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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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(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).

sohn and Williamson[11] reported the formation of $3Na_2O{\cdot}7UO_3$ and $Na_2O{\cdot}7UO_3$. These investigators made X-ray diffraction measurements on mixtures of the solids, and they further reported that the two compounds exist not only as anhydrous entities but also, in each case, as hydrates with both 12 and 16 moles of water per "formula." At the same time, however, they noted the effect of washing in changing the final composition.

The only previous phase rule study involving alkali "uranates" seems to be that of Flatt and Hess[12] on a portion of the quaternary system uranyl nitrate–potassium hydroxide–water, at room temperature and at the boiling point. The few measurements made indicated, but not very precisely, the formation of solids of the compositions $2K_2O{\cdot}5UO_3$ and $K_2O{\cdot}7UO_3$.

The relations in very high concentrations of alkali, or up to saturation with either sodium hydroxide or potassium hydroxide, were not studied in any of the previous work.

It seemed desirable therefore to attempt to determine the actual equilibrium phase relations in the system sodium oxide–uranium trioxide–water, especially since the information so obtained might be expected to prove useful in connection with certain uranium recovery processes. The various difficulties to be expected in such a study were already known. The solids involved are not well crystallized when formed from aqueous reactions, and they are incongruently soluble, so that they are decomposed by washing, separated only imperfectly from mother liquor, and not obtainable in a pure state for direct analysis. In addition, the solubilities involved are very low, and equilibrium with respect to solid phases is expected to be approached with extreme slowness, especially in low alkali concentrations. If an equilibrium state could be approached in a fairly satisfactory manner, however, it seemed possible that the compositions of the solids might be determined by the indirect methods of isothermal phase diagrams.

The general plan then was to prepare synthetic "complexes" or mixtures of known quantities of the three components, to bring these to equilibrium by stirring at constant temperature, to analyze the liquid phase, and from the two compositions involved for each experiment to extrapolate the tie-line to the composition of the saturated solid or mixture of solids.[13]

Materials and Analysis.—The uranium trioxide was supplied, in two ten-pound batches, by the United States Atomic Energy Commission. The uranium content was determined both by ignition to U_3O_8 at 1000° and by the standard procedure[14] of reduction with zinc in a Jones reductor, treatment with air to adjust the oxidation state to IV, and titration with ceric sulfate or potassium permanganate, either potentiometrically or, more conveniently, with ferroin as indicator. These solutions were standardized both with iron and with pure black oxide, U_3O_8.[15] The two samples of the yellow trioxide contained some water (about 1 and 5%, respectively); also, since the titration results were higher than those by ignition in both cases, the discrepancy indicated the probable presence of nitrate, amounting to about 2% and 1% in terms of uranyl nitrate, respectively. The presence and the amount of nitrate were then verified by colorimetric determination, performed with a Beckman model B spectrophotometer, involving the extent of decoloration of a constant amount of indigo carmine,[16] by comparison with known standards containing nitrate.

The material was therefore purified, in 50-g. batches, by boiling in a large quantity of water, followed by washing, filtration and drying. The product contained less than 0.1% of nitrate, determined by a spot test with brucine, as described by Feigl.[17] Many experiments were run with this purified uranium trioxide, but all of them were eventually discarded, as it became evident that the solid used failed to come to equilibrium in the aqueous system in any reasonable time.

All the experiments reported were run with a more active form of uranium trioxide prepared from the peroxide essentially according to a procedure described by Kraus.[18] The original uranium trioxide was dissolved in nitric acid and treated at 90°, with 10% H_2O_2 solution added dropwise and very slowly, with vigorous stirring, to precipitate the peroxide. Too rapid addition of hydrogen peroxide gives a non-settling precipitate which cannot be washed by decantation or filtration. After thorough washing on a büchner funnel, the peroxide, prepared in 50-g. batches, was finally converted to the trioxide (dark orange in color as compared to the original yellow material) by ignition, with occasional grinding, for about ten hours at 250–300°. The product, partially hydrated UO_3, contained only negligible amounts of peroxide, of U^{IV} and of nitrate (the latter not greater than 0.05 to 0.1%), and its UO_3 content, assayed as U_3O_8, varied, in the various batches, between 94.7 and 98.7%.

In solutions of very low uranium content the uranium was determined by a spectrophotometric method involving dibenzoylmethane, recently described by Yoe, Will and Black.[19] The absorption measurements were made both with the model B and with the model DU Beckman instruments.

The sodium oxide for the ternary complexes was introduced by weight as carbon dioxide-free sodium hydroxide solutions of known concentrations. The sodium oxide content of the final saturated solutions of the ternary system was determined either by titration or by flame photometry, depending on the size of sample and its concentration. Titrations were made with various standard sulfuric acid solutions (from 0.1 to 1 *N*) by means of weight burets, with methyl red as indicator, carbon dioxide being boiled out at the end-point. The Beckman model B spectrophotometer with flame attachment was used for the flame photometry measurements, which were based on calibration curves prepared with various standard sodium chloride solutions. In a few cases the sodium content was determined gravimetrically by weighing as NaCl after evaporation with aq. HCl, this being possible because the uranium oxide content was negligible. In the analysis of aliquots of wet residues the sodium was determined either with the flame photometer or gravimetrically as the triple sodium–zinc–uranyl acetate; in these wet residue analyses the uranium content was determined by titration.

Experimental Procedure.—For the majority of the experiments, covering the range below about 30% Na_2O in the liquid, complexes, ranging from 150 to 300 g. in total weight, were prepared, in long-necked round-bottom Pyrex flasks, from known weights of assayed UO_3, NaOH solution and water. Each flask was clamped in position, almost totally immersed, in a large constant temperature water-bath, and it was fitted with the stainless steel two-bladed stirrer of an individual stirring motor, run at about 1000 r.p.m. The stirring shaft was passed through a close fitting hole in layers of "parafilm" and filter paper at 50°, and of filter paper and aluminum foil at 75°, closing the mouth of the flask, and sealed around its rim with cellophane tape. This arrange-

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(11) C. A. Wamser, J. Belle, E. Bernsohn and B. Williamson, THIS JOURNAL, **74**, 1020 (1952).

(12) R. Flatt and W. Hess, *Helv. Chim. Acta*, **21**, 1506 (1938).

(13) A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

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(16) C. J. Rodden, editor-in-chief, "Analytical Chemistry of the Manhattan Project," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 213.

(17) F. Feigl, "Qualitative Analysis by Spot Tests," 2nd ed., Nordemann Publ. Co., Inc., New York, N. Y., 1939, p. 212.

(18) C. A. Kraus, U.S.A.E.C. literature, A-360, Oct., 1942.

(19) J. H. Yoe, F. Will and R. A. Black, *Anal. Chem.*, **25**, 1200 (1953).

ment was found to be convenient for continuous vigorous agitation, carried on in some cases for a total of 16 days, and it did not result in too much evaporation. Evaporation caused a change in the calculated composition of the total complex being stirred, and for the purpose of the necessary correction to be applied the extent of evaporation was determined by recording the loss of weight of the flask and contents (including the stirrer). On the basis of several experiments followed in this way the average rate of evaporation at 50° was found to be ~ 0.3% by weight per day for solutions containing not more than ~20% Na_2O. For higher concentrations the change was negligible and at very high concentrations, near saturation with sodium hydroxide, there was actually a gain in weight. At 75°, the evaporation for dilute solutions was ~0.06% per hour, falling off somewhat for the highest concentrations. Absorption of carbon dioxide by the alkaline solutions was found either negligible or entirely absent, on the basis of differential titration with two indicators.

For analysis of the solution after a certain period of stirring, the flask was first allowed to stand at room temperature for the solid to settle, if it would settle at all. Samples of the liquid were then taken either by centrifuging or by suction filtration through ultrafine sintered glass büchner-type funnels. For solutions of very low concentration the sodium oxide content of the first portions filtered was usually too low, and it was necessary to establish, by many tests on a variety of samples, a suitable procedure ensuring that after the discarding of a certain number of "washing" or "priming" portions, a sample would be obtained representing the final constant value for the solution being analyzed. In many cases successively filtered portions were analyzed until constant, regardless of the pre-established routine. The first portion, moreover, often was turbid, but the retention of solid improved after a distinct layer of it had accumulated on the filtering disc.

