[Contribution from the Department of Chemistry, New York University]

The Ternary System Na_2SO_4–$NaBrO_3$–H_2O, and a Sixth Possible Type of Solid Solution Formation between Two Components in the Roozeboom Classification

By John E. Ricci

Introduction.—The present measurements on the system sodium sulfate, sodium bromate and water have been made as part of the general purpose of investigating certain cases of the formation of double compounds between salts, to learn if possible the properties of the constituent salts which determine such complex formation. In a previous investigation[1] of a series of ternary systems involving sodium bromate, complex formation was noted between sodium bromate and sodium sulfate at 45°, which, it was suggested, might prove to resemble the compounds known to be formed between sodium sulfate and sodium iodate, namely, $NaIO_3 \cdot 3Na_2SO_4$ and $NaIO_3 \cdot 4Na_2SO_4$.[2] In the further study of the $NaBrO_3$–Na_2SO_4–H_2O system, however, the complex has been found to be a solid solution and not a definite compound at all. As another example of the tendency of sodium sulfate toward formation of solid solutions, the data here presented may prove helpful in establishing regularities in the relationships of sodium sulfate to other salts and in the general problem of complex formation between salts, in which extensive data and classification are still required.

Experimental Methods.—The experimental procedure and analytical methods have already been described in the previous publication on the 25° isotherm of the system.[1] Two weeks of stirring were generally allowed for equilibrium. The method of algebraic extrapolation of tie-lines[3] for the determination of solid phases was supplemented, in the case of the solid solution, by analysis of residues and of crystals formed by isothermal evaporation of solutions calculated to precipitate the solid solution.

Table I

10 and 30° Isotherms

Original complex, wt. % Na_2SO_4	Original complex, wt. % $NaBrO_3$	Saturated solution, wt. % Na_2SO_4	Saturated solution, wt. % $NaBrO_3$	Density	Solid phase
10°					
...	0.00	8.26	0.00	1.079	$Na_2SO_4 \cdot 10H_2O$
16.91	3.96	6.96	5.40	1.112	$Na_2SO_4 \cdot 10H_2O$
13.97	11.00	5.20	14.21	1.175	$Na_2SO_4 \cdot 10H_2O$
13.54	15.34	4.41	19.93	1.230	$Na_2SO_4 \cdot 10H_2O$
13.49	17.50	4.41	20.10	1.228	$Na_2SO_4 \cdot 10H_2O$ + $NaBrO_3$
5.22	32.97	4.37	20.12	1.228	$Na_2SO_4 \cdot 10H_2O$ + $NaBrO_3$
Average	...	4.40	20.11	1.227	$Na_2SO_4 \cdot 10H_2O$ + $NaBrO_3$
2.98	34.55	3.61	20.67	1.226	$NaBrO_3$
1.52	34.97	1.83	21.96	1.217	$NaBrO_3$
0.00	...	0.00	23.24	1.211	$NaBrO_3$
30°					
...	0.00	29.14	0.00	1.286	$Na_2SO_4 \cdot 10H_2O$
30.93	4.00	26.92	5.18	1.312	$Na_2SO_4 \cdot 10H_2O$
30.49	5.99	26.02	7.85	1.333	$Na_2SO_4 \cdot 10H_2O$
29.67	8.19	25.28	10.43	1.351	$Na_2SO_. \cdot 10H_2O$
28.67	9.69	24.95	11.46	1.361	$Na_2SO_4 \cdot 10H_2O$ + $NaBrO_3$
24.27	21.96	25.03	11.36	1.364	$Na_2SO_4 \cdot 10H_2O$ + $NaBrO_3$
Average	...	25.02	11.38	1.362	$Na_2SO_4 \cdot 10H_2O$ + $NaBrO_3$
17.74	27.51	21.04	13.86	1.343	$NaBrO_3$
10.28	33.93	12.43	19.89	1.311	$NaBrO_3$
0.00	...	0.00	29.85	1.284	$NaBrO_3$

Results.—The results of the solubility measurements are given, for the five isotherms studied in the present paper, in Tables I and II; the results at 25° have already been published.[1] The curves for the first three temperatures, 10, 25 and 30°, in which the solid solution is not found, are shown together in condensed form in Fig. 1. These isotherms require no discussion; no complex formation is found, the only solid phases at each temperature being $Na_2SO_4 \cdot 10H_2O$ and $NaBrO_3$. The quintuple point representing the transition between $Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4

