accurately the liquidus and solidus curves. It is obvious, also, that this method can be used in the reverse manner to determine the activities of the constituents of solid solutions from their activities in the liquid phase and the known liquidus and solidus curves.

The experimental data for the copper–nickel system, Fig. 2, were taken from the work of Guertler and Tammann;[5] for the silver–palladium system, Fig. 3, from the work of Ruer,[6] and for the gold–platinum system, Fig. 4, from the work of Doerinckel.[7] The heats of fusion, per gram atom, used in the calculations were: Cu, 2655 cal.; Ni, 4280 cal.; Ag, 2795 cal.; Pd, 3850 cal.; Au, 3130 cal.; Pt, 5250 cal.

Summary

1. A graphical method is developed for determining the liquidus and solidus curves for binary systems which solidify with the formation of solid solutions, from the fugacities or activities of the components in the two phases.

2. Equations are derived for calculating the liquidus and solidus curves from the temperatures and heats of fusion of the two pure solids and the assumption that both solutions are perfect.

PITTSBURGH, PA. RECEIVED AUGUST 14, 1933

(5) Guertler and Tammann, *Z. anorg. Chem.*, **52**, 25 (1907).

(6) Ruer, *ibid.*, **51**, 315 (1906).

(7) Doerinckel, *ibid.*, **54**, 333 (1907).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE NEW YORK STATE AGRICULTURE EXPERIMENT STATION]

The Solubility of Potassium Acid Tartrate. I.[1] In Tartaric Acid and Dipotassium Tartrate Solutions

BY D. C. CARPENTER AND G. L. MACK

A large number of investigators have reported values for the solubility of potassium acid tartrate in pure water at various temperatures, but agreement between the results is not particularly good. Low values are obtained by shaking unsaturated solutions with excess salt, while high values are the result of crystallizing salt from supersaturated solutions. The two investigations[2] in which both methods were used show medial results, in essential agreement with those presented in this paper. In both of these cases, however, insufficient time was allowed for equilibrium to be established. With mechanical shaking, undersaturated solutions reach equilibrium much sooner than supersaturated ones, but without agitation the reverse is true. The time required for equilibrium to be established varies considerably with the temperature. Thus at 25° twenty-four hours is amply sufficient, while at 0° equilibrium is not attained in less than seven days.

Experimental Part

Preparation of Materials.—Potassium acid tartrate was prepared from C. P. potassium hydroxide and tartaric acid by slowly adding the calculated amount of a solution of the former to a cooled solution of the latter, stirring meanwhile. Potassium acid tartrate crystallized out promptly and was filtered off on a Buchner funnel and washed with successive amounts of cold water. The salt was recrystallized three times from hot water and finally dried at 100° and stored in a desiccator over phosphorus pentoxide. The purity of the salt was determined by a potassium analysis.

Anal. Calcd. for $KHC_4H_4O_6$: K, 20.78. Found: K, 20.74, 20.78.

Dipotassium tartrate was prepared by slowly adding a solution of C. P. potassium hydroxide to a cold solution of tartaric acid until a test portion showed a P_H of 6.35 with brom thymol blue indicator. The solution was concentrated over a steam-bath and set aside for crystallization of the salt $K_2C_4H_4O_6{\cdot}0.5H_2O$. The salt was recrystallized from hot water three times, dried *in vacuo* at 40° to constant weight and bottled. Purity of the salt was established by a potassium analysis.

Anal. Calcd. for $K_2C_4H_4O_6{\cdot}{}^1/_2H_2O$: K, 33.24. Found: K, 33.25, 33.32, 33.28, av. 33.28.

The tartaric acid used in this work was a sample of the acid of C. P. Baker analyzed grade. This was not further purified inasmuch as the equivalent weight was found to be 75.108, 75.005 and 74.998, mean 75.037 (calcd., 75.035), against standard alkali with brom thymol blue indicator.

Experimental Method

Concentrated stock solutions of dipotassium tartrate and of tartaric acid were prepared from the pure compounds, for use in preparing the various concentrations of each required in the solubility studies recorded below.

Appropriate quantities (usually 5 to 10 ml.) of these stock solutions were added as required to an excess of potassium acid tartrate in a clean dry 125-ml. Erlenmeyer flask

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[1] Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 5.

[2] Noyes and Clement, *Z. physik. Chem.*, **13**, 412 (1894); Klapproth, *Z. anal. Chem.*, **61**, 1 (1922).

and the mixture made up to the final concentration with approximately 100 g. of distilled water recently boiled to remove carbon dioxide. By carefully adding the same amount of each liquid, a number of duplicate solutions of almost exactly equal concentration could be prepared. Half of these solutions were supersaturated with respect to potassium acid tartrate by immersing the flasks in hot water and shaking until all the salt was dissolved. The flasks were kept tightly stoppered so that no water vapor escaped during this process. The other half of these solutions were left undersaturated with respect to solid potassium acid tartrate, so that equilibrium was approached from both sides in the two series.

