

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SMITH COLLEGE]

Solid Solutions of the Alkali Halides. I. The Systems $\text{KBr-KCl-H}_2\text{O}$, $\text{RbBr-RbCl-H}_2\text{O}^1$ and $\text{RbBr-KBr-H}_2\text{O}^2$ at 25°

BY GEORGE S. DURHAM, ELIZABETH J. ROCK AND JOAN S. FRAYN

RECEIVED FEBRUARY 10, 1953

The ternary systems $\text{KBr-KCl-H}_2\text{O}$, $\text{RbBr-RbCl-H}_2\text{O}$ and $\text{RbBr-KBr-H}_2\text{O}$ have been studied under equilibrium conditions at 25° . All of these systems show type II solid solution formation according to Roozeboom's classification.

In the course of a theoretical investigation now in progress concerning solid solutions among the alkali halides,³ it became necessary to have reliable experimental data for ternary systems of isomorphous alkali halides and water. Although the system $\text{KBr-KCl-H}_2\text{O}$ had already been investigated by Amadori and Pampanini,⁴ it was felt worthwhile to restudy it, since they showed no proof of the attainment of equilibrium and since some of their data seemed inconsistent. Soon after the present work on this system was completed, the paper of Flatt and Burkhardt,⁵ containing results for the same system, appeared.

Experimental

I. $\text{KBr-KCl-H}_2\text{O}$.—Both salts, which met A.C.S. standards of purity, were recrystallized from water, centrifuged and dried to constant weight. The chloride, which was bromide-free, was shown by weighing as silver chloride and by the Caldwell modification of the Volhard analysis for halide to have an acceptable purity factor of 99.8%. Similar methods led to a value of 100.1% for the bromide. By the McAlpine test⁶ for chloride in the presence of bromide, the presence of approximately 0.2% potassium chloride was indicated in the latter salt. In preparing the complexes (initial mixtures) for the ternary system, corrections for the chloride present in the bromide were made on this basis.

The solubilities of the separate salts were determined from both under- and over-saturation; each sample was analyzed by the Caldwell-Volhard method, as well as by evaporation to constant weight at 170° .

In order to prove the attainment of equilibrium, each ternary complex was made up quantitatively in duplicate, the only difference being in the order of addition of the salts; thus for each point equilibrium in the solid phase was approached from two directions.⁷ The solubility tubes, each containing two glass marbles to keep the solid phase finely ground, were rotated in a thermostat kept at $25.00 \pm 0.02^\circ$. Under these conditions, the solid phases of duplicate complexes showed the same composition within experimental error after three to four weeks, except in the case of complexes IA and IB, for which a difference of 1% was found.

Samples of the liquid were taken for analysis by means of suction pipets, the tips of which were covered with filter paper and cotton. The solid phases were centrifuged, immediately weighed, and then dried at 170° to constant weight. From the weight of water lost on drying and the composition of the conjugate liquid solution, corrections were made for the solid left on evaporation of the residual mother liquor.

Analysis for potassium chloride and potassium bromide was made indirectly by means of a determination of total solids and a Caldwell-Volhard titration for total halide.

Although the use of such indirect methods magnifies errors, in this case because of the large relative difference in the formula weights of potassium chloride and potassium bromide and the high precision of each of the determinations involved, the error was no greater than that usually found when one component is determined by difference. The procedure was tried on known mixtures of widely varying compositions; for the component present in larger amount the results were accurate to within two parts per thousand.

The consistency of the analytical results was also checked by comparing the compositions of the solid phases with values obtained by algebraic extrapolation of the tie lines through the compositions of the liquid solution and the original complex. The average absolute deviation, in terms of potassium chloride, is 0.68%. Since the liquid and complex compositions lie so close together, an error in either will be multiplied by a factor of ten in the extrapolation; hence this deviation is considered satisfactory.

