probably are formed at the container walls. This technique also has been employed successfully for the preparation of magnesium diboride, MgB_2.

The AlB_2 structure is the prototype of the structure of many of the transition metal diborides which have been reported.[6] The space group of the hexagonal unit cell is C^6/mmm; $Z = 1$. The structure may be described in terms of close-packed layers of aluminum atoms separated by layers of boron atoms; both types of layers are perpendicular to the C axis. The unit cell dimensions of AlB_2, determined from Norelco geiger counter diffractometer measurements using Cu Kα radiation are: $a_0 = 3.009 \pm 0.001$ Å., $c_0 = 3.262 \pm 0.001$ Å. The X-ray diffraction pattern is given in Table I.

BROOKLYN, N. Y.

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(6) R. Kiessling, *J. Electrochem. Soc.*, **98**, 166 (1951).

[CONTRIBUTION FROM OAK RIDGE NATIONAL LABORATORY, UNION CARBIDE NUCLEAR COMPANY]

Studies in the Carbonate–Uranium System

BY C. A. BLAKE, C. F. COLEMAN, K. B. BROWN, D. G. HILL, R. S. LOWRIE AND J. M. SCHMITT

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Portions of the phase diagram for the four component system UO_3–Na_2O–CO_2–H_2O have been investigated at 26°. Solubilities have been determined for UO_2CO_3 in sodium carbonate solutions and for $Na_4UO_2(CO_3)_3$ in sodium carbonate and other salt solutions as a function of the concentration of co-solute. A solubility of 320 g. U/l. was obtained at molar ratio CO_2:Na:U close to 2:2:1 and *p*H close to 7. From solubilities and spectrophotometric measurements, evidence has been obtained for the existence of $UO_2(CO_3)_2^{-2}$ and $UO_2(CO_3)_3^{-4}$, with an estimate of the stability of the latter, and also for an additional complex ion having the molar ratio CO_2:U = 0.5.

It has long been known that uranyl compounds show considerable solubility in sodium carbonate solutions, indicating the formation of stable complex ions. This rather unique property of uranium has been useful in analytical separation procedures and in industrial uranium separation processes. Prior to the time that the present investigation was made[1-3] no thorough study of the carbonate–uranium system had been published although the particular compound sodium uranyl tricarbonate, $Na_4UO_2(CO_3)_3$, had been prepared and identified[4] and its solubility had been measured.[5] In addition Haldar[6] observed discontinuities in conductometric titrations of uranyl nitrate with carbonate solutions at points corresponding to carbonate:uranium mole ratios of 3:1 and 2:1. Bachelet, Cheylon, Davis and Goulette[7] have studied the preparation and properties of some alkali and alkaline earth carbonates and Bullwinkel[8] has confirmed the existence of two of the aqueous complexes described in this paper, discussing some of the chemical properties of these complexes and of uranyl carbonate.

Experimental

The uranium trioxide used in this investigation was prepared by precipitating uranium peroxide ($UO_4 \cdot xH_2O$) from uranyl nitrate solution (*p*H held at 2.5) with subsequent decomposition of the precipitate at a temperature of 325°. The uranium trioxide thus produced is a fluffy, reactive material, free from peroxide.

In the preparation of uranyl carbonate (UO_2CO_3), 20 g. of uranium trioxide, 10 ml. of water and a considerable excess of crushed Dry Ice were loaded into a small stainless steel bomb. Consistently good results (U:CO_3 mole ratios ranging from 1.01 to 1.03) were obtained by agitation of the bomb for 5 hr. at temperatures between 90–105° and pressures between 2500 and 3000 p.s.i. The product was very pale yellow and is stable at 109°.[9]

Sodium uranyl tricarbonate was prepared according to a general method proposed previously.[5] In this method sodium polyuranates are first prepared by precipitation from uranyl nitrate solution with sodium hydroxide. This precipitate is washed thoroughly and dissolved in a solution of sodium bicarbonate. The solid tricarbonate is obtained by evaporating to a low volume while passing carbon dioxide through the solution. A recrystallization from water was made to purify the material, which was bright yellow and stable at 240°. Carbonate:uranium mole ratios in the product varied from 3 to 3.2.

Reagent grade sodium carbonate, sodium bicarbonate and tank carbon dioxide were used in making the experimental mixtures.

Solubility equilibrations were made in Pyrex or in plastic (polyfluoroethylene) bottles. The solids and solutions were shaken for sufficient time (at least 10 days, usually 3 weeks or more) to ensure equilibrium. The agitation was carried out in a constant temperature room at 26 ± 2°. The contents of a bottle were then centrifuged, and usually both solid and solution were analyzed for uranium, sodium and carbonate. Solution densities were measured and the solubilities were calculated in weight per cent. The solid residues were complex in tests in the high solubility region near the invariant point, in tests in basic solutions and in tests starting with uranium trioxide. Application of Schreinemakers'[10] method of wet residues to the analyses of the wet solids permitted the calculation of the solid phase in only a few cases.