After sampling and analysis the complex was returned to the thermostat for further stirring, and the procedure was repeated in order to verify the attainment of equilibrium. For the experiments at 50° dealing with liquid concentrations below 0.05% Na_2O, from three to eight such successive analyses were generally necessary. In some cases the material remaining from a completed experiment was then used as the start of a new total complex, after addition of further small quantities of the components. In addition to the desirability of economizing in material, this procedure made it possible to start with the solid phase or phases already close to the new equilibrium state being investigated.

Since the greatest difficulty in the low alkali region seemed to be the slowness with which the mixtures came to equilibrium, several variations were tried in the order of mixing, in stirring of the uranium trioxide with water before addition of the sodium hydroxide solution, etc., but with no observable improvement in any case.

While the experiments at 75° were carried only to ~30% Na_2O in the liquid, those at 50° were extended to saturation with $NaOH \cdot H_2O$. In this high alkali region preliminary experiments were made with "open compexes" as described above, but on a smaller scale, for the sake of the very effective high speed stirring thus possible. It was found, however, that the solutions took up water from the air so irregularly that the total complex composition at the time of analysis of the liquid phase became too uncertain. Since these experiments did indicate that equilibrium in this region was being attained much more rapidly than in the dilute region, the final experiments for the high concentration region were made in closed tubes without internal stirring, and simply rotated on a wheel in the water-bath for periods up to 10 days. Re-analysis showed that the stirring time used had been sufficient. The liquid phase in these experiments, very close to or at saturation with sodium hydroxide, could be neither filtered nor centrifuged, because the temperature could not be allowed to fall. The mixtures were simply allowed to settle in the water-bath, and the clear liquid was rapidly withdrawn through a hot pipet for analysis.

Results and Discussion

Relations at 50°.—The principal data for the experiments at 50° are listed in Table I. Columns *A* and *B* give the composition of the total complex as calculated from the weights of the components

TABLE I

THE SYSTEM Na_2O–UO_3–H_2O AT 50°

In weight percentage.

No.	*A* % UO_3 in complex	*B* % Na_2O in complex	*C* % Na_2O in liquid	*D* % Na_2O in "solid"	Hr. stirring	Notes on method
Liquid + solid I ($NaOH \cdot H_2O$)						
1	0	...	45.20		4	*a,j*
Liquid + solid I + solid II						
2	0.3	48	45.15	95	6	*a,i*
3	1.74	45.61	45.25	54.4	2	*a,i*
4	5.12	45.08	45.26	43.3	18	*a,i*
5	9.4	44.1	45.16	38	36	*a,i*
6	9.65	43.67	45.15	35.2	18	*a,i*
7	9.87	43.47	45.18	33.7	18	*a,i*
Liquid + solid II (hydrated compound)						
8	3.89	43.78	44.28	36.1	144	*a,j*
9	5.40	43.59	44.26	36.4	240	*a,j*
10	3.91	43.33	43.88	34.7	144	*a,j*
11	5.47	43.23	43.82	37.0	240	*a,j*
12	5.30	42.83	43.62	33.8	96	*a,j*
13	3.86	42.86	43.33	35.5	144	*a,j*
14	5.41	42.42	43.15	34.3	240	*a,j*
Liquid + solid II + solid III						
15	5.46	42.25	43.07	33.0	216	*a,j*
16	5.46	42.12	42.94	32.9	240	*a,j*
17	3.88	42.26	42.91	31.4	144	*a,j*
18	5.44	41.80	42.98	27.2	240	*a,j*
19	5.43	41.55	42.75	26.5	216	*a,j*
20	5.38	41.38	42.77	23.7	216	*a,j*
21	5.39	41.17	42.66	20.8	240	*a,j*
22	5.41	40.78	42.42	17.4	240	*a,j*
23	5.46	40.87	42.54	17.2	240	*a,j*
Liquid + solid III (solid solution)						
24	5.66	40.40	42.26	14.00	360	*a,j*
25	5.39	39.43	41.18	12.90	168	*a,j*
26	5.46	38.37	40.09	12.54	168	*a,j*
27	5.44	37.42	39.10	11.89	168	*a,j*
28	12.94	34.37	38.31	11.50	3	*a,g*
29	5.40	36.35	37.95	11.82	168	*a,j*
30	5.48	35.45	37.00	12.15	168	*a,j*
31	9.73	33.91	36.66	11.91	2	*a,g*
32	5.41	34.47	35.94	12.04	168	*a,j*
33	12.79	26.26	28.85	11.06	5	*a,g*
34	13.10	18.59	19.98	10.59	3	*a,g*
35	9.772	17.874	18.79	10.36	2	*a,g*
36	8.889	15.533	16.11	10.3	5	*a,g*
37	3.173	14.774	14.93	10.6	5	*a,g*
38	8.403	9.532	9.458	10.3	4	*a,g*
39	7.256	7.630	7.408	10.22	5	*a,g*
40	6.861	6.353	6.037	10.23	4	*a,g*
41	5.233	3.657	3.255	10.19	4	*a,g*
42	5.460	2.549	2.062	10.09	4	*a,g*
43	5.410	1.971	1.462	9.95	4	*a,g*
44	5.508	1.320	0.770	9.79	13	*a,g*
45	1.817	0.778	.592	9.88	26	*a,g*
46	17.058	2.196	.420	9.84	115	*a,g*
47	5.0916	0.8992	.381	9.60	24	*a,g*
48	4.7788	.7459	.257	9.60	40	*a,g*
49	0.7055	.2659	.1943	9.57	62	*a,g*
50	2.925	.4666	.184	9.00	17	*b,h*
51	0.7535	.2558	.1791	9.46	23	*a,g*
52	2.954	.4501	.161	9.07	17	*b,h*
53	2.964	.4297	.145	8.89	17	*b,h*
54	1.324	.2540	.124	9.04	16	*b,h*
55	1.9214	.3115	.123	9.04	22	*b,d,h*
56	2.960	.4158	.1208	9.19	21	*a,b,g*
57	5.011	.5775	.0958	8.86	31	*b,c,h*
58	5.044	.5497	.0713	8.73	35	*b,h*
59	5.070	.5213	.0544	8.48	24	*b,h*
60	1.348	.1498	.0304	8.16	7	*b,h*
61	1.357	.1342	.0196	7.80	7	*b,h*
62	0.2326	.03404	.0176	6.66	65	*b,h*
63	1.373	.1276	.0151	7.59	7	*b,h*
64	0.2524	.03221	.0146	6.59	65	*b,h*
65	3.154	.2580	.014	7.19	35	*b,h*

TABLE I (*Concluded*)

