[CONTRIBUTION FROM THE WATSON LABORATORIES OF INTERNATIONAL BUSINESS MACHINES]

Phase Equilibria in the System K_2CO_3–Nb_2O_5 by the Method of Differential Thermal Analysis

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The heterogeneous equilibria in the solids produced by the reaction of K_2CO_3 and Nb_2O_5 have been investigated by the method of differential thermal analysis. Five compounds corresponding to the formulas:[1] (I) $3K_2O \cdot Nb_2O_5$, (II) $K_2O \cdot Nb_2O_5$, (III) $2K_2O \cdot 3Nb_2O_5$, (IV) $K_2O \cdot 3Nb_2O_5$ and (V) $3K_2O \cdot 22NbO_5$ have been found. I melts congruently at an undetermined temperature. II, IV and V melt incongruently at 1039, 1234 and 1279°, respectively. III melts congruently at 1163°. A region suitable for the growth of single crystals of II has been determined although the technological aspects have not been completely perfected. The problems encountered were those normally attendant with high temperature studies of oxide systems.

Introduction

The growing interest in dielectric materials, specifically those of the perovskite type, led to the initiation of fundamental studies of the system K_2CO_3–Nb_2O_5, in which potassium metaniobate (II), is known to exist. Several investigators have reported methods of growing single crystals of II.[2-5] These crystals have been described as white, yellow, blue or black. X-Ray analyses indicate that they have essentially the same structure, and it is believed that the color variations are probably due to impurity content or different states of reduction. It was felt that resolution of the phase diagram would establish optimum conditions for the growth of potassium metaniobate single crystals having the desired ferroelectric properties, and perhaps explain the color variations. The complete diagram would also serve to clarify the ambiguities concerning the number of compounds existing in the system,[6] and the discrepancies concerning the melting point of II.[7]

Experimental Procedure

The niobium pentoxide was purchased from the Fansteel Metallurgical Co. and contained a maximum of 0.2% Ta_2O_5 as the major contaminant. The potassium carbonate was Mallinckrodt analytical reagent dried for one hour at 285° to remove moisture. Neither chemical was subjected to any further purification prior to use. Norton Refractory Grain, 90 mesh R R Alundum was used as the reference material in all runs.

Ground charges of the reactants sufficient to give melts weighing approximately 8 g. after CO_2 loss were weighed to the nearest 0.1 mg. The charges were then fused and heated until CO_2 evolution ceased. Spattering of the melts during the vigorous reaction was avoided by a relatively slow preheat outside of the furnace. 4–6 analyses were conducted at each mole % to determine reproducibility, and to establish the effect of different heating and cooling rates, and of seeding and stirring. In all approximately 500 determinations were performed.

A diagram of the platinum-wound furnace used in the 0–50 mole % K_2CO_3 range is shown in Fig. 1. A smaller Kanthal wound furnace was used for the 50–100 mole % K_2CO_3 range. The platinum wound furnace contained an additional inner alundum thimble to protect the core supporting the platinum wire from the corrosive vapors of the reaction mixture. The thimble provided a more uniform heating zone.