The solutions were placed in a mechanical shaker immersed in a water thermostat controlled to within ±0.05° and agitated continuously until equilibrium was established. At the end of this time the solutions for analysis were drawn off by suction through a capillary tube the end of which was tightly packed with cotton to remove any suspended crystals of acid tartrate. In order to eliminate possible changes in composition due to selective adsorption or to a temporary displacement of the temperature equilibrium, the first 10 ml. of the filtrate was always discarded.

A weighed quantity of the filtrate was titrated with standard potassium hydroxide using brom thymol blue indicator. The alkali was carbonate free and contained no excess barium. The same sample was subsequently analyzed for potassium, the amount added during the titration being subtracted from the total. Separate samples were also analyzed for potassium.

The potassium was determined gravimetrically as perchlorate. Morris[3] states that tartrates interfere with the determination of potassium by this method and suggests a preliminary separation as cobaltinitrite. It was found that the tartrate radical can be oxidized completely by evaporating to dryness four or five times with nitric acid. While this takes some time, the nitric acid solutions do not spatter and require very little attention. The salt is thus obtained as the nitrate and can be treated with perchloric acid in the usual way.

Anhydrous ethyl alcohol containing 0.2% perchloric acid was used as the wash liquid. The small but appreciable amount of potassium perchlorate dissolved in the wash liquid was determined by analysis of pure potassium chloride and potassium hydrogen tartrate. The amount dissolved by a constant volume of liquid was found to vary with the total amount of the precipitate in an approximately exponential manner. A smooth curve showing the amount of the blank correction to be added to a given weight of potassium perchlorate was constructed through the points obtained from the analysis of various quantities of the pure salts.

All solutions were made up by weight and corrected to weight *in vacuo*. For conversion to volumetrical units, the densities of the saturated solutions were determined at the equilibrium temperature with a pycnometer of about 50 ml. capacity. The analytical weights were compared directly with a set calibrated by the U. S. Bureau of Standards.

Results

In Tables I and II are recorded the solubility of potassium acid tartrate in dipotassium tartrate and tartaric acid solutions at various temperatures. The data contained in the tables were read off a large scale graph of a series of mean values obtained from several closely agreeing individual determinations, in which equilibrium was approached from both the undersaturated and supersaturated sides. The maximum differences between duplicate determinations approached from either side did not exceed 1.3%.[4]

TABLE I

SOLUBILITY OF POTASSIUM ACID TARTRATE IN DIPOTASSIUM TARTRATE SOLUTIONS

Concn. K_2T, g. per 100 g. soln.	Concn. KHT, g. per 100 g. soln.	Density at $t°/4°$
	0°	
0.000	0.2305	1.0012
.025	.2010	1.0010
.050	.1772	1.0009
.100	.1394	1.0011
.200	.0978	1.0014
.300	.0758	1.0018
.400	.0617	1.0024
.500	.0523	1.0031
.600	.0480	1.0038
.700	.0433	1.0046
.800	.0379	1.0052
	5°	
0.000	0.2870	1.0016
.025	.2562	1.0016
.050	.2322	1.0017
.100	.1936	1.0021
.200	.1437	1.0025
.300	.1098	1.0029
.400	.0902	1.0035
.500	.0784	1.0041
.600	.0703	1.0047
.700	.0638	1.0053
.800	.0562	1.0059
	10°	
0.000	0.3579	1.0020
.025	.3272	1.0020
.050	.3000	1.0021
.100	.2557	1.0024
.200	.1924	1.0027
.300	.1540	1.0030
.400	.1317	1.0036
.500	.1143	1.0042
.600	.1039	1.0048
.700	.0935	1.0054
.800	.0824	1.0060
	15°	
0.000	0.4338	1.0016
.025	.4050	1.0017
.050	.3793	1.0017
.100	.3307	1.0018
.200	.2651	1.0021
.300	.2186	1.0025
.400	.1890	1.0028
.500	.1652	1.0031
.600	.1492	1.0037
.700	.1357	1.0043
.800	.1220	1.0049
	20°	
0.000	0.5323	1.0012
.025	.5010	1.0012
.050	.4737	1.0013
.100	.4228	1.0014
.200	.3492	1.0016
.300	.2939	1.0020
.400	.2532	1.0024
.500	.2208	1.0029
.600	.1977	1.0035
	25°	
0.000	0.6412	1.0003
.025	.6120	1.0003
.050	.5894	1.0004
.100	.5424	1.0005
.200	.4560	1.0008
.300	.3898	1.0011
.400	.3428	1.0017
.500	.3060	1.0024
.600	.2773	1.0028
.700	.2522	1.0032
.800	.2292	1.0036

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(3) Morris, *Analyst*, **45**, 349 (1920).