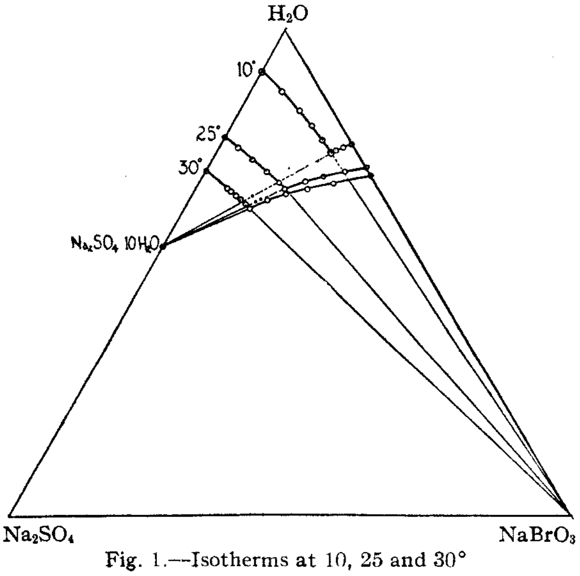

Fig. 1.—Isotherms at 10, 25 and 30°

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[1] Ricci, This Journal, **56**, 299 (1934).

[2] Foote and Vance, *Am. J. Sci.*, **19**, 203 (1930).

[3] Hill and Ricci, This Journal, **53**, 4305 (1931).

in the ternary system, although not here determined, must lie between 30 and 32.48°, the binary transition temperature. In this system, therefore, as much as 11.4% $NaBrO_3$ in the solution is not sufficient to lower the transition temperature of the Na_2SO_4 system 2.5°, which is in line with the generally small effect on this transition temperature of many other added salts besides $NaBrO_3$, such as $MgSO_4$, Na_2CO_3 and $(NH_4)_2SO_4$.

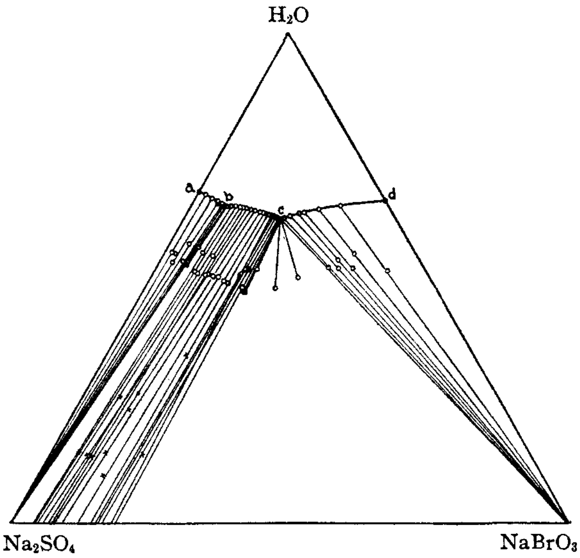

Fig. 2.—Isotherm at 45°.