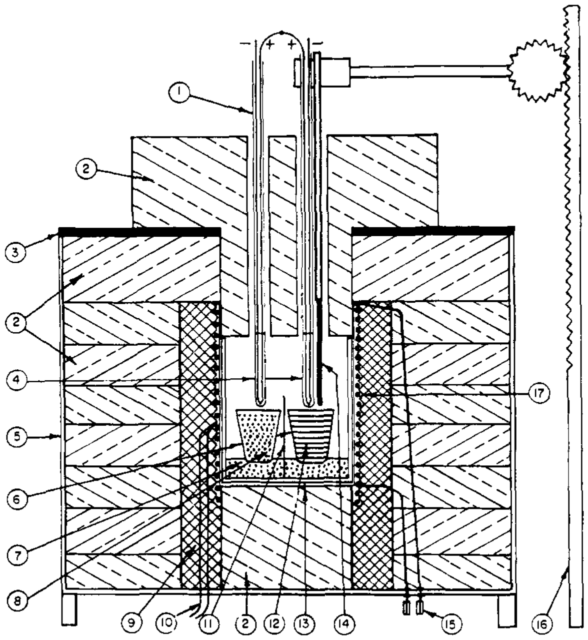

Fig. 1.—Schematic diagram of platinum-wound furnace and thermocouple assembly: 1, thermocouple 14″ long; 2, refractory brick; 3, $^{3}/_{16}''$ transite; 4, 2″ platinum cap cover on thermocouple; 5, $^{1}/_{6}''$ aluminum wall; 6, crucibles; 7, alundum powder; 8, reference material; 9, insuloxide; 10, core thermocouple; 11, partition; 12, charge; 13, alundum thimble; 14, bubbler—3″ platinum tip; 15, furnace lead wires; 16, rack and pinion; 17. $^{1}/_{6}''$ pitch thread.

Temperatures were measured with Pt–10Rh thermocouples supported in alundum protecting tubes. The assembly was lowered by means of a rack and pinion until contact was made with the melt. The thermocouple was then lowered a fixed distance into the melt. Bare thermocouples were initially used, but these were badly corroded by the molten alkali which tended to creep along the wire and eventually attack the alundum supporting tubes. In the range 0–67 mole % K_2CO_3, 5 mil platinum thermocouple protective capsules were fitted snugly over the alundum supporting tubes. These capsules were fitted as closely as possible to the thermocouple tips without shorting. Above 67 mole % K_2CO_3, platinum is severely attacked by the molten alkali, and gold capsules and crucibles were substituted in this relatively low temperature range.

The thermocouples were calibrated with K_2CO_3 in the gold region and with NaCl in the platinum region. Temperature measurements were reproducible to ±2°, but it is believed that the accuracy of measurement was probably of the order ±5°.

Temperatures and temperature differences were recorded on a #69950 Leeds and Northrup Speedomax X-Y recorder. Melt temperatures were recorded on the y-axis, provision being made to divide the signal voltage in order to accom-

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[1] These formulas are used for uniformity and do not necessarily represent the true structural formula.

[2] A. Joly, *Ann. Sc. de l'Ecole norm.*, **16**, #2, 125 (1877).

[3] B. T. Matthias, *Phys. Rev.*, **75**, 1771 (1949).

[4] E. A. Wood, *Acta Cryst.*, **4**, 353 (1951).

[5] P. Vousden, *ibid.*, **4**, 68 (1951).

[6] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., New York, N. Y., 1952, pp. 862–868.

[7] A. V. Lapitskii, *J. Gen. Chem.* (*U.S.S.R.*), **22**, 379 (1952).