(4) The writers are indebted to Dr. J. J. Kucera for certain results on the solubility of potassium acid tartrate in water, which results have been averaged with our own in arriving at the average values given in Tables I and II.

TABLE II

SOLUBILITY OF POTASSIUM ACID TARTRATE IN TARTARIC ACID SOLUTIONS

Concn. H_2T, g. per 100 g. soln.	Concn. KHT, g. per 100 g. soln.	Density at $t°/4°$
	0°	
0.000	0.2305	1.0012
.025	.2162	1.0013
.050	.2075	1.0013
.100	.1962	1.0014
.200	.1842	1.0016
.400	.1680	1.0024
.600	.1600	1.0035
.800	.1503	1.0047
	10°	
0.000	0.3579	1.0020
.025	.3457	1.0020
.050	.3352	1.0021
0.100	0.3205	1.0021
.200	.3003	1.0026
.400	.2715	1.0033
.600	.2502	1.0042
	25°	
0.000	0.6412	1.0003
.025	.6220	1.0003
.050	.6063	1.0004
.100	.5842	1.0005
.200	.5558	1.0008
.400	.5243	1.0014
.600	.4981	1.0021
.800	.4716	1.0027

As regards the solubility of potassium acid tartrate in water at various temperatures, the writers have found that the equation

$$C_t = k + at + bt^2$$

where $k = 0.2305$, $a = 0.010018$, $b = 0.0002564$ and $t = °C.$, fits the data with an accuracy of about ±1% over the temperature range studied, when concentration is expressed in grams per 100 grams of saturated solution.

The writers have found that the solubility of potassium acid tartrate in solutions of dipotassium tartrate and tartaric acid can be expressed as a function of the concentrations of the latter substances. These relationships are given in the following empirically derived equations

$$C_{KHT} = a + b \log C_{K_2T} \qquad (1)$$

$$C_{KHT} = k\, C_{H_2T}^{-n} \qquad (2)$$

where a, b, k and n are constants at a given temperature. For equation (1) these constants have the values at the respective temperatures of 0, 5 and 10° as follows: $a = 387, 475, 450$; $b = -124, -144.5, -197.5$. For equation (2) the constants have the values at the respective temperatures of 0, 10 and 25° as follows: $k = 0.15385, 0.24776, 0.49212$; $n = 0.1017, 0.10551$ 0.07248.

The first equation yields values deviating from those experimentally determined by ±3.1% on the average (with one exception) at 0, 5 and 10°, and any single determination has a probable error of ±2.8%. The equation fails at higher temperatures. The second equation is found to hold within ±1.9% over the whole temperature range from 0 to 25°, and any single determination has a probable error of ±2.0%. At higher tartaric acid concentrations the relationship begins to fail, but in tartaric acid solutions up to at least 0.5% the agreement is good.

The results here reported for the solubility of potassium acid tartrate in water agree closely with the values reported by other workers. The solubility expressed in grams per 100 grams of water is reported by Warington[5] and also by Paul[6] to be 0.363 and 0.366, respectively, at 10°. Magnanini[7] and Paul report 0.532 and 0.533, respectively, at 20°. Our results calculated to the same basis give the values 0.3592 at 10° and 0.5352 at 20°.

Summary

1. The solubility of potassium acid tartrate in tartaric acid solutions has been determined at 0, 10 and 25°, and in dipotassium tartrate solutions at 0, 5, 10, 15, 20 and 25°. The series of tartaric acid and dipotassium tartrate solutions had an approximate range of concentration between 0 and 1%.

2. The solubility of the acid tartrate is decreased by increasing concentrations of tartaric acid or of dipotassium tartrate, the latter having the greater effect.

3. The solubility of the acid tartrate in tartaric acid solutions follows the equation $C_{KHT} = kC_{H_2T}^{-n}$ fairly closely where k and n are constants for a given temperature.

4. The solubility of the acid tartrate in dipotassium tartrate solutions follows the equation $C_{KHT} = a + b \log C_{K_2T}$ at low temperatures, where a and b are constants at a given temperature.

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RECEIVED AUGUST 16, 1933

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[5] Warington, *J. Chem. Soc.*, **28**, 946 (1875).

[6] Paul, *Arb. Reichgesundh.*, **57**, 94 (1926).

[7] Magnanini, *Gazz. chim. ital.*, **31**, (II), 432 (1901).