TABLE II

37.5, 45 AND 52° ISOTHERMS

Original complex, wt. %		Saturated solution, wt. %			
Na_2SO_4	$NaBrO_3$	Na_2SO_4	$NaBrO_3$	Extrapolation	Solid phase
		37.5°			
...	0.00	32.70	0.00		
39.41	2.64	31.20	2.99	+0.02% $NaBrO_3$	Na_2SO_4
38.28	4.25	30.68	4.77.	−0.04	Na_2SO_4
37.43	5.02	30.53	5.57	+0.01	Na_2SO_4
...	...	(30.4)	(5.7)		Na_2SO_4 + S.S.
37.96	5.20	30.36	5.80	+0.30	S.S.
37.43	5.64	29.56	6.33	+0.21	S.S.
35.46	7.52	28.04	7.85	+4.58	S.S.
34.02	9.50	26.45	9.83	+6.67	S.S.
32.46	11.52	25.11	11.78	9.10	S.S.
32.06	13.22	24.08	13.38	11.88	S.S. + $NaBrO_3$
23.09	26.27	24.18	13.31		S.S. + $NaBrO_3$
Average	...	24.14	13.35		S.S. + $NaBrO_3$
22.96	25.51	25.67	12.39	+9.43% Na_2SO_4	$NaBrO_3$ (m)
21.41	26.91	25.01	12.75	+2.86% Na_2SO_4	$NaBrO_3$ (m)
20.71	27.11	24.71	12.95	0.14% Na_2SO_4	$NaBrO_3$ (m)
19.31	27.99	23.01	14.11	.07% Na_2SO_4	$NaBrO_3$
12.96	31.96	15.28	19.61	.20% Na_2SO_4	$NaBrO_3$
0.00	...	0.00	(32.08)		
		45°			
...	0.00	32.07	0.00		Na_2SO_4
44.45	2.51	30.35	3.12	+0.09% $NaBrO_3$	Na_2SO_4
42.41	4.61	29.18	5.64	+0.10	Na_2SO_4
42.11	5.41	28.82	6.29	+1.59	Na_2SO_4 + S.S.
42.03	5.61	28.79	6.30	2.57	Na_2SO_4 + S.S.
37.95	5.98	28.74	6.37	3.36	Na_2SO_4 + S.S.
Average	...	28.78	6.32		Na_2SO_4 + S.S.
52.14	3.92	30.44	4.50	2.64	S.S. (m)
49.92	4.30	29.95	5.01	2.53	S.S. (m)
49.93	4.59	29.52	5.45	2.48	S.S. (m)
49.80	5.18	29.21	5.85	4.21	S.S. (m)
37.43	7.00	27.76	7.53	3.62	S.S.
39.49	8.33	26.56	9.23	4.13	S.S.
38.96	9.51	25.85	10.12	6.66	S.S.
37.94	11.50	24.18	12.56	6.72	S.S.
36.97	13.52	22.92	14.38	9.66	S.S.
36.46	14.50	22.77	14.65	13.80	S.S.
32.12	16.28	21.58	15.96	14.40	S.S.
34.95	17.17	20.94	17.00	17.77	S.S.
34.75	17.85	20.76	17.22	19.89	S.S. + $NaBrO_3$
23.48	26.47	20.90	17.15		S.S. + $NaBrO_3$
Average	...	20.86	17.17		S.S. + $NaBrO_3$
19.00	29.97	22.47	16.00	+1.62% Na_2SO_4	$NaBrO_3$ (m)
19.18	29.47	22.19	16.23	3.19	$NaBrO_3$ (m)
17.19	33.76	21.59	16.62	0.30	$NaBrO_3$ (m)
17.04	33.02	21.09	17.03	.07	$NaBrO_3$ (m)
16.68	30.99	19.81	17.93	+0.10	$NaBrO_3$
14.17	31.98	16.54	20.38	+0.28	$NaBrO_3$
6.49	41.96	8.10	27.14	+0.21	$NaBrO_3$
0.00	...	0.00	34.22		$NaBrO_3$
		52°			
...	0.00	31.47	0.00		Na_2SO_4
42.50	2.52	29.71	3.03	+0.21% $NaBrO_3$	Na_2SO_4
41.53	4.50	28.17	5.47	+0.24	Na_2SO_4
39.95	6.20	27.73	7.19	+1.39	Na_2SO_4 + S.S.
39.66	6.93	27.64	7.45	4.50	Na_2SO_4 + S.S.
Average	...	27.7	7.3		Na_2SO_4 + S.S.
39.01	8.02	26.03	9.24	2.53	S.S.
36.75	12.03	23.17	13.24	7.02	S.S.
34.82	15.31	21.39	15.96	12.77	S.S.
31.77	18.83	19.26	18.98	18.23	S.S.
31.63	20.42	18.12	20.80	19.03	S.S. + $NaBrO_3$
14.95	34.63	18.15	20.69	−0.06% Na_2SO_4	S.S. + $NaBrO_3$
Average	...	18.13	20.77		S.S. + $NaBrO_3$
15.99	33.94	19.60	19.61	6.33% Na_2SO_4	$NaBrO_3$ (m)
17.25	32.64	19.03	20.06	7.72	$NaBrO_3$ (m)
13.32	35.98	16.27	22.19	−0.38	$NaBrO_3$
7.01	41.25	8.62	28.49	−0.44	$NaBrO_3$
0.00	...	0.00	36.09		$NaBrO_3$

S.S. = solid solution. m = metastable. ( ) = by graphic extrapolation.