No.	*A* % UO_3 in complex	*B* % Na_2O in complex	*C* % Na_2O in liquid	*D* % Na_2O in "solid"	Hr. stirring	Notes on method
Liquid + solid III + solid IV						
66	3.165	0.2315	0.0119	6.50	56	*b,h*
67	0.1872	.0232	.0104	6.46	120	*b,h*
68	1.394	.0996	.0091	6.11	72	*b,h*
69	0.4999	.0403	.0083	6.03	15	*b,d,e,h*
70	0.2543	.02875	.0127	5.99	64	*b,h*
71	3.479	.2286	.0080	5.98	72	*b,h*
72	0.4608	.0381	.0111	5.56	64	*b,g,h*
73	.4994	.0353	.0085	5.12	15	*b,d,e,h*
74	.2239	.0222	.0109	4.88	87	*b,h*
75	.2304	.0238	.0123	4.79	87	*b,h*
76	3.221	.1702	.0113	4.71	127	*b,h*
77	0.2100	.0212	.0111	4.69	140	*b,h*
78	.4676	.0323	.0102	4.54	68	*b,g,h*
79	0.9896	.01374	.0092	4.42	44	*b,h*
80	3.221	.1596	.0127	4.38	135	*b,d,h*
81	0.2318	.0212	.0109	4.30	87	*b,h*
82	0.6183	.0358	.0115	3.82	114	*b,g*
83	3.253	.1366	.0128	3.69	93	*b,h*
Liquid + solid IV ($Na_2O \cdot 6UO_3$)						
84	0.4995	0.03045	0.0108	3.82	125	*b,d,e,h*
85	3.2543	.1391	.0094	3.85	114	*b,h*
86	0.09886	.01305	.0092	3.8	67	*b,h*
87	.1012	.0123	.0086	3.6	91	*b,g*
88	.4725	.0269	.0081	3.85	64	*b,g,h*
89	1.4380	.0607	.0080	3.55	117	*b,h*
90	0.1008	.0116	.0076	3.9	44	*b,h*
91	0.1016	.0109	.0075	3.4	136	*b,h*
92	3.214	.1243	.0073	3.53	136	*b,d,h*
93	0.4997	.0254	.0065	3.67	84	*b,d,e,h*
94	.1021	.0102	.0063	3.7	91	*b,h*
95	.1017	.0094	.0057	3.6	64	*b,h*
96	1.4416	.0579	.0056	3.51	106	*b,h*
97	0.1022	.0090	.0054	3.4	64	*b,h*
98	1.437	.0599	.0045	3.72	89	*a,h*
99	0.1009	.00805	.0044	3.5	64	*b,h*
100	.1016	.0074	.0039	3.4	64	*b,h*
101	.4966	.0215	.0033	3.53	98	*b,h*
102	.1016	.0068	.0033	3.3	43	*b,h*
103	1.4453	.0551	.0030	3.52	52	*b,h*
104	0.1027	.0063	.0028	3.3	43	*b,h*
105	1.4473	.0532	.0022	3.41	22	*b,h*
106	1.4463	.0533	.0022	3.41	22	*b,h*
107	0.0986	.0057	.0022	3.4	66	*b,h*
108	0.4997	.0203	.0021	3.52	41	*b,d,e,h*
109	1.441	.0525	.0020	3.38	22	*b,h*
110	0.4962	.0194	.0016	3.47	22	*b,f,h*
111	3.3004	.1031	.0011	2.99	73	*b,h*
112	0.1002	.0045	.0010	3.4	240	*b,h*
113	.1002	.0041	.0009	3.1	240	*b,h*
114	.5010	.0171	.0008	3.15	260	*a,g*
115	.5396	.01799	.00050	3.15	300	*b,h*
116	.5277	.01797	.00045	3.22	123	*b,f,h*
117	3.4651	.1181	.00045	3.28	114	*b,h*
118	0.5010	.01708	.00045	3.22	130	*b,f,h*
119	0.4516	.01656	.00040	3.46	100	*b,h*
Liquid + solid IV + solid V						
120	.5156	0.01603	0.00043	2.94	123	*b,h*
121	.5070	.01507	.00044	2.81	123	*b,h*
122	3.292	.08935	.00077	2.62	159	*b,d,h*
123	0.09789	.00333	.00086	2.48	136	*b,h*
124	.5041	.01297	.00045	2.42	160	*b,h*
125	.5138	.01193	.00071	2.14	19	*b,h*
126	.5132	.01110	.00059	2.01	16	*b,f,h*
127	3.3247	.06880	.00068	2.01	76	*b,h*
137 (4)			.00081	1.92	68	*b,d,e,g*
128	0.09856	.00255	.00062	1.81	21	*b,h*
129	.4481	.00870	.00053	1.79	100	*b,h*
130	.5019	.00950	.00048	1.77	200	*b,h*
136 (3)			.00069	1.77	30	*b,d,e,g*
137 (3)			.00064	1.75	22	*b,d,e,g*
131	.09514	.00200	.00043	1.62	21	*b,h*
136 (2)			.00049	1.59	32	*b,d,e,g,h*
137 (2)			.00044	1.59	32	*b,d,e,g,h*
Liquid + solid V (solid solution)						
132	.4957	.00805	0.00030	1.54	16	*b,f,h*
133	.4956	.00805	.00028	1.58	16	*b,d,h*
136 (1)			.00021	1.43	20	*b,d,e,h*
137 (1)			.00020	1.43	20	*b,d,e,h*
139 (2)			.00018	1.22	60	*b,d,e,g,h*
134	.4243	.00587	.00018	1.32	22	*b,d,h*
135	.4244	.00587	.00016	1.33	22	*b,f,h*
Liquid + solid V + solid VI ($UO_3 \cdot 2H_2O$)						
136			0.00012	1.23→0	24	*b,d,e,g*
137			.00012	1.23→0	24	*b,d,e,g*
139 (1)			.00014	1.22	22	*b,d,e,h*
138	0.4807	0.00544	.00013	1.09	84	*b,h*
139			.00008	1.05→0	60	*b,d,e,g*
140	0.5154	0.00474	.00011	0.89	40	*b,h*

[a] Na_2O in liquid determined by titration. [b] Na_2O in liquid determined by flame photometry. [c] Na_2O in liquid determined as NaCl by evaporation with HCl. [d] UO_3 pre-stirred with water, for one hour to a day, before addition of NaOH solution. [e] NaOH solution added in successive small increments. [f] UO_3 stirred for one day with NaOH solution and 50 ml. of water before addition of further 150 ml. of water. [g] Liquid phase isolated by centrifuging. [h] Liquid phase isolated by ultra-fine filtration. [i] Liquid phase sampled by pipet after settling. [j] Complexes rotated in closed tubes (clear liquid obtained by settling); all others internally motor-stirred, open to air.

taken at the start of the run. Column *C* gives the sodium oxide concentration of the liquid phase. The value listed is that which is considered to be the most probable value representing equilibrium for the mixture. It is averaged from determinations made in a series of consecutive samplings upon repeated stirring, each sample being analyzed in duplicate in almost every case. The sixth column lists the total time of stirring to which the liquid concentration listed in column *C* corresponds.

The actual individual average analyses, for each stirring time, are listed separately in Table IA.[20] Examination of this table shows that in most of the experiments the attainment of equilibrium was definite. In some cases the final values were not quite constant, but it was nevertheless clear that the system was not far from equilibrium. It will be seen later, moreover, that the effect of small uncertainties in the final value of % Na_2O in the liquid upon the calculation of the composition of the solid phase, at least for experiments with liquids with very low sodium oxide concentration, is very small.

Although the uranium content of the liquids was also determined in many cases, the values found are not included in Table I. The values were erratic and not reproducible, and the most that can be said is probably simply that the solubility of uranium trioxide in these solutions is roughly of the order of 10 mg. per liter. The difficulties may have been partly in analysis, partly in imperfect separation of solid suspensions from the liquid to be analyzed, and partly in the possible effect of traces of carbon dioxide absorbed during the stirring; but the principal difficulty was probably the lack of attainment of true solubility equilibrium. There seems to be no question that equilibrium was

(20) This table, and the similar Table IIIA mentioned later, for the data at 75°, have been deposited as Document number 4426 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints, or $1.25 for 35 mm. microfilm in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

attained in the experiments with respect to the formation of the correct solid phases as function of the sodium oxide concentration of the liquid. This is the process followed by successive analysis of the liquid for its sodium oxide content. But the attainment of saturation or solubility equilibrium of the solid phases with the liquid solution, which would be followed through the uranium trioxide content of the liquid, may well be a very much slower process, in view of the very low solubilities (uranium trioxide concentration in the liquid) involved.

Calculation of Composition of Solid.—Direct analysis of solid phases, satisfactorily free of mother liquor, was obviously impossible in this system. Centrifuging, and centrifuging followed by suction filtration, gave nothing better than a smooth wet paste; and continued washing could not be used because of the incongruent solubility relations of the solid phases.

What was done, therefore, was to calculate the tie-lines fixed for each experiment by the compositions of the total complex and of the liquid phase, and to consider the possible solid phase compositions on the basis of the behavior and disposition of the tie-lines in the various regions of the system. The directions of the tie-lines were determined by algebraic extrapolation to the anhydrous base of the composition triangle of the system. The percentage (D) of sodium oxide on the base of the triangle, to which each tie-line extrapolates, is calculated from the data of Table I by the formula

$$D = B + (100 - A - B)\frac{(B - C)}{(A + B) - (C + U)} \qquad (1)$$

in which U, the percentage of UO_3 in the liquid, may be neglected without error. The possible presence of nitrate to the extent of one or two parts per thousand of the uranium trioxide used is also negligible in its effect upon this extrapolation. The quantities A and B used for the calculation, moreover, were not in every case those actually listed in the table. They were first corrected if necessary, for the evaporation occurring during the stirring of the complex up to the time of the analysis of the final solution taken as representing equilibrium. [This correction simply involved dividing B or $(A + B)$ by the factor $(1 - tr)$, in which t = time and r = weight fraction lost by evaporation per unit time; $r = 0.3\%$ per day at 50°, and $\sim 1.4\%$ per day at 75°.]