Concentrated solutions resulting from the dissolution of uranyl carbonate in aqueous sodium carbonate were very viscous and difficult to centrifuge. The solutions were also in equilibrium with appreciable carbon dioxide pressure. Equilibrium concentrations in these particular solutions, therefore, could not definitely be established.

Analyses of high level uranium samples were obtained by reducing the uranium and titrating potentiometrically with ferric sulfate solution.[11] On low level samples the ascorbic acid colorimetric procedure[12] was used. Sodium was determined with the flame photometer and the usual absorption–gravimetric method was used for carbonate.

For the spectrophotometric investigations, it was neces-

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(1) C. A. Blake, R. S. Lowrie, D. G. Hill and K. B. Brown, Report AECD-3280, 1951.

(2) K. B. Brown and J. M. Schmitt, Report AECD-3229, 1951.

(3) C. A. Blake, R. S. Lowrie, K. B. Brown and D. G. Hill, Report Y-794, 1951.

(4) M. Ebelman, *Ann.*, **43**, 302 (1842); *Ann. chim. phys.*, [3] **5**, 206 (1842).

(5) W. E. Bunce, N. H. Furman and R. T. Mundy, Report M-4238, (revised), May, 1947.

(6) B. C. Haldar, *J. Indian Chem. Soc.*, **24**, 503 (1947).

(7) M. Bachelet, E. Cheylon, M. Davis and J. C. Goulette, *Bull. soc. chim. France*, 55 (1952), Jan.-Feb.; 565 (1952), May-June; 173–9 (1954), Feb.

(8) E. P. Bullwinkel, Report RMO-2614, 1954.

(9) Bullwinkel[8] describes the preparation of uranyl carbonate by passing a stream of carbon dioxide at one atmosphere pressure through a water slurry of freshly precipitated uranium trioxide.

(10) F. A. H. Schreinemakers, *Z. physik. Chem.*, **11**, 81 (1893).

(11) C. J. Rodden, "Analytical Chemistry of the Manhattan Project," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 70.

(12) Ref. 11, p. 107.

sary to prepare solutions having carbonate:uranium mole ratios varying from zero to 40. The *p*H of each solution was measured and its absorption spectrum was determined, and the final carbonate:uranium ratio was obtained from chemical analysis. For solutions having ratios greater than 3, sodium carbonate in the desired amount was added to sodium uranyl tricarbonate solutions. Most of the solutions with ratios less than 3 were prepared by the addition of the appropriate amounts of hydrochloric acid to solutions of sodium uranyl tricarbonate. Immediately upon addition of the acid, the solutions were scrubbed with moist nitrogen gas, the *p*H rising gradually. The scrubbing was continued until, in one series of tests, a constant and reproducible optical density was obtained, or, in two other series, until a desired *p*H level was reached. In the first case precipitation frequently occurred shortly after a constant optical density was reached. In addition, some solutions were prepared by adding sodium carbonate or sodium uranyl tricarbonate to solutions of sodium uranyl dicarbonate and by equilibrating sodium uranyl dicarbonate solutions with carbon dioxide at a known partial pressure. (In the latter case, the sodium:uranium ratio remained constant.)

The light absorption measurements were made with a Beckman Model DU spectrophotometer using a tungsten lamp and silica cells having light paths ranging from 1 mm. to 10 cm. The wave length scale calibration was checked against hydrogen discharge lines in the range 275–492 mμ.

A Beckman *p*H meter, Model G, equipped with saturated calomel and high alkalinity glass electrodes was used for the *p*H determinations.

Results

The regions investigated in the four component system UO_3–Na_2O–CO_2–H_2O are shown by the three-dimensional diagram (26° isotherm) represented in Fig. 1. The most interesting cross-section of the system, the UO_2CO_3–Na_2CO_3–H_2O plane, is shown in Fig. 2. Some of the important saturated solutions in this plane are described in Tables I (solid phase = UO_2CO_3) and II (solid phase = $Na_4UO_2(CO_3)_3$).

The complete phase equilibrium data from this investigation, together with certain measurements from other laboratories[5,13,14] which have been calculated to the same basis, are available from the American Documentation Institute.[15] These include compositions, *p*H and density at points near the Na_2O–CO_2–H_2O face, in the UO_3–Na_2O–H_2O face, in and near the UO_2CO_3–Na_2CO_3–H_2O cross-section and in the $Na_4UO_2(CO_3)_3$–$NaHCO_3$–H_2O, UO_3–Na_2CO_3–H_2O, UO_3–$NaHCO_3$–H_2O and UO_2CO_3–Na_2O–H_2O cross-sections.