The solid phases stable in the ternary system at the three higher temperatures studied are as follows, as seen in Fig. 2, which gives the curve for the 45° isotherm: anhydrous Na_2SO_4 for solutions between points a and b; solid solution (anhydrous) for solutions b–c; and $NaBrO_3$ for solutions c–d. As shown in Table II, the solubility curve b–c for the solid solution, extends metastably into the region of anhydrous Na_2SO_4; a similar metastable extension for the solubility curve of $NaBrO_3$, past the isothermally invariant point c, was noted at all three of the higher temperatures studied. The figure represents only the stable equilibria; the metastable points cannot be shown on the same diagram with any clearness at all. The curves for 37.5 and 52° are very similar to that for 45°, but cannot be shown on the same figure because of the overlapping of curves caused by the retrograde temperature solubility relations of Na_2SO_4 as compared with the normal behavior of $NaBrO_3$. It is to be stated at this point that for economy of space in publication only about half of the experimental points actually obtained for this system are published in the two tables. The "averages" shown for the isothermally invariant points, for example, are in each case based on a sufficient number of determinations, and the curves themselves are known definitely to be smooth. In Table II the column headed "Extrapolation" gives the result of the algebraic extrapolation of the tie-lines connecting saturated solution with original complex, to the base of the triangle: *i. e.*, to 0% H_2O.

The Solid Solution.—That the phase in equilibrium with solutions on the curve b–c in Fig. 2 is a solid solution—a solid phase of varying composition—is seen at once from the behavior of the tie-lines in that region. The small crosses in the figure represent the compositions of some of the residues (some wet and some centrifuged) analyzed in these experiments. Algebraic extrapolation of the tie-lines gives the following limits, in percentage of $NaBrO_3$ for the solid solution: at 37.5°, 0.5 to 10%; at 45°, 2.5 to 18%; and at 52°, 3 to 18.5%. These extrapolations and the analyses of residues, however, can fix only the salt ratio, and not the hydration, of the solid solution. Because of the rapidity with which Na_2SO_4 combines with solution water during the unavoidable cooling, the analyses show an average of 12% H_2O even in the centrifuged solid phase. Crystals of the solid solution were therefore obtained by isothermal evaporation of solutions on the curve b–c at 45°; the analysis, with particular precautions taken to prevent hydration of Na_2SO_4, showed an average of 3.1% H_2O for crystals from two different points on b–c. The solid is therefore reported as anhydrous.

The limits found for the solid solution, even at its greatest extent, do not correspond to any definite stoichiometric ratio of the two salts. In the system Na_2SO_4–$NaIO_3$–H_2O, the complex formed between the salts, also having, as in the present system, a lower temperature limit of about 30°, is resolved into two definite compounds of very similar composition: $NaIO_3 \cdot 3Na_2SO_4$ and $NaIO_3 \cdot 4Na_2SO_4$, although the results of x-ray examination of the solid phases involved tend to indicate that the second of these compounds may represent a solid solution of Na_2SO_4 in $NaIO_3 \cdot 3Na_2SO_4$.[2] A similar behavior might therefore be suspected in the sodium bromate combination. However, the hypothetical $NaBrO_3 \cdot 4Na_2SO_4$ compound, containing 21.0% $NaBrO_3$, is outside the limits found for the solid solution; even the 1:5 compound (17.5% $NaBrO_3$) is excluded at 37.5°. It is impossible, then, with these observations, to consider this phase as a solid solution of Na_2SO_4 in such a compound.

On a Sixth Possible Type of Solid Solution Formation (in the Roozeboom Classification).—To sum up, the general nature of this system at those temperatures at which the solid solution exists, involves the following sequence of solid phases on an isotherm: first a pure component, Na_2SO_4; second, an anhydrous solid solution (with limits inside the base of the triangle, and not corresponding to any stoichiometric compounds); and third, another pure component, $NaBrO_3$. This means that in the binary system Na_2SO_4–$NaBrO_3$ at these temperatures, the miscibility is incomplete, and yet there is not a pair of conjugate solid solutions, but a single limited phase of solid solution. Such a binary system does not belong to any of the "five possible types" of binary systems forming solid solutions in the classification of Roozeboom;[4] nor does such a ternary system belong to any of the "five possible cases" deduced for water plus two salts with a common ion with formation of solid solution, also given by Roozeboom,[5] and repeated, for example, in the monograph by Blasdale, "Equilibria in Saturated Salt Solutions."[6] Three of the five types are concerned with complete miscibility of the solid components. The other two types refer to systems in which the miscibility is incomplete, and in which there are always two series of solid solutions (conjugate solid solutions). It is assumed, in other words, that if the mutual solubility is not unlimited, solid solutions always exist in conjugate pairs.