II. $\text{RbBr-RbCl-H}_2\text{O}$.—In general the methods used for this system were similar to those described above. The rubidium salts were of C.P. grade obtained from the A.D. Mackay Company, and after being dried to constant weight at 190° were used without further purification. The chloride gave a negative test for bromide; by the method of Andrews,⁸ the bromide was found to contain less than 0.1% rubidium chloride. Caldwell-Volhard analyses showed the rubidium chloride to contain 0.6% potassium chloride and the bromide 0.7% potassium bromide.

In the analytical calculations for the ternary system, it was necessary to correct for the potassium present, since otherwise the calculated results would be too high in rubidium chloride. By means of the semi-empirical distribution equation of Hill, Durham and Ricci,⁹ and the experimental data for the $\text{RbCl-KCl-H}_2\text{O}^{10}$ and $\text{RbBr-KBr-H}_2\text{O}$ systems, it was calculated that for a K/Rb molar ratio of 0.010 in the liquid the K/Br ratio in the solid for these two systems would be 4.6×10^{-4} and 1.6×10^{-3} , respectively. Since seven-eighths of the solid used in making up the complexes for the $\text{RbBr-RbCl-H}_2\text{O}$ system went into the aqueous phase, and since according to the above distributions, only a relatively small amount of potassium would be expected in the solid phase, it was assumed for purposes of calculation that the molar K/Rb ratio in the aqueous phase was the same as in the original salts (0.010 in each case) and that the potassium content of the solid was negligible. On the basis of these considerations the analytical calculations for the liquid were made with formula weights for rubidium bromide and chloride which had been corrected for the potassium present. The weighted averages used were 165.0 and 120.4, respectively. In this system, therefore, the compositions of the complexes and the ternary aqueous phases are given in terms of the potassium-containing rubidium salts used.

The solubilities of the separate salts were obtained from both under- and over-saturation, by means of evaporation to constant weight at 190° . Since in each case the amount of solid phase was relatively small, it was assumed, from the considerations outlined above, that the potassium-rubidium ratio in the liquid was equal to that in the original salt. With this information and data from the appropriate ternary systems, solubilities for the pure salts were obtained by extrapolation.

Because of the limited supply of rubidium salts, only two complexes were prepared in duplicate, one being chosen so that its solid phase was rich in rubidium chloride, and the

(1) Results for this system taken from the thesis presented by E. J. Rock for the M.A. degree at Smith College, 1948.

(2) Experimental work carried out as a senior research problem by J. S. Frayn, 1949.

(3) G. S. Durham and J. A. Hawkins, *J. Chem. Phys.*, **19**, 149 (1951).

(4) M. Amadori and G. Pampanini, *Atti accad. Lincei*, [II] **20**, 473 (1911).

(5) R. Flatt and G. Burkhardt, *Helv. Chim. Acta*, **27**, 1605 (1944).

(6) R. K. McAlpine, *THIS JOURNAL*, **51**, 1065 (1929).

(7) A. E. Hill and N. Kaplan, *THIS JOURNAL*, **60**, 550 (1938).

(8) L. W. Andrews, *ibid.*, **29**, 275 (1907).

(9) A. E. Hill, G. S. Durham and J. E. Ricci, *ibid.*, **62**, 2723 (1940).

(10) J. d'Ans and P. Busch, *Z. anorg. allgem. Chem.*, **232**, 337 (1937).

other so that its solid phase was rich in rubidium bromide. If equilibrium were established in these two cases, it seemed reasonable that it would be reached also in the other complexes. Analysis after rotation at $25 \pm 0.1^\circ$ for 2.5 weeks showed the solid-phase compositions in the first pair to be within 0.84% absolute of each other and those of the second pair to be within 0.55%. This agreement was considered to be reasonably satisfactory. The average absolute deviation between analyzed and extrapolated compositions for the four solid solutions is 0.83%, with a multiplication-of-error factor in the extrapolation of about sixteen.

In order to obtain samples of the solid solutions suitable for X-ray diffraction measurements, a portion of each solid phase was washed with alcohol and ether after filtration, in order to minimize the amount of non-equilibrium solid resulting from the mother liquor.