TABLE I

SOLUBILITY OF URANYL CARBONATE IN SODIUM CARBONATE SOLUTIONS AT 26°

Na_2CO_3, *M*	UO_2CO_3, *M*	$d_{25°}$, g./ml.	*p*H
0.094	0.087	1.029	7.3
.189	.174	1.061	7.3
.377	.338	1.121	7.2
.566	.521	1.188	7.1
.755	.742	1.257	7.0
.943	.886	1.314	6.7
1.13	1.09	1.373	7.0
1.41	1.35	1.421	6.9

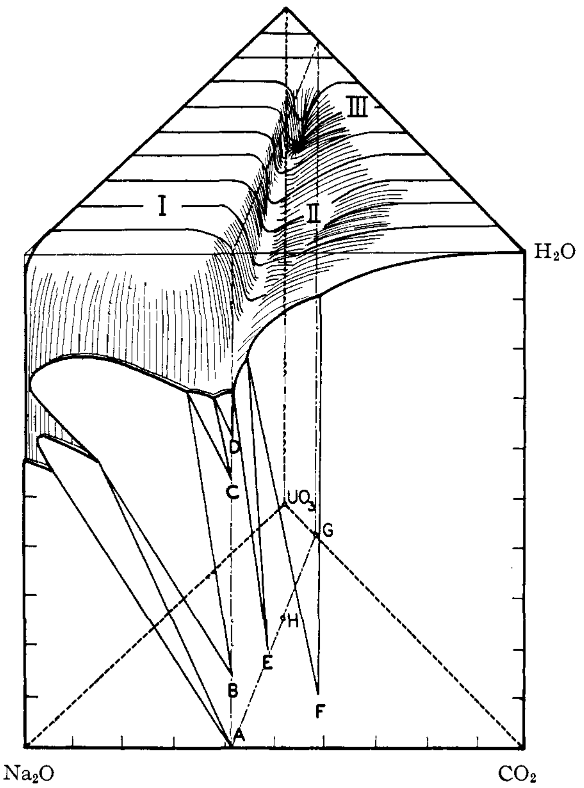

Fig. 1.—Phase diagram for system UO_3–Na_2O–CO_2–H_2O at 26°: I, solutions in equilibrium with sodium uranates; II, solutions in equilibrium with sodium uranyl tricarbonate; III, solutions in equilibrium with uranyl carbonate: A, Na_2CO_3; B, $Na_2CO_3 \cdot H_2O$; C, $Na_2CO_3 \cdot 7H_2O$; D, $Na_2CO_3 \cdot 10H_2O$; E, $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ (Trona); F, $NaHCO_3$; G, UO_2CO_3; H, $Na_4UO_2(CO_3)_3$.

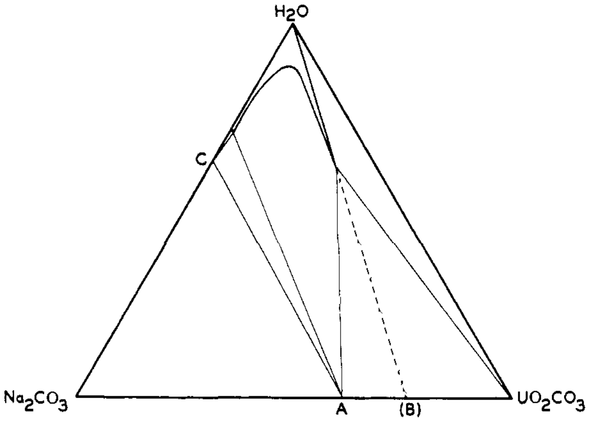

Fig. 2.—The UO_2CO_3–Na_2CO_3–H_2O cross-section at 26°: A, $Na_4UO_2(CO_3)_3$; B, calculated composition for $Na_2UO_2(CO_3)_2$; C, $Na_2CO_3 \cdot 10H_2O$.

Absorption spectra are listed in Table III for solutions at carbonate:uranium mole ratios from 0.5 to 5, together with the spectrum of uncomplexed uranyl ion (uranyl perchlorate in dilute perchloric acid). The analysis of the system by the method of continuous variations as used by Yoe[16] is shown in Fig. 4 for those solutions in which the carbon dioxide partial pressure was lowered as

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[13] P. D. Miller, H. A. Pray and H. P. Munger, Report BMI-JDS-206.

[14] E. Bersohn and E. L. Brady, Report MonC-109, March 1, 1946.

[15] For this supplementary material, order the American Documentation Institute Document No. 5079, remitting for it in advance $2.50 for photoprints or $1.75 for 35-mm. film, by check or money order payable to Chief, Photoduplication Service, Library of Congress, Washington 25, D. C.