Experimentally, however, there are first of all a great number of binary systems, and also several ternary systems, in which this is not the case: the miscibility is incomplete, and yet there is evidence of but one solid solution phase, at a given temperature. The following ternary systems serve as examples.

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(4) Roozeboom, *Z. physik. Chem.*, **30**, 385 (1899).

(5) Roozeboom, *ibid.*, **8**, 521 (1891).

(6) Blasdale, "Equilibria in Saturated Salt Solutions," Chemical Catalog Co., New York, 1927.

1. Na_2SO_4–K_2SO_4–H_2O:[7] The phase glaserite, $3K_2SO_4 \cdot Na_2SO_4$, dissolves some Na_2SO_4, but there is no corresponding conjugate solid solution of glaserite (or K_2SO_4) in Na_2SO_4.

2. Na_2SO_4–Na_2CrO_4–H_2O:[7] solid phases at 25°: solid solution of $Na_2CrO_4 \cdot 10H_2O$ in $Na_2SO_4 \cdot 10H_2O$, Na_2SO_4 and $Na_2CrO_4 \cdot 6H_2O$; again only one solid solution with incomplete miscibility of the two components.

3. Na_2CO_3–K_2CO_3–H_2O:[8] a single solid solution phase inside the triangle, consisting of a solution of $K_2CO_3 \cdot 6H_2O$ and $Na_2CO_3 \cdot 6H_2O$.

4. NH_4Cl–$CuCl_2$–H_2O:[7] a single solid solution with composition extending slightly to either side of the point corresponding to $CuCl_2 \cdot 2NH_4Cl \cdot 2H_2O$.

5. NH_4Cl–$CoCl_2$–H_2O at 25°:[7] solid phases: solid solution of $CoCl_2 \cdot 2H_2O$ in NH_4Cl, and $CoCl_2 \cdot 6H_2O$.

6. NH_4Cl–$NiCl_2$–H_2O at 25°:[7] similar to No. 5.

7. $KClO_3$–KNO_3–H_2O at 25°:[7] solid phases: solid solution of KNO_3 in $KClO_3$, and KNO_3.

8. The present system, Na_2SO_4–$NaBrO_3$–H_2O, appears to be another case.

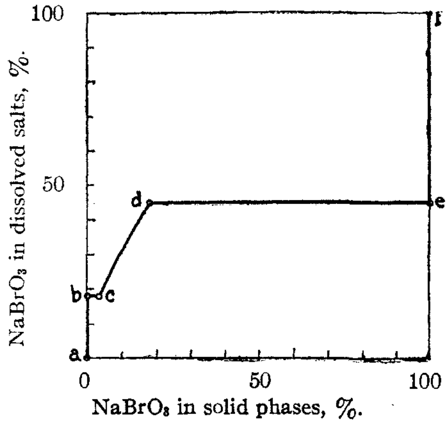

Fig. 3.—Isotherm at 45°.

In all these cases the miscibility of the solid is incomplete, unless in each case both ends of the solid solution are assumed to represent definite compounds. In some of the above systems (Nos. 1, 2 and probably 3) one end of the solid solution does correspond to a definite compound, but certainly not both ends, in any of the systems. Furthermore, while the miscibility must therefore be regarded as incomplete, there is in each case only one solid solution, not a pair, *i. e.*, not "two series of solid solutions." Unless again, as Rivett[9] points out, even the so-called pure phases are regarded as solid solutions with limits too small for detection; but this is not necessary.

In Fig. 3 the system, at 45°, is plotted by the method adopted in his book by Blasdale. Such diagrams are ordinarily used only for systems in which the solid phases are made up entirely of solid solutions, continuous or discontinuous. In the present case the abscissa represents the percentage $NaBrO_3$ in the solid phase or mixture of solid phases, whatever its nature may happen to be. On such a diagram then, a vertical portion of the curve indicates a definite compound (which, however, may or may not be hydrated) as the solid phase; a horizontal portion indicates an isothermally invariant point (with two solid phases, corresponding to the two ends of the horizontal line); and all other parts of the curve, oblique and curved portions, indicate solid phases of varying compositions, or solid solutions. That both ends of any one horizontal portion of such a curve should be of the same type, *i. e.*, both vertical (definite compounds) or both oblique (conjugate solid solutions) does not seem to be a thermodynamic necessity. All that appears necessary on this diagram is that each vertical or oblique portion should terminate, at either end, in a horizontal portion. That is to say, for each change of phase there must be an isothermally invariant liquid solution.