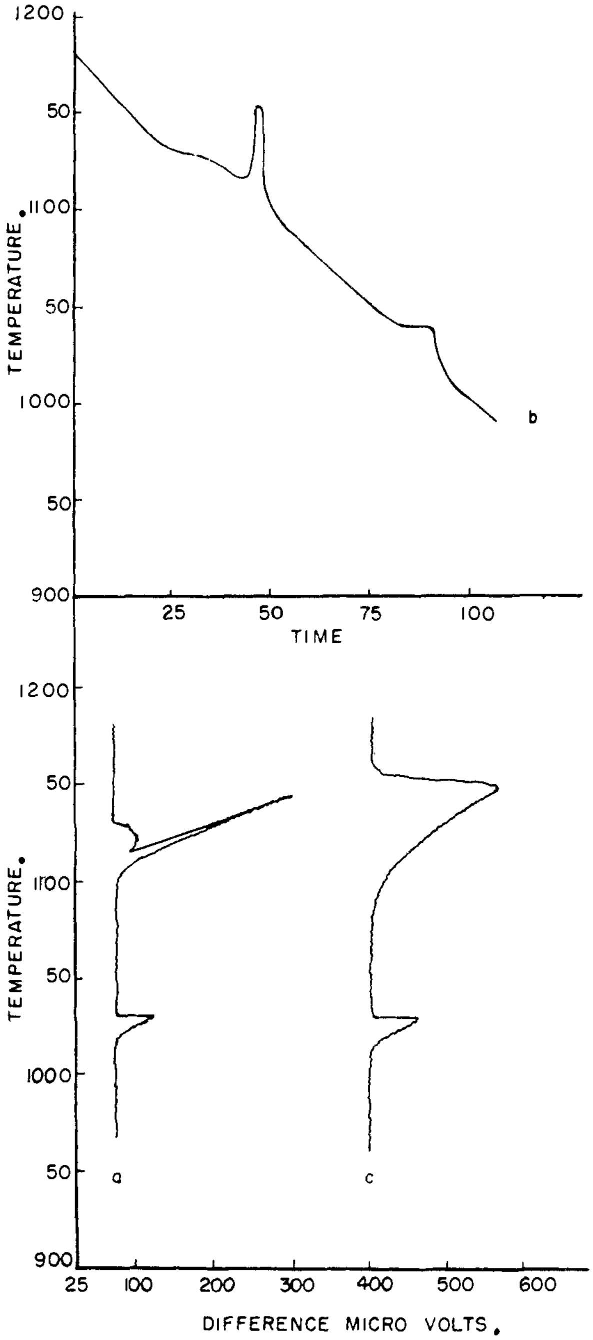

Fig. 2.—Cooling curves in 35–50 mole % K_2CO_3 region: (a) non-equilibrium D.T.A. curve; (b) non-equilibrium time–temperature cooling curve; (c) equilibrium D.T.A. cooling curve.

modate the instrument's maximum range of 10 mv. The full 2.5 mv. range of the x-axis was used to obtain differences. A bucking potential was applied to the x-axis to center the pen. The noise and insensitivity encountered in the higher temperature regions, initially, made it practically impossible to read transition points. Grounding of the thermocouple capsules, X-Y recorder and furnace casing eliminated this noise and increased the sensitivity of the recorder.

Oxygen bubbled through gold or platinum tubes provided excellent agitation of the molten charges and diminished reduction of the Nb_2O_5. The bubbling tube passed through a sufficiently long hot zone, and the bubbling rate was adjusted so as not to affect the temperatures of the melts.

Constant temperature at the thermocouple cold junctions was achieved by the use of a boiling water reflux bath.

Transition temperatures were taken as the first detectable change in slope of the cooling curve for both the liquidus and solidus. The first detectable change in slope during a heating cycle was chosen as the solidus. The maximum of the liquidus for a heating cycle was found to approximate the first crystallization found in the cooling curve, but, as liquidus points obtained during heating cycles were not too well defined, all liquidus data were taken from cooling curves.

Temperature control was effected by the use of variac drive with a 47 v./hr. maximum speed. Any fraction of this speed could be obtained by the use of a proportional timer.

For the majority of runs cooling and heating rates were of the order 2–3°/min., although some analyses were made at rates as high as 20°/minute.

The liquidus in the range 0–35 mole % K_2CO_3 was readily established with cooling curves. Seeding and stirring prevented supercooling. Seeds weighing approximately 0.2 mg. were obtained from pre-runs and were introduced into the melts at 5° cooling intervals. The platinum crucibles examined after cooling in the 12–25 mole % region exhibited considerable swelling. It was evident that pressure was a variable in this part of the system, and the solidus temperatures obtained were inconsistent. The 0–25 mole % K_2CO_3 solidus temperatures were established by cooling to about 50° below the expected transition, holding the material at this temperature for about two hours and then heating at 1°/min. The precise composition of compound V could not be established by this technique because of the difficulty of attaining complete equilibrium below the liquidus. Samples in the range 0–16 mole % K_2CO_3 were prepared for X-ray analyses in the following manner. The charges were heated until molten and programmed to cool through the liquidus at 0.5°/min. and then held at the transitions for 24 hours prior to cooling to room temperature. At the compound line in question there should not be any Nb_2O_5 lines, but, even with this procedure for attaining equilibrium, it was not possible to precisely locate the compound. This method gave a compound range from 11.5–12.5 mole % K_2CO_3, and the mid-point was arbitrarily chosen as the compound line.