[16] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

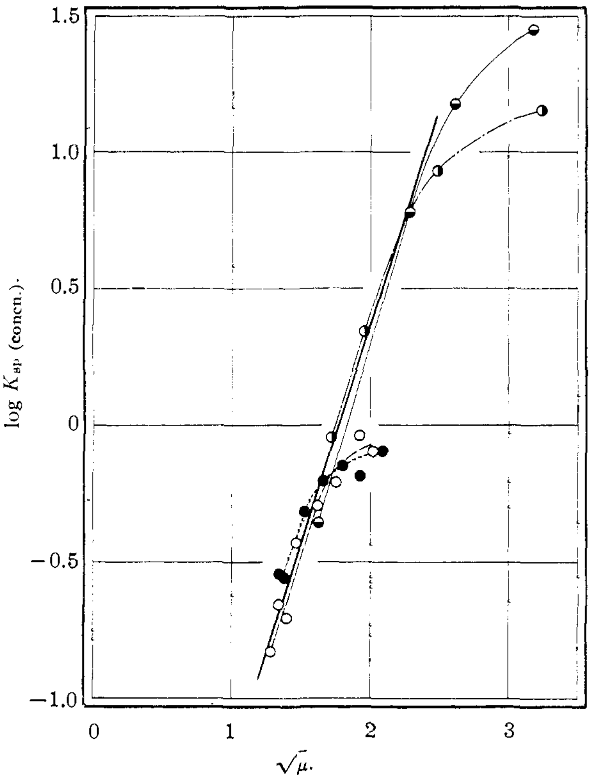

Fig. 3.—Concentration solubility product of sodium uranyl tricarbonate in sodium salt solutions *vs.* square root of ionic strength at 26°: ○, $NaClO_4$; ◑, Na_2CO_3; ◒, Na_2SO_4; ●, NaCl.

far as possible and in Fig. 5 for those in which it was adjusted to reach a set *p*H. Most of these test solutions (all those containing 0.035 *M* uranium) were also examined at wave lengths close to 430, 450 and 460 mμ, with results similar to those shown at 438 mμ.

TABLE II

SOLUBILITY (*M*) OF $Na_4UO_2(CO_3)_3$ IN SOLUTIONS OF SODIUM SALTS

Co-solute, *M*	26°					30°[b]	
	Na_2CO_3	NaCl–Na_2CO_3[a]	NaCl	Na_2SO_4	$NaClO_4$	Na_2CO_3	$NaHCO_3$
0	0.286					0.265	
0.3	.173			0.168			0.178
0.5	.130	0.126		.135	0.134	.136	.144
1.0		.063	0.075		.056	.071	.078
1.5		.034	.034	.045	.028		
2.0		.020	.020	.035	.015	.025	
2.5			.012		.008		
3.0			.006	.011	.005	.010	
3.5			.003		.002		
4.0			.0025				

[a] 0.28 *M* NaCl, remainder Na_2CO_3.

TABLE III

ABSORPTION SPECTRA OF URANIUM SOLUTIONS[a]

Optical density for 0.035 *M* uranium, 1 cm. path length, 26°

λ, mμ	A	B	C	D	E
388	0.258	0.282	0.392		0.143
398	.385	.396	.466		.196
400	.420	.438	.500		.218
402	.470	.488			.232
403					.235
404	.498	.522	.604		.226
406	.515	.537			.213
408	.538	.568	.719		.214
410	.575	.600			.228
412	.618	.649	.844		.250
414	.635	.676			.255
416	.642	.683	.933		.242
418	.658	.704	.980	2.60	.218
420	.692	.745	1.072		.193
422	.730	.777	1.125		.188
424	.740	.788	1.188		.193
426	.695	.761	1.219		.197
428	.675	.735	1.199	3.47	.187
430	.705	.761	1.209		.161
432	.775	.829	1.270		.137
434	.835	.887	1.333		.118
435	.855	.920			
436	.850	.913	1.406		.103
438	.755	.814	1.417	3.80	.097
440	.640	.705	1.333		.092
442	.618	.667	1.240		.085
444	.703	.740	1.219	3.80	.074
446	.820	.850	1.240		.064
448	.935	.970	1.302	3.62	.056
449	.945	.980			
450	.930	.975	1.386		.048
452	.748	.808	1.386		.044
454	.558	.610	1.229		.042
456	.468	.506	1.036		.036
458	.488	.516	.927	2.92	.032
460	.565	.589	.880		
462	.665	.683	.880		
463	.665	.690			
464	.650	.680	.891		
466	.496	.531	.873		
468	.295	.345	.765	2.04	
478	.043	.066	.288	1.46	

[a] A: sodium uranyl tricarbonate in sodium carbonate solution, $5CO_3$:U, *p*H 11.2. Tricarbonate spectrum. B: sodium uranyl tricarbonate in water, $3CO_3$:U, *p*H 9.3. Tricarbonate spectrum with absorption increased slightly by presence of hydrolyzed uranyl species. C: uranyl carbonate in sodium carbonate solution, $2CO_3$:U, *p*H 7.7. Dicarbonate spectrum with absorption increased considerably by presence of hydrolyzed uranyl species. D: hydrolyzed uranyl species, $0.5CO_3$:U, *p*H 7.8. Prepared by eliminating carbon dioxide from acidified sodium uranyl tricarbonate solution; 0.122 *M* NaCl present. E: Uranyl perchlorate in perchloric acid solution, *p*H 1.2. *Cf.* absorption peaks at 404, 416, 428 mμ reported by E. Rabinowitch, "Absorption Spectra of Uranyl Compounds in Solution," Report ANL-5173, December, 1953; ~ 401, 414, 426 mμ from spectral curve given by S. Ahrland, *Acta Chem. Scand.*, **3**, 377(1949).