Theoretically, the accuracy of such extrapolation for the solid composition depends on having the second term of equation 1 small compared to the term B, and on the precision of the differences represented by numerator and denominator of the fraction; geometrically, then, it depends on the distance, in the usual triangular plot of the ternary isotherm, between the two points fixing the tie-line involved, namely, the liquid composition and the complex composition. For this reason it would seem still better to use the analysis of a wet residue to fix the second point. Many experiments were made, in fact, by the wet residue method,[21] but they were all discarded. What would seem to be gained by the method was overbalanced by the much lower analytical accuracy with which a wet residue point could be fixed. For either method the only analytical determination necessary for fixing the liquid composition was that of sodium oxide since the uranium trioxide content was negligible. But whereas a synthetic total complex can usually be prepared with almost any desired degree of accuracy by direct weighing of the components, the wet residue has to be analyzed for both sodium and uranium, and it furthermore entails errors of handling that are difficult even to estimate. Unless, for example, the whole wet residue sample is dissolved and aliquoted for analysis, the portions used for the two different determinations do not pertain to the same total composition. But after dissolving in acid, the sodium oxide content cannot be determined by titration, but only gravimetrically or by flame photometry, and the precision thus possible is not sufficient for the distinctions in question.

The use of the total complex brings the second point of the tie-line close to the liquid composition, and it was, in addition, deliberately brought very close (which simply means that very little uranium oxide was used in the complexes), in the low alkali region because of the slowness with which the solid phases came to their equilibrium compositions even with the violent stirring used, and in the very high alkali region because of the bulkiness of the solid phase formed and the difficulty of obtaining sufficient clear liquid for analysis through settling. The approach to equilibrium was slower the lower the sodium oxide concentration of the liquid, and most of the experiments dealt with solutions containing less than 0.02% Na_2O. Actually, however, the accuracy of the extrapolation is higher in this region than in the region of higher concentrations, where more solid was used. In the higher range, the quantity $(B - C)$ of equation 1 is the difference of two large quantities, and a very high accuracy is therefore required in the titrations for both B and C. In the low alkali region, on the other hand, C is so small compared to B, except in a few cases in which extremely little solid was used, that the error of the extrapolation hardly depends on the relative accuracy of the determination of the sodium oxide content of the liquid, which was done by flame photometry. In this case the principal uncertainty is simply that resulting from the extreme slowness of equilibration of the solid phases. These relations may easily be verified by substitution of the numerical values from the table. The number of decimals recorded for D (% Na_2O on the Na_2O-UO_3 base of the composition triangle, or % Na_2O in the solid if this is assumed to be anhydrous), in Table I, is based on consideration of the uncertainties in the analysis of the liquid, in the agreement of successive analyses (Table IA), in the time of stirring, and in the rate of loss of water by evaporation. Except for experiments in very high alkali concentrations, the scattering of the experimental points seen in Figs. 2 and 5, therefore, is not the result of analytical difficulty but of incomplete equilibrium, or of a (partially) false equilibrium which persisted despite the long and vigorous stirring and despite the use of very small amounts of solid.

In a few special experiments of Table I, those

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(21) F. A. H. Schreinemakers, *Z. physik. Chem.*, **11**, 75 (1893).

numbered 136(1–3), 137(1–4) and 139(1–2), the solid composition was calculated a little differently. The final liquid and solid compositions for these experiments are listed in Table I, in order to have the results together for comparison, but the data used in calculation of the solid composition are given separately in Table II. These mixtures were based on the material remaining from a completed experiment, such as number 136 itself. Taking into account material removed for analysis from the original total complex, such as No. 136, a new total composition was prepared by addition of further small amounts of the components. Since the bulk of the original Na_2O and UO_3 was always in the solid phase, none of which, in most cases, was removed in the sampling of the liquid, the next total composition, such as No. 136(1), is known quite accurately with respect to the actual weights of UO_3 and Na_2O in it, but the total weight of the complex is known only approximately. When solid phase was also removed in the preceding sampling, the amount removed was also taken into account. The data here therefore comprise the actual weights of UO_3- ($= a$) and of Na_2O ($= b$) in the total mixture, the (approximate) total weight of the mixture ($= c$), and the percentage of Na_2O in the equilibrium liquid ($= d$). Then the percentage of Na_2O, on the anhydrous basis, in the equilibrium solid ($= e$) is calculated as

$$e = 100 \times \frac{b - d(c - a - b)/100}{a + b - d(c - a - b)/100} \qquad (2)$$

in which it is assumed, again, that the UO_3 content of the liquid is negligible, and, with altogether negligible, error, that the weight of the liquid phase is equal to $(c - a - b)$.

TABLE II

DATA FOR THE SPECIAL EXPERIMENTS IN TABLE I (50°)

No.	Wt. of UO_3 in mixture, a	Wt. of Na_2O in mixture, b	Total wt. of mixture, c	% Na_2O in liquid, d	% Na_2O in solid, e
136	2.2314	0.02818	313	0.00012	1.23
136(1)	2.2314	.03293	283	.00021	1.43
136(2)	2.2314	.03754	323	.00049	1.59
136(3)	2.2314	.04224	293	.00069	1.77
137	2.2310	.02818	311	.00012	1.23
137(1)	2.2310	.03292	265	.00020	1.43
137(2)	2.2310	.03754	320	.00044	1.59
137(3)	2.2310	.04170	290	.00064	1.75
137(4)	2.2310	.04658	345	.00081	1.92
139	2.6442	.02834	200	.00008	1.05
139(1)	2.6442	.03309	280	.00014	1.22
139(2)	2.6442	.03316	265	.00018	1.22

If a group of tie-lines radiates, practically, from the water apex of the triangle—as is obviously the case for all those involving liquids of very low alkali concentration—it is clear that they can give no information regarding the water content of the solid phase. At the same time, however, these tie-lines give the actual ratio of Na_2O to UO_3 in the solid regardless of its water content. On the other hand, if a group of tie-lines does not radiate from the water apex, they can fix even the water content of the solid if they have a common intersection in the triangle; but in the absence of such an intersection the value of D obtained by extrapolation does not represent the percentage of Na_2O in the solid unless this is actually anhydrous.

The corresponding values of C and D listed in Table I are plotted in Figs. 1 and 2. In order to show the results for the low concentration region on one diagram the vertical coördinate in Fig. 2 represents the logarithm of C (% Na_2O in the liquid) rather than the concentration itself.

The simplest interpretation of the high concentration results seems to be that suggested by the lines drawn through the points in Fig. 1; and our interpretation of the low concentration region (Fig. 2) is shown separately, for clarity, in Fig. 3. A horizontal represents an isothermally invariant solution saturated with two solid phases, and a vertical represents a range of solution concentrations saturated with a single solid of fixed composition and hence a solid "compound." Along other curves the solid composition varies with the liquid composition, representing, therefore, saturation with a solid solution of a certain range.

There are evidently then six solid phases, which will be distinguished as I for pure $NaOH \cdot H_2O$ to VI for pure $UO_3 \cdot 2H_2O$, with four intervening solid phases, II–V, containing both Na_2O and UO_3. Although the scale cannot bring out the variations in the liquid compositions near the water apex, the complete isotherm is shown in the usual triangular fashion in Fig. 4. The relations are also shown schematically, without regard to scale, in the diagram of Fig. 4a.

The most surprising of these solids is solid II, saturating liquids of composition on the roughly vertical section c-d of Fig. 1. Figure 4 shows that this solid contains more than two moles of Na_2O per mole of UO_3.