A typical time–temperature cooling curve for the region 35–50 mole % K_2CO_3 prior to the use of seeding techniques is shown in Fig. 2a. Figure 2b is the differential counterpart and Fig. 2c is the equilibrium curve obtained with seeding. It is believed that Figs. 2a and 2b do not represent simple supercooling phenomena. It is possible that a metastable phase has initially crystallized and when a lower temperature is reached the unstable crystallites undergo a transition with evolution of sufficient heat to raise the melt temperature above the temperature of initial crystallization. The seeding evidently induces nucleation of the stable phase. The cooling curves then obtained are in good agreement with the corresponding heating curves.

In the 67–100 mole % K_2CO_3 region the volatility of I necessitated the use of 15–20°/min. cooling rates with vigorous stirring through the liquidus temperature. 10°/min. cooling rates were then used to fix the solidus. No heating data could be obtained in this region because of this volatility. Similarly, the exact stoichiometry of I could not be determined by differential analysis, but was established by microscopic examination. Charges were weighed and heated in gold crucibles. The fused samples were thoroughly ground and specimens of the powders were examined using a modification of the hot wire technique described by Ordway.[8] Specimens were picked up by the hot wire and melted. The temperature was slowly lowered so that liquidus, solidus and the decomposition or phase transformation were observable. At 74 mole % K_2CO_3 the characteristic eutectic structure of the system I–II was observed. The eutectic solidification was followed by the decomposition or phase transformation of I. At 75 mole % the eutectic structure was that of the system I–K_2CO_3.

The liquidus points in this range, especially near the eutectic, were partly determined visually, because of the apparently low heat effect produced when I crystallized.

Discussion of the Phase Diagram

The equilibrium curves are represented in Fig. 3 and are based on the differential thermal analysis

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[8] F. Ordway, N.B.S. paper #61 (1952).