Discussion

The four-component diagram, Fig. 1, is represented as a triangular right prism with the UO_3–Na_2O–CO_2 system as its base and with H_2O plotted vertically; *i.e.*, the H_2O vertex of the usual tetrahedron is expanded into a triangle, all of which represents pure water. This form of the diagram serves to magnify the extremely narrow regions of important solubility, as also does the choice of weight per cent. as the concentration unit.

The front face is the system Na_2O–CO_2–H_2O.

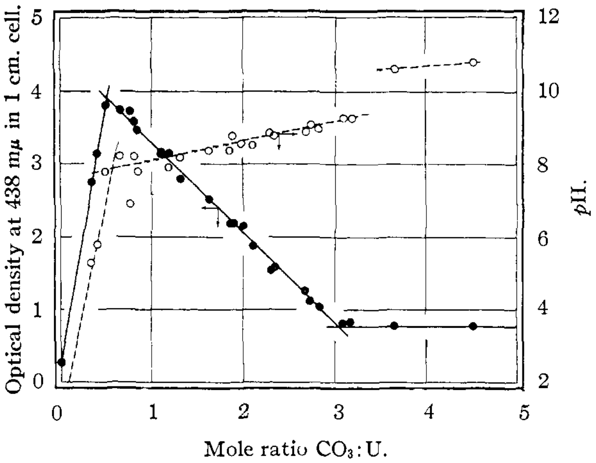

Fig. 4.—Variation of optical density with carbonate:uranium ratio at minimum carbon dioxide partial pressure: 0.035 *M* uranium, 1 cm. path length, 26°: ●, optical density; ○, *p*H.

This system is taken from the work of Freeth[17] from Na_2O to Na_2CO_3 and from that of Hill and Bacon[18] from Na_2CO_3 to $NaHCO_3$. No attempt was made to represent the other two vertical faces since the solubilities are extremely small until almost at the front face.

Solutions on the surface of field I are in equilibrium with solid compounds of hydrolyzed uranium. The problem of identification of these equilibrium solid phases was not attempted in the present investigation. Recently, Ricci and Loprest[19] have studied the phase relations in the system Na_2O-UO_3-H_2O at 50 and 75° and have identified several equilibrium solids.

This field of very low solubility breaks sharply to a region of soluble complex compounds, with a portion visible of the face for the field of stable tricarbonate, $Na_4UO_2(CO_3)_3$ (II). No solubilities were measured in the region of high carbon dioxide content; so the right-hand boundaries of field II were not defined and the solubility surfaces are not known beyond this area.

A two-phase line separates field I from field II and probably from a uranyl carbonate region at the rear (III), also not defined on the right. The line dips very steeply into a sink which is probably an isothermal invariant point. However, a two-phase line separating uranyl carbonate from sodium uranate was not established; so a solid solution is not excluded. Although the exact composition at the invariant point was not determined, the solution contains at least 26 wt.% UO_3 (22 wt.% U, 320 g. U/l.) at mole ratio CO_2:Na_2O:UO_3 = 1.8:1.0:1. Higher solubilities were measured, up to 32 wt.% UO_3, but might have involved supersaturation. In this region solutions are viscous and there is an appreciable carbon dioxide pressure ($\sim$20 mm.) so that sampling and analysis were difficult.

It seems probable that two-phase lines also exist very close to, and more or less parallel to, the front face, representing equilibria between uranate and sodium carbonate on the left and between tricarbonate and either sodium carbonate or bicarbonate on the right. The latter was shown in part, but the line on the left was not determined. These lines probably intersect the tricarbonate–uranate line in a second invariant point close to the sodium carbonate–trona region.