If point a, in Fig. 4a, represents the solubility of $NaOH \cdot H_2O$ in pure water at 50°, the first solubility curve, a-b, for saturation with this solid in presence of UO_3 in the liquid, is too short for detection, and the horizontal b-c, in Fig. 1, represents the solution saturated with both $NaOH \cdot H_2O$ and solid II, point b,c in Fig. 4(a). The concentration of this liquid is experimentally indistinguishable from the solubility of $NaOH \cdot H_2O$ alone, or 45.20% Na_2O, point a. The next horizontal section, d-e, represents liquid, with 42.7_8% Na_2O as its average composition, saturated with both solid II and solid III, which is clearly a solid solution covering a long range of composition. Between these invariant liquids or for concentrations between 45.2 and 42.8% Na_2O, the liquid is in equilibrium with a single solid (II), the composition of which must lie on the group of tie-lines (Fig. 4) joining the short solution curve c-d (Fig. 4(a)) and the base of the diagram at the narrow region labeled "II." These nine tie-lines, taken from points 6–14 of Table I, are not parallel to each other; nor do they have a common intersection in the triangle. They intersect irregularly; but this is the result of the low precision in the extrapolated value of D for this region, because of the inevitable uncertainties in the handling and analysis of the practically saturated sodium hydroxide solutions involved in determining both the total complex composition and the liquid composition. For

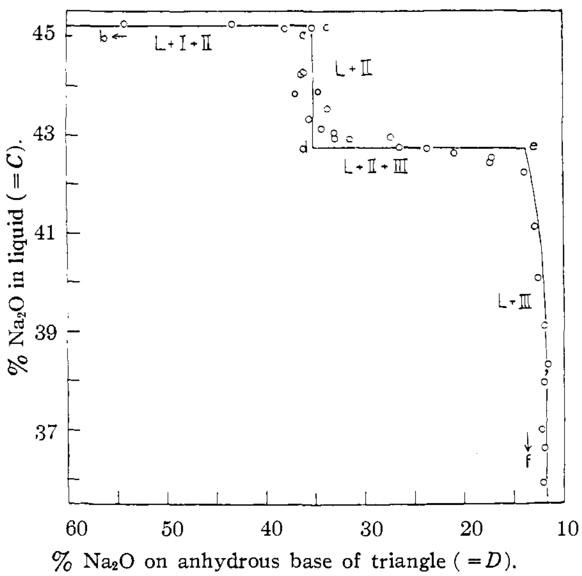

Fig. 1.—System Na_2O–UO_3–H_2O at 50°: tie-line relations for the high alkali concentration region.

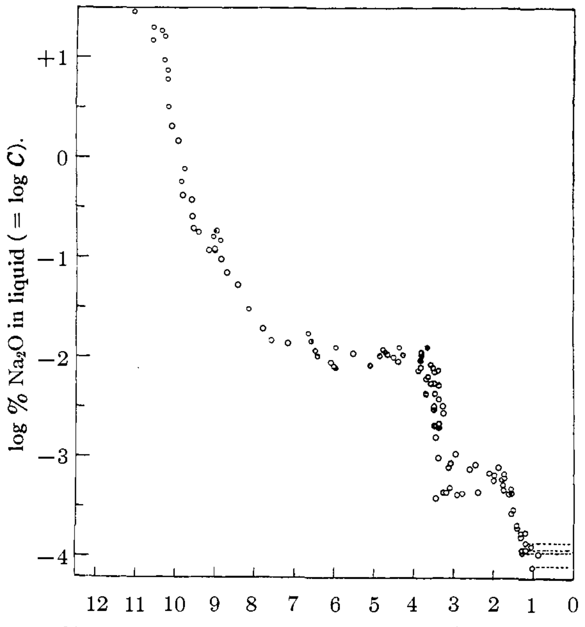

Fig. 2.—System Na_2O–UO_3–H_2O at 50°: tie-line relations for the low alkali concentration region.

an uncertainty of only one part per thousand in each of these two points fixing the tie-line the uncertainty of the extrapolated value of D at the base of the triangle is about ±1% Na_2O for a complex containing ~5% UO_3.

This solid II is bright pink in color, and along the section b-c of Fig. 1, with white solid $NaOH{\cdot}H_2O$ also present, the color varied accordingly as a mixture of the pink with white. The pink solid is extremely finely divided, and of great apparent bulkiness. Although it settles to leave a clear supernatant liquid, in some cases only 1 or 2 ml. of such liquid was visible even after many days of standing in a test-tube for a 50-g. complex containing only 5% UO_3. It seems likely therefore that this solid is hydrated, and probably rather highly hydrated.

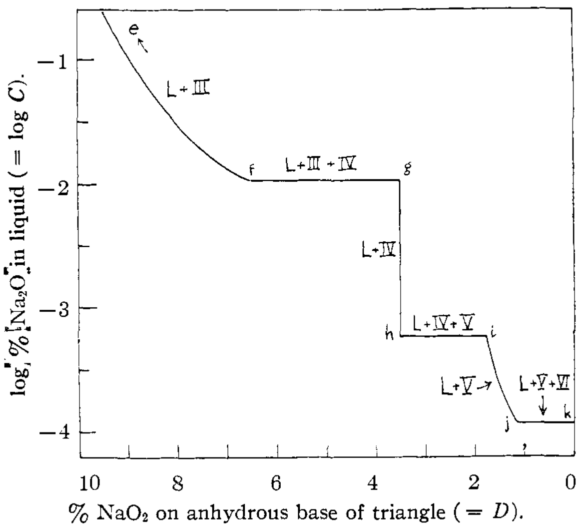

Fig. 3.—System Na_2O–UO_3–H_2O at 50°: phase relations on basis of results in Fig. 2.

If the compound were anhydrous, the extrapolations of the tie-lines to the base of the triangle would indicate, with an average of 35.2% Na_2O, a 5:2 mole ratio of Na_2O to UO_3, for which the theoretical percentage of Na_2O is 35.14. But since it is almost certainly hydrated, the Na_2O proportion must be still higher. For the mole ratios 3:1 to 6:1 the following formulas all fall on the bundle of tie-lines: $3Na_2O{\cdot}UO_3{\cdot}2H_2O$ (or $Na_2UO_4{\cdot}4NaOH$), $4Na_2O{\cdot}UO_3{\cdot}6.5H_2O$, $5Na_2O{\cdot}UO_3{\cdot}11H_2O$, and $6Na_2O{\cdot}UO_3{\cdot}15H_2O$. The agreement for either of the last two formulas is quite good, but only the last, which may be written as $Na_2UO_4{\cdot}10(NaOH{\cdot}H_2O)$, contains sufficient water for the hydration of all the excess of NaOH over "Na_2UO_4." Extrapolated to the theoretical value of 30.82% UO_3 for this formula, the nine tie-lines there give an average value of 39.9% Na_2O (average deviation, 0.5) compared to the theoretical figure of 40.07%. The intersection of the tie-lines with the line joining $NaOH{\cdot}H_2O$ and Na_2UO_4 thus occurs almost exactly (on the average) at the mole ratio 10:1.

Double compounds of "salts" with NaOH, or compounds with excess of Na_2O relative to the "acidic" oxide, are rather rare. Among those reported are $4Na_2O{\cdot}Al_2O_3{\cdot}10H_2O$ (= $8NaOH{\cdot}Al_2O_3{\cdot}6H_2O$), $2Na_2O{\cdot}B_2O_3{\cdot}H_2O$ (= $NaOH{\cdot}NaBO_2$), $NaOH{\cdot}3Na_3AsO_4{\cdot}H_2O$, $NaOH{\cdot}Na_3AsO_4{\cdot}10H_2O$ and $NaOH{\cdot}Na_2C_4H_4O_6{\cdot}3H_2O$ (tartrate).[22] The classical example is perhaps "tetrasodium chromate," $Na_4CrO_5{\cdot}13H_2O$[23] (= $2NaOH{\cdot}Na_2CrO_4{\cdot}12H_2O$).

In contrast to solid II, the next one, solid III, a solid solution, ranges in color from bright orange at its high Na_2O end (point e) to plain yellow at the low Na_2O end (point f); and while also extremely finely divided it settles more readily than does the

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[22] All cited in A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," D. Van Nostrand, N. Y., Third Edition, 1940 (Vol. I, pp. 1146, 1150), and Supplement to Third Edition, 1953 (pp. 415, 429).