III. RbBr-KBr-H₂O.—The methods used were very similar to those described under I. The potassium bromide contained 0.1% potassium chloride. The rubidium bromide was prepared from a mixture of rubidium chloride and bromide originating from system II. Rubidium sulfate was first formed by means of sulfuric acid and was then converted to rubidium bromide by metathesis with barium bromide. After two crystallizations, the product was found to

TABLE I

TERNARY SYSTEMS OF ALKALI HALIDES WITH WATER AT 25°

No.	Original complex		Liquid phase			Solid solution	
	A, wt. %	B, wt. %	A, wt. %	B, wt. %	(A + B), moles	A, wt. %	A, mol. frac.
I. KBr(A)-KCl(B)-H ₂ O							
1	0.00	...	0.00	26.42	0.000	0.00	0.000
2A ^a	10.00	25.00	10.01	20.91	.231	7.89	.050
B ^b	10.00	25.00	10.28	20.69	.237	6.87	.044
3A	21.00	22.00	20.21	15.31	.451	26.95	.188
B	21.00	22.00	20.13	15.39	.450	26.99	.188
4A	25.00	21.00	22.85	13.83	.504	37.78	.276
B	25.00	21.00	22.75	13.92	.503	37.29	.272
5A	34.00	18.00	26.62	11.56	.590	60.0	.488
B	34.00	18.00	26.42	11.71	.586	59.9	.487
6A	37.00	10.00	30.46	8.74	.686	81.1	.730
B	37.00	10.00	30.50	8.70	.686	81.0	.729
7A	39.00	5.00	35.09	4.89	.818	92.9	.890
B	39.00	5.00	35.21	4.75	.820	92.9	.890
8	...	0.00	40.57	0.00	1.000	100.0	1.000
II. ^c RbBr(A)-RbCl(B)-H ₂ O							
1	0.00	...	0.00	48.48	.000	0.00	.000
(48.60)—extrapolated to zero % KBr							
2	4.29	45.33	0.066	1.06	0.008
3A	13.97	41.06	13.78	37.90	.210	17.72	.136
B	13.97	41.06	13.63	37.95	.208	16.82	.128
4	21.41	31.87	.329	39.8	.326
5	24.85	28.82	.387	54.4	.465
6A	37.77	18.81	34.79	18.69	.576	82.9	.779
B	37.77	18.81	34.90	18.69	.576	82.3	.773
7	44.84	8.35	.797	94.6	.927
8	...	0.00	52.72	0.00	1.000	100.0	1.000
(52.75)—extrapolated to zero % KCl							
III. RbBr(A)-KBr(B)-H ₂ O							
1	0.00	...	0.00	40.65	0.000	0.00	0.000
2A	12.95	38.17	12.89	32.08	.224	13.40	.100
B	12.94	38.17	12.87	32.14	.223	13.22	.099
3A	23.92	29.04	22.94	25.29	.395	33.60	.267
B	23.92	29.03	23.08	25.26	.395	33.70	.268
4A	33.64	21.43	30.88	19.41	.534	58.9	.508
B	33.64	21.43	31.01	19.30	.537	58.9	.508
5A ^d	39.58	16.54	(36.14)	15.20	.631	72.5	.665
B	39.72	16.39	35.78	15.44	.618	74.5	.678
6A ^d	45.68	11.32	(41.21)	10.85	.732	84.5	.797
B	45.84	11.16	40.97	10.87	.730	86.4	.820
7A ^d	51.07	7.01	(45.54)	6.95	.825	93.2	.908
B	51.25	6.83	45.22	6.97	.824	93.9	.917
8 ^d	...	0.00	52.23	0.71	1.000	100.0	1.000
(53.03)—extrapolated to zero % KBr							

^a A complexes were prepared with salt A as the initial solid phase. ^b B complexes were prepared with salt B as the initial solid phase. ^c The RbBr used in this system contained 0.7% KBr; the RbCl 0.6% KCl. ^d These complexes were prepared with RbBr remaining from system II.

contain 0.35% potassium bromide and less than 0.1% of rubidium chloride. For some of the complexes the rubidium bromide described under II was used.