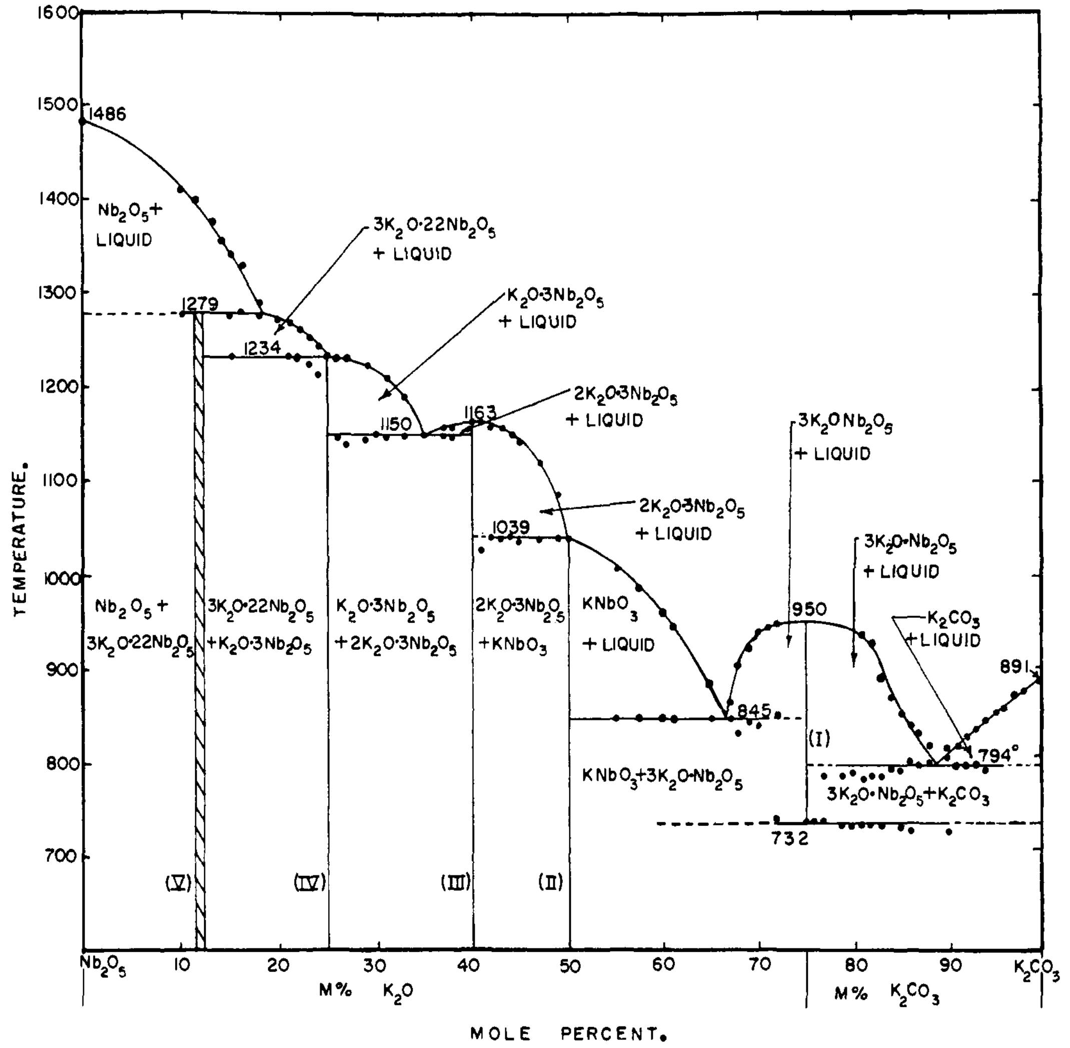

Fig. 3.—Phase diagram of the system K_2CO_3 or K_2O–Nb_2O_5.

results tabulated in Table I. It is evident from the phase diagram that, in the region 0–75 mole %, potassium carbonate serves solely as a source of K_2O. In the region 75–100 mole %, K_2CO_3 is actually present as a component of the system. Figure 3 has been explicitly labeled to indicate the exact function of the K_2CO_3. No discontinuity in the phase diagram arises since one mole % of K_2O is equivalent to one mole % of K_2CO_3.

It can be seen from the diagram that there are five compounds corresponding to the compositions: (I) $3K_2O{\cdot}Nb_2O_5$, (II) $K_2O{\cdot}Nb_2O_5$, (III) $2K_2O{\cdot}3Nb_2O_5$, (IV) $K_2O{\cdot}3Nb_2O_5$ and (V) $3K_2O{\cdot}22Nb_2O_5$. Compounds I and III melt congruently, II, IV and V melt incongruently.

The region 75–100 mole % K_2CO_3 represents equilibrium conditions between I and K_2CO_3. The eutectic point is fixed at 89 mole % K_2CO_3 and 794°.

A heat effect is observed at 732°, which may possibly be the result of a phase transformation or a decomposition. Because of the difficulty in isolating the components and because of the hygroscopic character of the cooled reaction mixtures, neither chemical nor X-ray analysis could be employed to establish the nature of the phenomenon. It is known that, in the region 50–75 mole %, compound II exists at room temperature and that from 75–100 mole %, K_2CO_3 exists at room temperature. If a decomposition is the explanation then the compound decomposing is evidently I. If the heat effect represents a phase transformation involving compound I then the diagram would be completed by extending the compound I line to the abscissa and extending the 732° tie line between 50 and 100 mole %.

