant K_i, is expressed by the simple equilibrium equation

$$\frac{(H^+)(\bar{In})}{(HIn)} = K_i. \qquad (1)$$

If, then, the hydrogen ion concentration of the indicator solution is fixed, the ratio $(\bar{In})/(HIn)$ at equilibrium can be determined. It has been shown in the original paper[5] that the percentage transmission of a solution, such as that of rosolic acid, containing two absorbing components is given by the equation

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[1] *Z. physik. Chem.*, **68**, 89 (1909).

[2] This investigation has been carried out with the aid of a grant from the Carnegie Institution of Washington to H. C. Jones.

[3] THIS JOURNAL, 37, 776 (1915).

[4] The behavior of rosolic acid as a dibasic acid will be discussed later.

[5] *Loc. cit.*