All complexes were made up in duplicate as described under I and were rotated for three weeks in a thermostat kept at $25.0 \pm 0.1^\circ$. Analyses for the solubilities of the separate salts were made both by drying to constant weight at 190° and by the Caldwell-Volhard method. A period of three weeks proved sufficient for the attainment of equilibrium in the ternary system. The methods of analysis and sampling were similar to those used in the RbBr-RbCl-H₂O system. A value for the solubility of pure rubidium bromide was obtained by extrapolating the analytical data to zero % potassium bromide. The average absolute deviation between analyzed and extrapolated solid solution compositions was 0.51%, with an average multiplication-of-error factor in the extrapolation of about eight.

Results

The solubility data are given in Table I and are plotted in the form of Roozeboom distribution

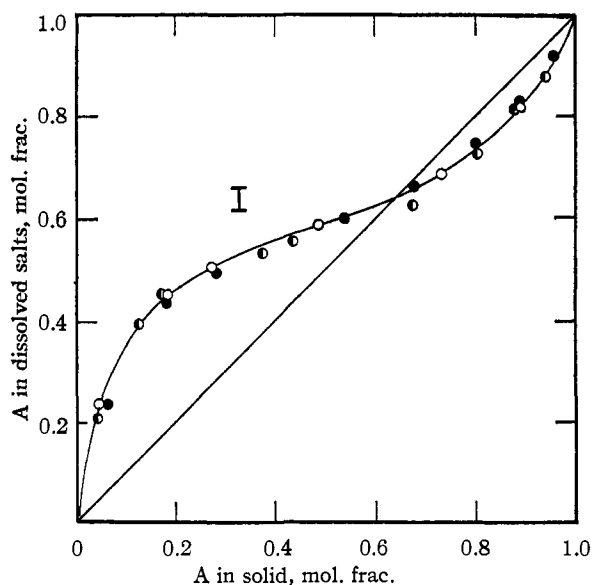


Fig. 1.—Distribution of KBr(A) and KCl between aqueous and solid solution at 25°: O, this research; ◐, Amadori and Pampanini⁴; ●, Flatt and Burkhardt.

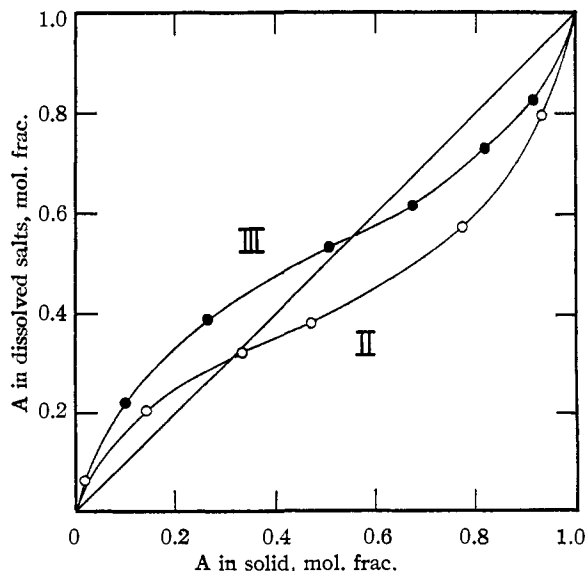


Fig. 2.—Distribution between aqueous and solid solution at 25°: II, RbBr(A)-RbCl; III, RbBr(A)-KBr.

curves in Figs. 1 and 2. All three systems show type II solid solution according to the Roozeboom classification. Plotted also in Fig. 1 for comparison are data for the KBr-KCl-H₂O system as determined by Amadori and Pampanini⁴ and by Flatt and Burkhardt.⁵ The present results, which are more consistent than those of Amadori and Pampanini, indicate the congruent crystallization end-point to be at mole fraction 0.64 of potassium bromide as compared to the latter's value of 0.60. Although in this respect we agree with Flatt and Burkhardt, their results as compared with ours show a somewhat smaller fraction of potassium bromide in the liquid before this point, a larger one after.