The precise melting point of I could not be established, because of the high K_2O volatility in this region. Extrapolation of the solubility curves placed the melting point at about 950°. The high volatility observed is not unexpected in view of the flat congruent area which indicates extensive dissociation of I in the liquid state.

The region 50–75 mole % K_2CO_3 represents the system I–II. The eutectic is fixed at 66.5 mole % K_2CO_3 and 845°. II can be seen to melt incongruently at 1039° and 50 mole % K_2CO_3. This serves to explain some of the discrepancies concerning the melting point of II. If caution is not exercised in drying the K_2CO_3 prior to use, or if the contained moisture is not taken into account, weighed 50 mole % charges will actually contain an excess of

TABLE I

D.T.A. DATA FOR THE SYSTEM K_2CO_3 OR K_2O–Nb_2O_5

Temperature of heat effects, °C.

Compn., mole % K_2CO_3	Nb_2O_5	M.p., °C.	Liquidus	Solidus	Transition
100	0	891			
98	2		873		
97	3		870		
96	4		856		
95	5		851	793	
94	6		841	790	
93	7		834	794	
92	8		825	794	
91	9		816	795	
90	10		813	805	721
89	11		799	794	
88	12		815	798	
87	13		830	795	
86	14		837	799	723
85	15		840	790	726
84	16		867	789	731
83	17		889	781	727
82	18		927	781	730
81	19		936	779	730
80	20			787	730
79	21			783	731
77	23			783	735
76	24				735
75	25				735
72	28		947	845	
71	29		943		736
70	30		939	839	
69	31		924	840	
68	32		910	830	
67	33		863	844	
65	35		879	845	
61	39		944	844	
60	40		957	844	
57.5	42.5		985	848	
55	45		1005	843	
50	50	1039			
49	51		1085	1039	
47	53		1120	1039	
45	55		1141	1037	
44	56		1153	1042	
43	57		1157	1039	
42	58		1159	1039	
41	59		1163	1025	
40	60	1163			
38	62		1157	1147	
37	63		1156	1150	
35	65			1151	
33	67		1191	1151	
31	69		1208	1149	
30	70			1150	
29	71		1224	1145	
27	73		1231	1141	
26	74		1232	1147	
25	75	1234			
24	76		1244	1213	
23	77		1253	1225	
22	78		1262	1232	
21	79		1270	1232	
20	80		1272		
18	82		1291		1279
16	84		1331		1281
15	85		1343	1234	1278
14	86		1358		
13	87		1377		
11	89		1400		
10	90		1411		1280
0	100	1486			

Nb_2O_5. As the ascending curve from the peritectic is quite steep, slight non-stoichiometry will result in appreciably higher melting points. Similarly, porcelain thermocouple protective capsules as used by Lapitskii[7] will result in incorrect melting points because of the reaction of II with the porcelain. The 50–67 mole % region is seen to be the only one suitable for growth of crystals of II; and the most promising dielectric crystals have been grown from 55 mole % K_2CO_3. The crystals extracted from this melt were white, but had a rather high conductivity for a good dielectric. The white crystals however had lower conductivity than any of the other, colored, varieties, with $\rho = 5.06 \times 10^8$ ohm cm.

The tendency of II to lose oxygen, especially in the vicinity of the peritectic, was quite marked. Weight losses of the order of 0.1% accompanied the reduction and the crystals exhibited dark blue to black coloration. Very slow cooling of the melt in an oxygen atmosphere gave pale yellow to white crystals. X-Ray studies of these crystals showed them to be orthorhombic, with lattice constant in agreement with previous reports.[3,4]

The system II–III is seen to exist from the peritectic at 50 mole % to the congruency at 40 mole %. III melts at 1163° and the region 25–40 mole % K_2CO_3 depicts the binary system III–IV. The eutectic in this system is present at 35 mole % K_2CO_3 and 1150°. The white crystals of III were found to be birefringent, and similar in appearance to mica, having a lamellar type of growth. Crystals of IV were pale yellow rectangular plates exhibiting birefringence.