[23] Ref. 22, Third Edition, p. 1255. For the phase diagram of the system Na_2O–CrO_3–H_2O at 30°, see F. A. H. Schreinemakers, *Z. physik. Chem.*, **55**, 71 (1906).

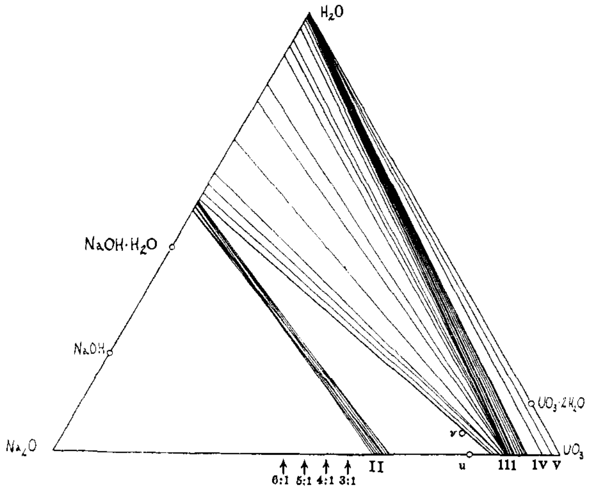

Fig. 4.—System Na_2O–UO_3–H_2O: tie-line relations at 50°; u = "Na_2UO_4," v = $Na_2UO_4 \cdot H_2O$ or $2NaOH \cdot UO_3$.

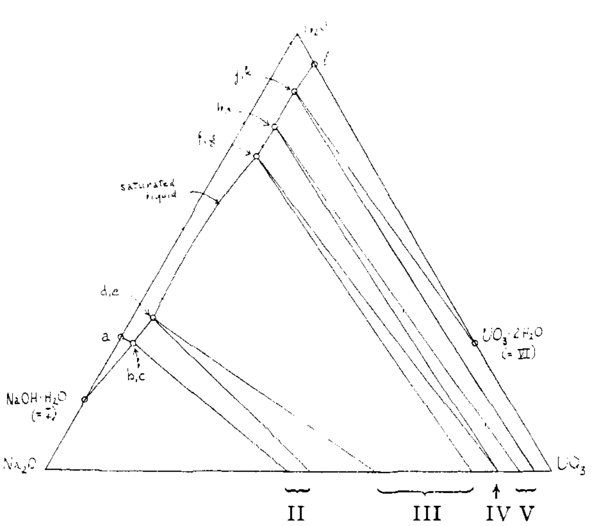

Fig. 4(a).—Schematic diagram of the phase relations at 50°.

compound II. Along the section d-e of Fig. 1, the mixture of these solids showed the expected variation of color from distinct pink to distinct orange and an immediate improvement in settling as the solid solution became part of the mixture. The change between the solids is reversible. The compound II is very incongruently soluble, being stable only in contact with highly concentrated alkali. Dilution with water rapidly changes the color from pink to orange, indicating hydrolytic decomposition of the compound to the solid solution III; the reverse change, by addition of concentrated NaOH to the yellow or orange solid, is much slower but easily observable.

The long curve labelled e-f (Figs. 1, 2, 3) represents the major part of the phase diagram (Fig. 4). Here the liquid, with alkali concentrations ranging from 42.8% Na_2O (point e) down to 0.01% Na_2O (point f), is saturated with a single continuous solid phase of variable composition. If this solid is anhydrous its composition (values of *D* in Table I, or the region "III" at the base of Fig. 4) runs from ~13.5% Na_2O (point e) to ~6.5% Na_2O (point f). (The value 6.5% Na_2O for point f is estimated not from the logarithmic plot of Fig. 2 but from a direct plot of *C* against *D* on an appropriate scale for this region.) Since there is a gap in solid composition between compound II and the edge of solid solution III, these results definitely rule out the existence, as a distinct equilibrium phase in the aqueous system at this temperature, of an anhydrous "normal" or mono-uranate, "Na_2UO_4" (theoretical % Na_2O = 17.82; point u on Fig. 4), although such a formula, as already suggested, may be involved as part of compound II.

If the solid solution III is anhydrous, then, it covers at this temperature the $Na_2O:UO_3$ mole ratios from ~8:11 (theoretical, 13.62% Na_2O) to ~1:3 (theoretical, 6.74% Na_2O), so that the "diuranate," "$Na_2U_2O_7$" (with 9.78% Na_2O), is merely a point in this range of variable solid. If the solid solution is hydrated, however, it would cover a greater range of $Na_2O:UO_3$ ratios in its composition. The solid, however, may well be anhydrous. If it is hydrated its high Na_2O edge would be some point on the limiting tie-line running to 13.5% Na_2O on the base of Fig. 4, and its edge might possibly be the formula "$Na_2UO_4 \cdot H_2O$," although the point representing this formula, with 4.92% H_2O (point v on Fig. 4), lies just outside and to the left of the limiting tie-line for the solid solution, which intersects the Na_2UO_4–H_2O line at 6.0% H_2O. If the water content of the solid solution is greater than 5–6% then its composition, according to its limiting tie-line, extends to $Na_2O:UO_3$ ratios greater than unity. The lower limit of ~1:3 for the mole ratio included in the solid solution (point f) is independent of the water content assumed for it. It seems likely, all things considered, either that this solid solution is anhydrous or that it has only a small water content.

Although the precision along some parts of the curve e-f is not high, it is nevertheless clear that the solid solution is continuous between the limits e and f, with no sufficient evidence of any break, or invariance in the liquid composition, to suggest a discontinuity in the solid solution. The middle part of the curve is very steep (Figs. 1, 2), so that over a considerable range of sodium oxide concentrations in the liquid the solid phase composition is almost constant, near ~10.3% Na_2O; but this does not correspond to any very simple mole ratio of the oxides. In terms of Fig. 4, this means a tendency for the tie-lines in this region to converge at a point on the base of the diagram. This possibility of a practically invariant composition at some point in the solid solution range vanishes, however, if the solid solution is hydrated, for then its composition lies somewhere above the base of the triangle.

(Figure 4 shows only a few of the actual tie-lines for the region Liquid + Solid III, and only a single token tie-line for each of the subsequent regions, Liquid + Solid IV and Liquid + Solid V.)

The solid solution III is the sole saturating phase for liquid compositions ranging from point e to point f, where the curve (Fig. 2) again becomes horizontal, indicating the appearance of an additional solid phase, solid IV. The horizontal f-g (Fig. 3) therefore represents a third isothermally invariant solution, saturated with the limit f of solid solution III and with solid IV. The concentration of sodium oxide in this solution, 0.0106%, is averaged from points 66–85 of Table I, with an average deviation of 0.0012. The range of solid composition (mixture of two solids) in equilibrium with this liquid is from 6.5% Na_2O (point f) to 3.5% Na_2O (point g).

Since the section g-h (Figs. 2, 3) is fairly vertical, the solid IV which saturates these liquids (between 0.0106 and 0.00058% Na_2O) appears to be one of fixed composition rather than a solid solution. Points 82–119 of Table I may be attributed to this section, and the average solid composition given by these points is 3.49% Na_2O, with an average deviation of 0.18 and with extremes of 3.9 and 3.0. The composition is therefore very close to the formula $Na_2O{\cdot}6UO_3$, with a theoretical sodium oxide percentage of 3.49; the theoretical values for the 1:5 and the 1:7 formulas are 4.16 and 3.00, respectively. There is a slight trend in the solid compositions, with higher values near point g and lower values near point h, but in view of the scattering of the points, the solid may be taken to be either a pure, definite compound or a solid solution of short range on either side of the 1:6 compound.