The solubilities here reported for potassium chloride, potassium bromide and rubidium chloride are in excellent agreement with literature values.¹¹ That for rubidium bromide, 52.9%, is appreciably lower than the figure 53.7% given by Seidell,¹¹ which was interpolated by Fajans and Karagunis (see Meyer and Dunkel¹²) from measurements by Reissig¹³ and Rimbach.¹⁴ Rimbach's solubilities were obtained by means of the determination of bromide; if his rubidium bromide contained potassium bromide, this method of analysis would lead to high results.

Complexes 5A, 6A and 7A in the RbBr-KBr-H₂O system were prepared from rubidium bromide

(11) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1940, Vol. I, pp. 747, 684, 1429.

(12) K. Meyer and M. Dunkel, *Z. physik. Chem., Bodenst. Suppl.*, 556 (1931).

(13) T. Reissig, *Ann.*, **127**, 33 (1863).

(14) E. Rimbach, *Ber.*, **38**, 1553 (1905).

described in the RbBr-RbCl-H₂O system. Although the same weights of materials were used as in the respective B complexes, the compositions of the complexes differed due to the different percentage of potassium bromide present as impurity, and duplicate solid solutions would not be expected to result. The deviations actually found, however, are greater than can be attributed to this cause alone and are accompanied by a higher rubidium bromide content in the aqueous phase for the A complexes. On the basis of the agreement between the directly determined and the extrapolated solid-solution compositions, the A results seem as consistent analytically as the B. The reason for these differences is not known, although a possible explanation might be the presence of a small amount of soluble non-isomorphous impurity in the original rubidium bromide. Since it is felt that in these three cases the B results are probably the more dependable, they have been used in plotting the distribution curve.

Due to the indirect method of analysis coupled with the impurity of the rubidium salts, it is felt that the absolute error in the individual solid phase compositions may be as high as 1% for systems II and III. While this means that the distribution ratios in the dilute solutions may be relatively inaccurate, the accuracy is sufficient to fix satisfactorily the Roozeboom distribution curves.

Acknowledgment.—We are extremely grateful to the Society of the Sigma Xi for a Grant-in-Aid which made possible the purchase of the rubidium salts used in this research.

NORTHAMPTON, MASS.

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

The System H₂O-NaPO₃

BY GEORGE W. MOREY

RECEIVED JULY 24, 1953

The solubility relations in the system H₂O-NaPO₃ up to the melting point of NaPO₃ were determined by the closed tube method, and the vapor pressures of the saturated solutions at the invariant points and at 400 and 500° were also measured.

Most of the phase equilibrium work of the Geophysical Laboratory has dealt with silicate systems, but to one interested in silicates the chemistry of the phosphates also is of interest. In both cases the structural element is a tetrahedral grouping of four oxygens around a central positive ion, and the various compounds are formed by repeated polymerization in which an oxygen atom is shared by two structural groups. Both the silicates and the phosphates are glass-formers because of the tendency toward repeated polymerization of tetrahedral groupings. Many of the differences between the silicates and the phosphates can be related to the difference in radii of the positive ions. Because of this interest in the phosphates as compared with the silicates, studies of some phosphate systems are nearing completion, and this paper is a report on one of these studies.

There is nothing in the literature about the system H₂O-Na₂O·P₂O₅ above 100°. The results below 100° included in Fig. 1 are recalculated from "International Critical Tables"¹; the experimental work is that of Imadsu.² The experimental results listed in Table I were all obtained by the closed tube method. The solubilities below 400° were made in sealed glass tubes rotated in an oven which was provided with an automatic temperature control.³ Runs above 400° were made in sealed glass tubes in an ordinary furnace without continuous rotation, but the tubes were inverted

(1) "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," Vol. 4, McGraw-Hill Book Co., Inc., New York and London, 1928, p. 237.

(2) Akira Imadsu, *Mem. Coll. Sci. Eng.* (Kyoto Imperial University), **3**, 257 (1912).

(3) F. C. Kracek, G. W. Morey and H. E. Merwin, *Am. J. Sci.*, **35A**, 143 (1938).