In the figure, the solid phases are as follows: for curve a–b, Na_2SO_4; for curve b–c, Na_2SO_4 + solid solution; for curve c–d, solid solution; for curve d–e, solid solution + $NaBrO_3$; for curve e–f, $NaBrO_3$.

When so plotted this type of system is seen to be not altogether unrelated to the other five types. Blasdale points[10] out for example how a system of type I or II can, with varying temperature, become a system of type IV, by the flattening out of a curved oblique portion of the curve into a truly horizontal portion, *i. e.*, a change from a system with one continuous solid solution to a system with two solid solutions and an intervening isothermally invariant liquid. Similarly, it seems, if an almost straight vertical portion of the curve of a system of type IV or V should become truly vertical, the result would be a system of this additional unclassified "type VI," *i. e.*, a change from a system with the sequence solid

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(7) "International Critical Tables," Vol. IV, 1928.

(8) Hill and Miller, THIS JOURNAL, **49**, 669 (1927).

(9) Rivett, "The Phase Rule," Oxford University Press, 1921, p. 8.

(10) *Loc. cit.*, p. 99.

solution, isothermally invariant point, solid solution, to the sequence pure compound, isothermally invariant point, solid solution.

The classification of this type of solid solution formation is connected with the problem of the correctness or incorrectness of the principle of the universality of solid solutions. The argument for this principle, as given by Rivett,[9] is that the "composition" of a pure component being always the same, even at different temperatures, it cannot be in equilibrium with varying solutions (liquid or solid) at different temperatures. The fallacy is in assuming that "chemical composition" as we ordinarily express it (as percentage by weight) is a definitive thermodynamic variable; the thermodynamic variables used in the Phase Rule are temperature, pressure and concentration, and the concentration of any component is the mass of the component in unit volume. "Chemical composition" (weight per cent.) does not by itself give the true concentration, which determines the thermodynamic and the chemical potential.

Since specific volume changes with temperature, it follows that the concentration and therefore the chemical potential of a pure component do change with the temperature, and therefore the same component (chemically) can be in equilibrium, at different temperatures, with solutions of varying compositions. This applies both to liquid and to solid solutions, *i. e.*, both to the solid–liquid and to the solid–solid equilibrium. It is therefore not necessary to assume universal solid solutions in the temperature–composition diagram of solubility or freezing point for a two-component system at constant pressure, as was contended by Rivett. Therefore, too, it is possible to have a single solid solution phase, in an equilibrium of two components both solid, and with incomplete miscibility. The chemical potential of the undissolved pure component varies with temperature (since specific volume varies) and it can therefore be in equilibrium with a varying solid solution with varying temperature.

Hence what has been called above the "sixth" type of solid solution, which we know, experimentally, to occur in binary and ternary systems, is not impossible thermodynamically.

The argument, as put forward by Rivett[9] for the contention that all solid phases are solid solutions, implies that according to the Phase Rule there can never be a pure phase. This is not an uncommon misapprehension, resulting from thinking of materials from the point of view of atomic and kinetic theory. Under all present conceptions of the structure of matter as made up of particles relatively very far apart even in solid crystals, in lattices which can never, theoretically, be absolutely impenetrable by atoms of foreign substances, it is of course almost self-evident, atomistically, that the probability of any kind of contamination in any phase whatever is never absolutely zero, and that therefore no phase can ever be regarded as pure or of a definite composition. But the question as to whether this contamination represents solution and not merely adsorption, or mechanical occlusion, etc., is one of experiment, and makes the whole difference in the present argument. To say, as Rivett does,[11] that "so called" pure solids are actually solid solutions with limits too small for detection, is begging the question. The problem is entirely one of determining experimentally if possible whether or not a solid phase is a solid solution, since the Phase Rule, as theory, is indifferent to the result. The Phase Rule—thermodynamics—is concerned only with the relation of the number of phases to the number of components, and certain thermodynamic variables such as temperature and pressure, and not at all with the practical question of whether or not we can ever obtain a pure substance. In the derivation of the Phase Rule it is not necessary at any point to assume that each component must be present in every phase. The derivation may even incorporate the condition that "in certain phases certain of the components can enter only in definite proportions and certain other components can enter not at all."[12]