As may be seen from Fig. 2, the data for the horizontal section h-i of Fig. 3 are rather poor at this temperature, the attainment of equilibrium in this region being persistently slow. The simplest interpretation, however, is that this is a horizontal section representing a fourth isothermally invariant solution, now saturated with solid IV and with the limiting composition of another solid solution phase, at point i. The 24 points 113–137(2) of Table I give an average of 0.00058% Na_2O as the concentration of this liquid, with an average deviation of 0.00014, while the solid composition (mixture) ranges from 3.5 to ~1.7 or 1.8% Na_2O (point i). The next section of the curve of Fig. 3, or i-j, represents saturation with a solid solution, solid V, containing from 1.7 or 1.8 to 1.1 or 1.2% Na_2O, or covering the $Na_2O:UO_3$ mole ratios between ~1:12 and ~1:18. The interpretation of the section h-i as a horizontal for saturation with solids IV and V, although somewhat questionable on the basis of the 50° data alone, is strongly corroborated by the much clearer relations observed at 75° (Fig. 5).

Finally, the horizontal j-k represents the last isothermally invariant solution, that for saturation with solid V (point j) and $UO_3{\cdot}2H_2O$ (solid (VI)). The last six points of Table I give 0.00012% Na_2O as the concentration of this solution, with an average deviation of 0.000013. (There must also be a curve "k-l," of course, for saturation with $UO_3{\cdot}2H_2O$ alone, but this, like that for $NaOH{\cdot}H_2O$, was not detectable; Fig. 4(a).) The actual constancy of the liquid composition in this region was observed by starting with suspensions of $UO_3{\cdot}2H_2O$ in pure water and then adding successive small increments of very dilute NaOH solution. The original suspensions had the sodium content of the water used, namely, ~0.00005% Na_2O. Then through seven successive additions of NaOH solution in experiment 136, for example, the analysis gave repeatedly 0.00012% Na_2O (in each case also constant with time), up to and including the total composition for the mixture recorded in Table II as No. 136. At this point, then, the solid, with 1.23% Na_2O, was a mixture of $UO_3{\cdot}2H_2O$ and a solid solution of the composition of point j. With the next addition of sodium oxide, to give the total composition of complex No. 136(1) of Table II, the equilibrium concentration of sodium oxide in the liquid began to rise, and the percentage of sodium oxide in the solid also rose, so that we were now dealing with curve i-j of Fig. 3. Further additions of sodium oxide, with equilibration and analysis, gave the subsequent points of the series, 136(2) and 136(3). Similar procedures and observations are involved in the series numbered 137 and 139.

Relations at 75°.—A portion only of the 75° isotherm of the system was investigated, for the purpose of verifying the relations in the low alkali region, with the expectation that heterogeneous equilibrium might be attained more rapidly at the higher temperature. The higher alkali region, involving the solid phase II, the pink compound, was not attempted at 75°, and whether this solid persists as an equilibrium phase at 75° is not known.

For the part of the 75° isotherm studied, the data and results are listed in Table III and plotted in Fig. 5. The information given in Table III is similar to that in Table I. The liquids for experiments 1–6 were sampled by centrifuging and titrated for sodium oxide content. All others were sampled by ultra-fine filtration and analyzed for sodium by flame photometry. The actual successive analyses made in testing for equilibrium are listed separately in Table IIIA.[20] The procedure followed for the special experiments 17(1), 19(1), 23(1), 22(1),

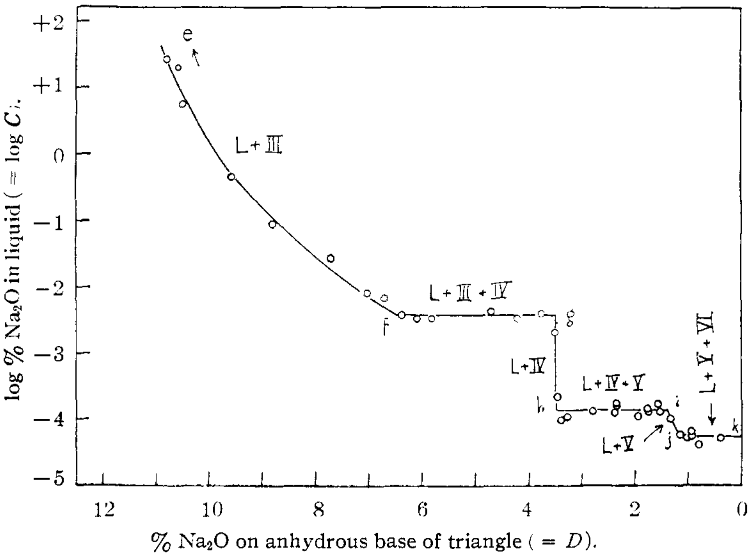

Fig. 5.—System Na_2O–UO_3–H_2O at 75°: tie-line relations for the low alkali region.

24(1,2) and 25(1,2,3) was the same as that already explained for the corresponding experiments at 50° (Table II), and the data are given separately in Table IV.

TABLE III

THE SYSTEM Na_2O–UO_3–H_2O AT 75°

(In weight percentage.)

	Composition of complex				
	A	B		C	D
No.	% UO_3	% Na_2O	Hr. stirring	% Na_2O in liquid	% Na_2O in "solid"
Liquid + solid III (solid soln.)					
1	9.785	27.204	4	29.31	10.8
2	12.553	18.744	3	20.12	10.6
3	5.322	5.962	3	5.682	10.5
4	1.9609	0.6434	43	0.456	9.57
5	1.9439	.2762	23	.0914	8.81
6	1.9897	.1908	76	.0268	7.69
7	1.9908	.1582	70	.0083	7.02
8	1.9997	.14974	179	.00714	6.69
Liquid + solid III + solid IV					
9	1.9778	0.1381	45	0.0038	6.37
10	1.9891	.13165	104	.00326	6.07
11	1.9853	.1255	65	.00358	5.79
12	1.9848	.10191	63	.00443	4.69
13	1.9651	.08967	70	.00358	4.20
14	1.9771	.08083	64	.00412	3.74
Liquid + solid IV ($Na_2O \cdot 6UO_3$)					
15	2.0150	0.07480	48	0.00214	3.49
16	2.0107	.07201	90	.00023	3.45
Liquid + solid IV + solid V					
17	1.9817	0.06916	40	0.000105	3.37
18	2.0224	.06823	42	.000113	3.26
19	1.9605	.05613	88	.000136	2.78
17(1)			41	.000126	2.37
20	2.0001	.04822	63	.000178	2.35
21	2.0076	.04814	42	.000168	2.34
19(1)			41	.000113	1.94
23(1)			66	.000153	1.75
24(2)			85	.000140	1.74
25(3)			67	.000168	1.55
22	1.9744	.03061	70	.000131	1.52
Liquid + solid V (solid soln.)					
24(1)			48	.000102	1.31
Liquid + solid V + solid VI ($UO_3 \cdot 2H_2O$)					
25(2)			41	0.000061	1.16
23	2.0279	0.02049	68	.000056	1.00
22(1)			90	.000058	0.94
24	1.9866	.01851	44	.000068	.92
25(1)			48	.000041	.77
25	1.9724	.007516	44	.000055	.38

TABLE IV

DATA FOR THE SPECIAL EXPERIMENTS IN TABLE III (75°)

No.	Wt. of UO_3 in mixture *a*	Wt. of Na_2O in mixture *b*	Total wt. of mixture *c*	% Na_2O in liquid *d*	% Na_2O in solid *e*
17(1)	3.266	0.07946	115	0.000126	2.37
19(1)	2.8133	.05583	101	.000113	1.94
23(1)	3.0362	.05425	145	.000153	1.75
24(2)	2.636	.04673	129	.000140	1.74
25(3)	2.9519	.04656	114	.000168	1.55
24(1)	2.958	.03927	139	.000102	1.31
25(2)	2.9519	.03478	124	.000061	1.16
22(1)	4.988	.04748	157	.000058	0.94
25(1)	2.9519	.02301	139	.000041	0.77

With respect to the sequence and nature of solid phases and invariant solutions, the results for this part of the system at 75° are seen to corroborate the conclusions drawn from the more widely scattering results at 50°; and the solids will therefore be identified by the same numerals as for the 50° isotherm. Solid III, saturating the liquids along the curve e-f, is again a solid solution, with its limit f still at ~6.5% Na_2O. Solid IV is again clearly very nearly the compound $Na_2O \cdot 6UO_3$ (theoretical, 3.49% Na_2O), and solid V is close to 1.3% Na_2O or ~16 UO_3 per Na_2O. The concentration in the liquid at each of the three invariants studied is lower than at 50°. For the liquid f-g saturated with solids III and IV, points 9–16 of Table III give an average value of 0.0038% Na_2O, with 0.00034 as average deviation. The eleven points 17–22 give, for liquid h-i, saturated with solids IV and V, an average of 0.00014% Na_2O with average deviation of 0.000020. For the last invariant, j-k, saturated with solids V and VI, the last six points of Table III give 0.000057% Na_2O (average deviation, 0.000006), which is just barely over the observed reading for the distilled water used.