Equilibrium conditions between IV and V exist from the peritectic at 25 mole % and 1234° to the peritectic at 18.5 mole % and 1279°. V reacts at 1234° according to eq. 1.

$$\text{V} + \text{liq.} \longrightarrow \text{IV} + \text{cal.} \qquad (1)$$

Crystals of V were found to be white, and fibrous in appearance.

The region from 12 to 18.5 mole % shows equilibrium between Nb_2O_5 and V and then between V and IV. The reactions involved are given by (eq. 2 and 1), respectively.

$$\text{Nb}_2\text{O}_5 + \text{liq.} \longrightarrow \text{V} + \text{liq.} + \text{cal.} \qquad (2)$$

In the region 0–12 mole % K_2CO_3 the equilibrium between Nb_2O_5 and V is shown with the reaction at the transition given by eq. 3

$$\text{Nb}_2\text{O}_5 + \text{liq.} \longrightarrow \text{V} + \text{cal.} \qquad (3)$$

The melting point of Nb_2O_5 has been reported as 1520° and more recently by Orr[9] as 1512°. Orr discusses a premelting phenomenon with a melting range of 1477–1512°. Table I shows the freezing point obtained in this study to be 1486° with no premelting apparent in the heating curves. X-Ray analysis of the compounds reported is presently in progress and will be presented at a later date.

(9) R. L. Orr, THIS JOURNAL, 75, 2808 (1953).

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NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Phase Relations in the System Sodium Oxide–Uranium Trioxide–Water at 50 and 75°[1]

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Equilibrium phase relations in the system sodium oxide–uranium trioxide–water at 50 and 75° have been investigated by phase rule methods. In addition to the terminal solids of $NaOH \cdot H_2O$ (I) and $UO_3 \cdot 2H_2O$ (VI), there are at 50° four intervening solid combinations of the two oxides, all incongruently soluble, the concentration of uranium trioxide in the liquids throughout being of the order of 10–20 milligrams per liter. For solutions almost saturated with sodium hydroxide, containing from 42.8 to 45.2% Na_2O (the solubility of $NaOH \cdot H_2O$), the saturating solid is a pink hydrated compound, solid II, with a high ratio of sodium oxide, probably 5 or 6 Na_2O per UO_3. The next solid phase, solid III, for liquid concentrations extending down to 0.0106% Na_2O, is a solid solution of considerable range in composition and ranging in color from bright orange to plain yellow. If it is anhydrous its upper sodium oxide limit is at $\sim 8Na_2O \cdot 11UO_3$, while if it is slightly hydrated it may just include the formula $Na_2UO_4 \cdot H_2O$; its lower limit is very nearly $Na_2O \cdot 3UO_3$. The familiar diuranate formula, $Na_2U_2O_7$, is therefore simply a point in the continuous range of this principal solid solution. This phase is followed, for liquid concentrations down to 0.00058% Na_2O, by the compound $Na_2O \cdot 6UO_3$, solid IV, which shows little, if any, tendency to take up adjacent solids in solid solution. There follows finally another solid solution, V, ranging approximately from $Na_2O \cdot 12UO_3$ to $Na_2O \cdot 18UO_3$, and saturation with both this solid and $UO_3 \cdot 2H_2O$ (VI) occurs at 0.00012% Na_2O in the liquid. The 75° isotherm was studied only for liquid concentrations below 30% Na_2O, showing in this region the same sequence, nature and compositions of solid phases as at 50°. The Na_2O concentrations of the three isothermally invariant liquids covered, each saturated with two solids, are lower than at 50°.