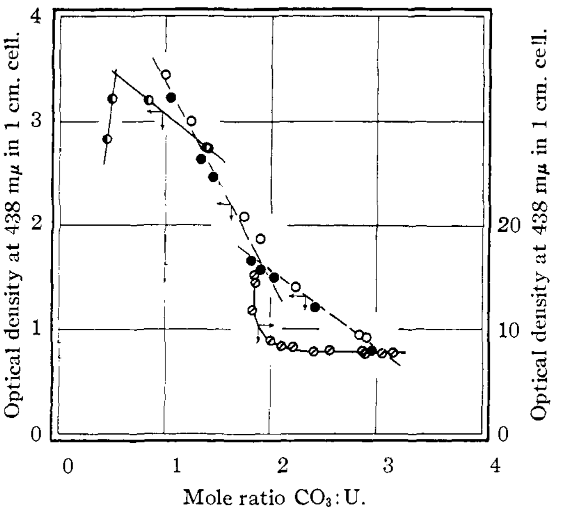

Fig. 5.—Variation of optical density with carbonate:uranium ratio at constant *p*H levels: 1 cm. path length, 26°: ○, 0.035 *M* uranium, *p*H 8.0; ●, 0.035 *M* uranium, *p*H 7.5; ◐, 0.035 *M* uranium, *p*H 5.7–5.8; ⦶, 0.35 *M* uranium, *p*H 6.5–7.5.

The UO_2CO_3-Na_2CO_3-H_2O cross-section, which is plotted in Fig. 2 without the expansion of the H_2O vertex used in Fig. 1, shows the exceedingly small range of composition in which high solubility is to be found. Despite the smallness of this region the high solubility is easily obtained by the dissolution of uranyl carbonate in aqueous sodium carbonate. When loss of carbon dioxide is prevented, the resulting saturated solutions in equilibrium with solid uranyl carbonate lie along the line running from the water apex toward the point on the base corresponding to the composition of sodium uranyl dicarbonate, which, however, was not identified as an equilibrium solid phase. (Solid alkali and alkaline earth uranyl dicarbonates have since been reported.[7,8]) This plane does not include the invariant point described above, which lies slightly to the Na_2O side; the point of greatest solubility shown in Fig. 1 lies on the very steep right wall of the deep sink. Dissolution of uranyl carbonate in sodium bicarbonate solutions resulted in immediate evolution of carbon dioxide and, eventually, solutions corresponding to those starting with sodium carbonate.

These solutions all have approximately equal molar quantities of uranyl carbonate and sodium carbonate so that the existence in solution of a complex having CO_3:UO_2 = 2 is suggested. It is interesting that the final *p*H of these aqueous solutions is very close to 7. In view of the sodium–uranium–carbonate balance and the neutral *p*H, the presence of bicarbonate, bicarbonate–carbonate or hydroxy–carbonate complexes seems unlikely. Polymerized hydroxy–bicarbonate com-

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(17) F. A. Freeth, *Phil. Trans.*, **233**, 35 (1922).

(18) A. E. Hill and L. R. Bacon, THIS JOURNAL, **49**, 2487 (1927).

(19) J. E. Ricci and F. J. Loprest, *ibid.*, **77**, 2119 (1955).

plexes cannot be excluded.[20] However, these would be isomeric with hydrated carbonate complexes and the data were not sufficient to distinguish between the two types. For simplicity the complex ion may be postulated as $UO_2(CO_3)_2^{-2}$ with the corresponding expression for the dissolution of uranyl carbonate in sodium carbonate solutions being

$$UO_2CO_3(s) + Na_2CO_3 \rightleftarrows 2Na^+ + UO_2(CO_3)_2^{-2} \quad (1)$$

The solubility of sodium uranyl tricarbonate in water is 7.2 wt.% UO_3 (6.0 wt.% U, 68 g. U/l.), decreasing with increasing concentration of sodium carbonate as shown in Fig. 2. Several other sodium salts, Table II, suppress sodium uranyl tricarbonate solubility to a similar extent. In fact, these data can all be fairly closely represented by a single empirical equation[21]

$$M(\mathrm{U}) = 0.35/(M \text{ co-solute} + 1.1)^2 - 0.0103 \quad (2)$$

The apparent dependence of solubility upon the total concentration of salts, whether of monovalent or divalent anions, rather than on the resulting concentration of sodium ion, led to a further analysis of the data in which the variation of the molal solubility product with ionic strength was considered.

A dissolution reaction for sodium uranyl tricarbonate may be written

$$Na_4UO_2(CO_3)_3(s) \rightleftarrows 4Na^+ + UO_2(CO_3)_3^{-4} \quad (3)$$

for which the molal solubility product would be expressed as

$$K_{\mathrm{sp(conc)}} = [Na^+]^4[UO_2(CO_3)_3^{-4}] \quad (4)$$

The spectrophotometric evidence discussed below is in agreement with a complex species having this carbonate:uranium combining ratio, and preliminary dialysis measurements indicate that the ion contains only one uranium atom. Values for $K_{\mathrm{sp(conc)}}$ were determined for individual solubility measurements in Table II, and the variation of $\log K_{\mathrm{sp(conc)}}$ with the square root of the corresponding ionic strength, μ, is shown on Fig. 3. The data are best expressed by a straight line, defined by the equation[22]

$$\log K_{\mathrm{sp(conc)}} = 1.64\sqrt{\mu} - 2.8 \text{ at } 26\text{–}30° \quad (5)$$

This shows how the high dependence of solubility concentration product upon ionic strength overshadows the variations in sodium ion concentration and accounts for the uniformity of the empirical relationship.