That the terminal solid VI is $UO_3 \cdot 2H_2O$ was determined by direct analysis. Solid rotated with water for two months at 25° was air-dried to constant weight and then assayed as U_3O_8 at 1000°, giving 89.06 and 88.99% UO_3. Solid stirred violently with water for 72 hours at 75°, and dried rapidly by washing with alcohol and ether, gave, by similar assay, 88.61 and 88.66% UO_3. The theoretical value for $UO_3 \cdot 2H_2O$ is 88.81% UO_3.

The various solid phases from III to VI differed little in apparent physical properties. The color of the principal solid solution, solid III, varied from yellow to bright orange with increasing sodium oxide content. With less than about 9% Na_2O in the solid it settled rather poorly from the mother liquor, which then contained less than 0.1% Na_2O. In the higher concentration range the solid settled well enough to permit sampling of the liquid by centrifuging. The remaining three solids, IV, V, VI, were all yellow; solids V and VI settled fairly well but solid IV, the compound $Na_2O \cdot 6UO_3$, seemed to be the most finely divided, settling extremely slowly. Long centrifuging and even weeks of standing failed to give a clear liquid, which was obtainable only by ultra-fine filtration. The presence of this solid could almost be established visually, in suspensions of mixed solids, by this characteristic. The solids in experiments 25, 25(1), and 25(2) at 75°, for example, settled fairly well, but when the total composition was changed to 25(3), to bring it from the invariant j-k, for solids V and VI, to the invariant h-i for solids IV and V, the change was visible, in agreement with the result of analysis. Similar observations were made, in reverse, in going from experiment 22 to 22(1), also at 75°.

The final numerical relations for the solid phases and isothermally invariant solutions for both temperatures may be summarized as follows

Solids

I, $NaOH \cdot H_2O$ at 50°; NaOH at 75°

II, hydrated compound with probably 5 or 6 moles of Na_2O per UO_3, at 50°; not studied at 75°

III, solid solution with $Na_2O:UO_3$ mole ratios from ~8:11 to ~1:3 at 50°; same lower limit at 75°

IV, compound, probably anhydrous, $Na_2O \cdot 6UO_3$, at 50° and 75°; possibly with slight solid solution on either side of this formula

V, solid solution with $Na_2O:UO_3$ mole ratios from ~1:12 to ~1:18 at 50°; ~1:16 at 75°

VI, $UO_3 \cdot 2H_2O$, from 25 to 75°.

Invariant liquids (% Na_2O)

	50°	75°
L + I	45.2	(58.5)[24]
L + I + II	45.2	
L + II + III	42.8	
L + III + IV	0.0106	0.0038
L + IV + V	.00058	.00014
L + V + VI	.00012	.00006

At the higher temperature the lower limit of the solid solution III appears to be about the same as at 50°. Solid IV remains close to the formula $Na_2O \cdot 6UO_3$ in composition, with very little, if any, tendency to take up adjacent solids in solid solution. The composition spread of solid V is possibly becoming narrower with increasing temperature. The fact that the sodium oxide concentrations of the invariant liquids involving the solids III–VI are lower at 75° than at 50° suggests that the actual solubilities of the various solids are decreasing with rising temperature. A solid of approximately the composition $Na_2O \cdot 16UO_3$ is formed at a sodium hydroxide concentration of $\sim 4 \times 10^{-5}$ *M* at 50° and $\sim 2 \times 10^{-5}$ *M* at 75°; and the solid $Na_2O \cdot 6UO_3$ requires NaOH at $\sim 2 \times 10^{-4}$ *M* at 50° but only 4.5×10^{-5} *M* at 75°

Although the solid phases found here to be the equilibrium solids in the aqueous system are not necessarily the same as those to be expected in the anhydrous system $Na_2O–UO_3$ at high temperatures, the results do seem to rule out the existence of a simple "mono-uranate," or $Na_2O \cdot UO_3$, at least as an equilibrium phase in the aqueous system, despite the formation of the unexpected solid II with a much higher $Na_2O:UO_3$ ratio. As for the familiar "diuranate" formula, $Na_2U_2O_7$, or $Na_2O \cdot 2UO_3$, we see that in these isotherms at least, this is merely a point in the continuous range of compositions comprising the principal solid solution III, although it may be that such a compound becomes a distinct phase in itself at much higher temperature. In some ignitions of wet mixtures of Na_2O and excess UO_3, made for the purpose of testing the result for possible use in analysis of wet residues, it was observed that the weight of the residue obtained at 1000° could be accounted for best (but roughly) in terms of a mixture of $Na_2U_2O_7$ and U_3O_8.

On the basis of the present results, then, all the formulas of sodium uranates previously reported (references 1, 4, 9, 10, 11) through the direct or indirect analysis of precipitates obtained from aqueous solutions, would have to be explained as representing portions of a solid solution, mixtures of equilibrium solids, or decomposed (hydrolyzed) residues of these. Thus the reported $Na_2O:UO_3$ mole ratios 1:2, 9:20, 3:7 and 2:5 would represent regions of the solid solution III; the "compounds" with ratios 2:7 and 1:4, if they were equilibrium solids, would be mixtures of the solids III and IV; and the "compounds" 1:7 and 1:8 probably represent solid IV, or $Na_2O \cdot 6UO_3$, partly decomposed by washing into a mixture of solids IV and V. From the behavior encountered in the present direct study of the system, and from the phase equilibria established, it may be said that it is highly improbable that equilibrium could be expected to hold in ordinary precipitations such as those used in attempting to determine the compositions of the solids by direct analysis or those occurring during the titration of uranyl salt solutions with alkali.

NEW YORK, N. Y.

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[24] Seidell (ref. 22), Vol. I, p. 1284; by interpolation.

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

The Separation of Europium from Samarium by Electrolysis[1]

BY E. I. ONSTOTT

RECEIVED OCTOBER 28, 1954

Europium is efficiently separated from samarium by electrolysis of the europium citrate complex ion at a lithium amalgam cathode. Samarium oxide containing 1.6% europium oxide is quantitatively freed of the europium with one electrolysis. Under optimum conditions, 99.9% of the europium is removed into the mercury phase, while less than 10% of the samarium is removed. Parameters affecting the electrolysis are discussed.

The separation of europium from samarium is not difficult, since europium is easily reduced to the divalent state.[2] However, an efficient method of separating a small amount of europium from a relatively large amount of samarium has not previously been reported.

Marsh[3] has used sodium amalgam to separate europium from samarium, but his method depends on the selective oxidation of samarium after extraction of both samarium and europium. Several extractions are necessary in order to obtain pure samarium. The ion-exchange separation of europium from samarium is possible, but not practical.[4]

McCoy[5] previously has shown that the mercury cathode separation of europium from samarium is practical. Actually the electrode employed by Mc-

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[1] Work done under the auspices of the Atomic Energy Commission.

[2] H. N. McCoy, THIS JOURNAL, **57**, 1756 (1935); **59**, 1131 (1937); L. F. Yntema, *ibid.*, **52**, 2782 (1930).

[3] J. K. Marsh, *J. Chem. Soc.*, 398 (1952); 531 (1943).

[4] B. H. Ketelle and G. E. Boyd, THIS JOURNAL, **69**, 2800 (1947); F. H. Spedding, E. I. Fulmer, J. E. Powell, T. A. Butler and I. S. Yaffee, *ibid.*, **72**, 4840 (1950); S. W. Mayer and E. C. Freiling, *ibid.*, **75**, 5647 (1953).

[5] H. N. McCoy, *ibid.*, **63**, 3432 (1941).