This is a report of the phase rule investigation of two isotherms of the system sodium oxide–uranium trioxide–water. The information in the literature regarding the composition of various "uranates" of sodium and their equilibrium relations is somewhat fragmentary and conflicting. Reference works in inorganic chemistry mention both the "normal" or mono-uranate, such as Na_2UO_4, from high temperature reactions, and a variety of "polyuranates," particularly the diuranates, both of sodium and of potassium, presumably known as definite compounds. The actual information, however, is meager, especially with regard to the question of equilibrium relations in aqueous systems.

"$Na_2U_2O_7$" has been reported as formed by high temperature reactions,[2] and from the ignition of precipitates obtained from uranyl salt solutions treated with excess of sodium hydroxide. The considerable variation in the final composition of such precipitated products has been attributed to a variety of effects. Jolibois and Bossuet,[3] observing the sodium oxide content to vary from 1 or 2 up to 8%, considered the precipitate to be merely hydrated uranium trioxide with adsorbed sodium hydroxide. Metzger and Heidelberger[4] reasoned that the original precipitate was probably actually $Na_2U_2O_7$ but that it suffered decomposition in washing to bring the composition down to the observed values of $9Na_2O \cdot 20UO_3$ and $2Na_2O \cdot 5UO_3$. Bersohn and Brady[2b] not only noted this important effect of washing in changing the composition of the solid before analysis but even suggested that the original solid might have been itself variable, in the nature of a solid solution. The results of the present investigation corroborate this surmise. With regard to the corresponding compound "$(NH_4)_2U_2O_7$," which had also been reported in the early literature,[5] we may note that Carston and Norton[6] failed in their attempt to prepare a solid of exactly such composition.

Still other formulas have been reported for precipitates obtained in connection with the study of the *p*H titration curves for the reaction of sodium hydroxide with uranyl salt solutions. The questionable nature of these results is apparent when it is noted that the first precipitate in such a neutralization is probably hydrated uranium trioxide, and that it would be very unlikely that equilibrium of solid phases would subsequently hold during the continued neutralization. On the basis of the characteristics of the *p*H titration curve, although without direct analysis, Britton[7] inferred that the first precipitate was "uranyl hydroxide." Similarly, in a study of the action of calcium hydroxide on uranyl nitrate solution, the first precipitate was found to contain hardly any calcium.[8] Guiter has reported the compound $2Na_2O \cdot 7UO_3$ as being formed in the titration of uranyl nitrate at room temperature,[9] and the compounds $Na_2O \cdot 4UO_3$ and $Na_2O \cdot 8UO_3$ from uranyl acetate solutions at room temperature and at the boiling point, respectively.[10] In the titration of uranyl nitrate, Wamser, Belle, Bern-

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[1] This work was supported by the United States Atomic Energy Commission under Contract No. AT.(30-1)-1256 with New York University. Part of the work described was done by F. J. Loprest in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] (a) C. Zimmermann, *Ann.*, **213**, 285 (1882); (b) R. Bersohn and E. L. Brady, U.S.A.E.C. literature, Mon. C-109, March, 1946.

[3] P. Jolibois and R. Bossuet, *Compt. rend.*, **174**, 1625 (1922).

[4] F. J. Metzger and M. Heidelberger, THIS JOURNAL, **31**, 1040 (1909). This paper contains references to earlier work on these precipitates.

[5] E. Peligot, *Ann.*, **43**, 255 (1842).

[6] A. I. Carston and T. H. Norton, *Am. Chem. J.*, **10**, 219 (1888).

[7] H. T. S. Britton, *J. Chem. Soc.*, **127**, 2148 (1925).

[8] C. Tanford, R. L. Tichenor and H. A. Young, AECD-2653, Feb., 1945.

[9] H. Guiter, *Bull. soc. chim. France*, 403 (1946).

[10] H. Guiter, *ibid.*, 275 (1947).