Solubility of sodium uranyl tricarbonate in sodium carbonate solutions is known to decrease with rising temperature[5]; however, preliminary experiments in the four-component system at elevated temperatures and pressures indicate that a region of high solubility continues to exist.

Since the solubility measurements had suggested the existence of at least two uranium carbonate complexes, the spectrophotometric properties of these solutions were examined to help identify the complex species. The spectrum of the $5CO_3$:U solution, Table III, is attributed to the uranyl tricarbonate ion; it was not changed by larger excesses of sodium carbonate up to $40CO_3$:U. Without excess sodium carbonate ($3CO_3$:U), in such dilute solution, an appreciable amount of the uranium was hydrolyzed, so that the absorption was increased without noticeable shift of the absorption peak wave lengths. The corresponding spectrum at $2CO_3$:U, *p*H 7, was affected even more by the contribution from highly colored hydrolytic species, but it still serves to show the similarities to and differences from the tricarbonate spectrum. The absorption peak wave lengths are close to those of the dicarbonate spectrum. The spectrum at $0.5CO_3$:U shows the much higher coloration of the hydrolyzed uranium.

The wave length of 438 mμ was chosen for use in the continuous variations analysis. The series at minimum carbon dioxide partial pressure is shown in Fig. 4, together with the final *p*H of each solution. Here the solutions at ratios above $3CO_3$:U were those prepared by adding sodium carbonate to sodium uranyl tricarbonate, and the others were those prepared by adding acid to tricarbonate solutions and scrubbing out carbon dioxide until a constant optical density was reached. This series shows a reasonably sharp break at $3CO_3$:U as expected for confirmation of the tricarbonate ion. It also shows a sharp maximum at $0.5CO_3$:U but no discernible break at $2CO_3$:U where some evidence of a dicarbonate ion was expected. The absorption at 4 and 5 CO_3:U, which remained unchanged on up to $40CO_3$:U, corresponds to a molar extinction coefficient of 22.0 at 438 mμ for the uranyl tricarbonate ion, which has been confirmed by Bachelet, *et al.*,[7] with a value of about 19 and by Bullwinkel[8] with a value of about 23.[23]

At ratios less than $3CO_3$:U the *p*H dropped, first gradually and then rapidly, with a sharp break at $0.5CO_3$:U. Since the *p*H changed in this fashion, it cannot be determined from this series whether the absorption maximum at $0.5CO_3$:U corresponds to a complex or whether it resulted only from the rapid change in *p*H. Accordingly, this region was examined again, using a series of solutions at constant *p*H, 5.7–5.8. At this *p*H level the absorption was lower, but it still varied with the carbonate concentration and showed the maximum at $0.5CO_3$:U (Fig. 5), favoring the interpretation that the hydrolyzed uranium forms a complex with carbonate at this ratio. This complex has been tentatively formulated as $U_2O_5OHCO_3^-$. Higher polymerization has not been ruled out, but the acid balance (3.5 moles hydrochloric acid per mole of

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[20] Preliminary dialysis experiments have shown that there is no diffusion through a cellophane membrane from these solutions at the particular concentration studied.

[21] For practical application, the primary value of these data arises from the fact that this empirical uniformity permits the prediction of the equilibrium solubility in a wide range of sodium salt solutions if only the total molar concentration of salts is known. In terms of the commonly used weight unit, U_3O_8, equation 2 becomes

$$\text{g. } U_3O_8/\text{l.} = 98/(M \text{ co-solute} + 1.1)^2 - 2.9.$$

[22] It may be noted that from eq. 5 log *K*sp(conc.) is equal to −2.8 at infinite dilution, or *K*sp (the activity solubility product) is equal to 0.002. From the solubility measurements in sodium perchlorate solutions an independent calculation has been made according to the method proposed by Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 476, for highly soluble salts. The calculated value for *K*sp is 0.01.

[23] These values were estimated from the respective spectral curves, after elimination of small discrepancies in the wave length scales by matching of the absorption peaks.

uranyl tricarbonate to reach the ratio of 0.5:1) does appear to rule out bicarbonate or hydroxy–bicarbonate complexes unless there is higher polymerization. It should be noted that the calculations which follow concerning the tricarbonate and dicarbonate complexes do not depend on this formulation nor even on the existence of a complex at this ratio.