The reason for stressing this point is that the classification of binary systems forming solid solutions, by Roozeboom, in which there is no place for the case of a pure solid in equilibrium with a solid solution (or with a liquid solution, as Rivett logically extended the argument), has been accepted and repeated in text-books on the Phase Rule, with the result that such experimental cases in which this "sixth type" of solid solution formation has been found, either have been laid down as cases in which the solid solution was "beyond detection," as in Rivett's book, or have not been referred to at all, as in the monograph by Blasdale, in which only such systems are chosen as

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(11) *Loc. cit.*, p. 9.

(12) Saurel, *J. Phys. Chem.*, **3**, 137 (1899).

illustrations, which find a place in the "five possible types" under discussion.

It seems to the writer therefore that the accepted classification of Roozeboom for the "five possible types" of solid solution formation between two components is not all inclusive, and that at least a "sixth type" must be added, to include those cases in which there is incomplete miscibility, with an equilibrium between a pure component (or compound) and a solid solution.

Summary

1. Solubility measurements are given for the system Na_2SO_4–$NaBrO_3$–H_2O at 10, 25, 30, 37.5, 45 and 52°. The two salts form no double compounds in this temperature range; but a solid solution is formed between anhydrous Na_2SO_4 and $NaBrO_3$, the composition of the solid extending from about 2% as a lower limit to about 10% $NaBrO_3$ at 37.5°, and to about 19% $NaBrO_3$ at 52°.

2. The binary system Na_2SO_4–$NaBrO_3$ therefore shows the existence of a single solid solution, at the temperatures studied, in equilibrium, not with a conjugate solid solution, but with the pure solid components. This type of solid solution formation is shown not to be impossible, and is added as a "sixth type" to the "five possible types" of Roozeboom.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF MICHIGAN]

The Kinetics of the Alkaline Hydrolysis of Ethyl Carbonate and of Potassium Ethyl Carbonate

BY NEVILLE F. MILLER AND LEE O. CASE

Introduction

As a result of his studies of the rate of saponification of ethyl carbonate, Skrabal[1] concluded that the secondary reaction—the decomposition of the monoethyl carbonate—is immeasurably fast. He therefore assumed a reaction mechanism which represented the saponification of ethyl carbonate as essentially a simple second order process.

Later, however, in a series of equilibrium and kinetic investigations of the monoalkyl carbonates, Faurholt[2] showed that the decomposition of ethyl potassium carbonate proceeds with measurable speed in alkaline solution. He showed that Skrabal had erred in using the methyl orange end-point for titration of his solutions. At this acidity, ethyl potassium carbonate decomposes almost instantly. By the use of the phenolphthalein end-point in the presence of excess barium chloride the residual potassium hydroxide may be titrated without decomposition of the ethyl potassium carbonate or the barium carbonate formed. Faurholt showed also that the secondary reaction is not a true saponification, since its velocity is independent of hydroxyl ion concentration but is dependent upon alcohol concentration.

From a study of the measurements of Faurholt (which were carried out at 0° and were concerned chiefly with the monomethyl carbonate), it appears probable that the reaction mechanism governing the alkaline hydrolysis of ethyl carbonate at ordinary temperatures is essentially that of two consecutive reactions, one of the second order followed by one of the first order. Until now this has not been verified.

The results of the present investigation strongly support this hypothesis. Special interest attaches to the general mechanism indicated, since so far as can be determined it has not heretofore received detailed treatment.

The velocity constants of both reactions were measured by two distinct methods and for different concentrations at a temperature of 25°. By means of additional measurements at 35° the temperature coefficients for both reactions were determined. Since a small amount of alcohol was necessary to keep ethyl carbonate in solution, the velocity constant for the second reaction was also measured in the absence of alcohol in order to determine the effect of this factor.

Relations Involved.—Omitting ionic considerations, the following abbreviated mechanism is proposed for the sake of convenience of mathematical treatment:[3]

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[1] A. Skrabal, *Monatsh.*, **38**, 305–318 (1917).

[2] Faurholt, *Z. physik. Chem.*, **126**, 211–226 (1927).

[3] The last two equations are intended as schematic only, being mathematically equivalent to the more detailed mechanism indicated by the extensive work of Faurholt.