The region around $2CO_3$:U was also re-examined using series at constant *p*H, here at *p*H 8.0 and 7.5. These absorptions match the former series at 1:1 (which was also at *p*H~8) and at $3CO_3$:U. With the effect of changing *p*H eliminated, these series show an appreciable break near $2CO_3$:U. However, the breaks are still not well defined, since at this uranium concentration level the absorption is still dominated by the highly colored hydrolytic species. The third series shown on this figure was made at uranium concentrations an order of magnitude higher,[24] with *p*H 6.5–7.5. These were prepared by equilibrating sodium carbonate solutions of uranyl carbonate with carbon dioxide at various known partial pressures. Here the higher concentration suppressed hydrolysis of the uranium, so that the break near $2CO_3$:U was well developed. From the optical densities of the solutions above $2.2CO_3$:U, which can be considered essentially free from the hydrolytic species, in combination with the coefficient already evaluated for the tricarbonate ion, the molar extinction coefficient of the dicarbonate ion was found to be 23.4 at 438 mμ. This has been confirmed by Bullwinkel[8] with a value of about 22.[23]

The chemical analyses of the solutions shown to be free of hydrolysis, together with the carbon dioxide pressure, were sufficient for evaluation of the approximate equilibrium concentration quotient for the dissociation of tricarbonate to dicarbonate

$$UO_2(CO_3)_3^{-4} \rightleftharpoons UO_2(CO_3)_2^{-2} + CO_3^{-2} \qquad (6)$$
$$K_{3(\mathrm{conc})} = C_D C_{CO_3}/C_T \approx 3 \times 10^{-4}\ (\mu \approx 2)$$

The amount of hydrolyzed uranium in the two solutions showing the highest optical density in this series was estimated by material balance, and the molar extinction coefficient of the hydrolyzed species was estimated to be in the order of 125 at 438 mμ in terms of monomeric uranium (*i.e.*, 250 for $U_2O_5OHCO_3^-$, if that formulation be correct). With the aid of the three extinction coefficients, concentrations were calculated for the solutions at low carbonate ratios. The estimate of $K_{3\text{-}(\mathrm{conc})}$ which results was in good agreement with that from solutions at the higher carbonate levels: 2.3×10^{-4} (μ = 1–3.6) average from the four solutions at $2CO_3$:U and lower, 3.6×10^{-4} (μ = 1.6–2.6) average from the six solutions at $2.2CO_3$:U and higher. Bullwinkel[8] has reported a constant of 6×10^3 for the reverse reaction, corresponding to about 1.7×10^{-4} for the reaction as written here, calculated presumably for infinite dilution.

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[24] The actual uranium concentrations varied from 0.22 to 1.3 *M*. The corresponding optical densities at 0.35 *M* were calculated after establishing conformation to Beer's law.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

The Anhydrous Reduced Halides of Zirconium and Hafnium[1]

BY EDWIN M. LARSEN AND JAMES J. LEDDY

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A study was made of reactions of the type $M(s) + 3MX_4(g) = 4MX_3(s)$, where M refers to zirconium or hafnium, and X refers to F, Cl, Br or I. A pseudo-equilibrium position, found by plotting the extent of reaction *versus* reaction time, occurred after the reaction had proceeded for 36 to 48 hours. It shifted in favor of the reaction product with increasing temperature, in the range 200 to 700°, and/or increasing pressure, in the range 5 to 15 atm. The ease of reduction of MX_4 increased considerably from chloride to iodide, and very slightly from hafnium to zirconium. No reaction was found to occur under the above conditions between MF_4 and M. The disproportionation reactions were followed both macroscopically and by an X-ray method. The rates of disproportionation appeared to be appreciable only at temperatures above 450°.

One aspect of the chemistry of zirconium and hafnium that has received little attention is the chemistry of the lower oxidation states. Earlier work on the reduction of zirconium tetrachloride with aluminum metal in liquid aluminum chloride[2] yielded a zirconium trichloride that was contaminated with aluminum oxide and zirconium oxide. Zirconium tribromide was prepared in a higher state of purity by reducing zirconium tetrabromide with aluminum wire in a hydrogen atmosphere at 650° in a "hot-cold" tube.[3] The only work on the hafnium trihalides was done by Schumb and Morehouse[4] who repeated the experiments of Young and Schumb[3] with hafnium tetrabromide. Although zirconium triiodide has been observed to form,[5] no samples were analyzed or studies made with this compound inasmuch as metal production was the object of the investigation. No significant difference between the behavior of the zirconium and hafnium bromides was reported. No work has been reported on the lower fluorides.

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[1] Based on a thesis submitted by James J. Leddy in partial fulfillment of the requirements for the degree of Doctor of Philosophy. General Electric Co. Fellow, 1954–1955. Work carried out in part under Task Order 4 of Contract N7-onr-28504 between the Office of Naval Research and the University of Wisconsin. Presented at the September, 1955, Minneapolis Meeting of the American Chemical Society before the Division of Physical and Inorganic Chemistry.

[2] O. Ruff and R. Wallstein, *Z. anorg. Chem.*, **128**, 96 (1923).

[3] R. C. Young and W. C. Schumb, THIS JOURNAL, **53**, 2148 (1931).

[4] W. C. Schumb and C. K. Morehouse, *ibid.*, **69**, 2696 (1947)

[5] J. D. Fast, *Z. anorg. allgem. Chem.*, **239**, 145 (1938).