[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF THE ARGONNE NATIONAL LABORATORY]

Studies on the Alkaline Earth Diuranates[1]

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Methods for the preparation of the alkaline earth diuranates have been examined and pure compounds obtained by thermal decomposition of the respective metal-uranyl acetates. The thermal stability of the metal diuranates in vacuum and in the presence of oxygen at temperatures up to 1100° has been investigated by tensimetric methods. The metal diuranate-oxygen systems have been found to be reversible below 1100°. Equilibrium dissociation pressures of oxygen so obtained permit outlining of the diphasic and monophasic regions of composition encountered, calculation of decomposition isotherms and isobars, and the heats of reaction, free energy changes and entropy changes involved. Qualitative studies on rates of oxidation of decomposition products to the diuranates have been made. X-Ray investigation of solids of composition MeU_2O_6 indicate the structural similarity of these compounds to uranium dioxide.

Although the uranium–oxygen system has been investigated in some detail as regards thermal stability, crystal structure, phase relationships and non-stoichiometry,[2] relatively little is known concerning the closely related metal–uranium–oxygen systems. Uranium in its hexavalent state forms several groups of these ternary oxides with alkali, alkaline earth and a number of other metal ions. Most frequently encountered are the uranates (M_2UO_4) and diuranates ($M_2U_2O_7$). In addition, the preparation of polyuranates containing as many as six uranium atoms per molecule ($M_2U_6O_{19}$) has been reported.[3,4] The work being described here deals with the diuranates of the alkaline earth metals: magnesium, calcium, strontium and barium.

A number of preparative methods have been described for the alkaline earth diuranates,[5-11] but none of them has been successfully applied to all four of these diuranates. The color of the alkaline earth diuranates has been reported as yellow-green, orange and yellow-brown, depending upon the method of preparation. They have been found to be insoluble in water, but easily soluble in dilute acids. Other than these general statements on color and solubility, the only other observations reported on physical or chemical properties is that the alkaline earth diuranates turn dark on long heating at a bright red heat. On the basis of one early observation, the decomposition of magnesium diuranate (and, by inference, all alkaline earth diuranates) might be expected to be reversible, since Wertheim[5] stated that the compound changed from an orange to a dark green color when heated in a reducing flame, and regained its original color when placed in an oxidizing flame. In the early phases of our work, we observed that the color change on ignition at high temperatures was reversible in that the original orange color of the compound was restored on slow cooling in air. In contradistinction, the uranium–oxygen system itself has been shown to be for much of its range an irreversible system.[12] Reversibility in the metal diuranate system would be of some interest in making data available for comparison with the uranium–oxygen system itself.

I. Preparation of Pure Alkaline Earth Diuranates

All of the six methods given above for the preparation of the alkaline earth diuranates were investigated in some detail. The ignition of the metal uranyl acetate was the only one to give a pure product free of an excess of either the alkaline earth metal or uranium oxide. Magnesium and barium uranyl acetates were easily obtained pure but the preparation of the corresponding calcium and strontium salts caused some difficulty because of their high solubilities and a marked tendency for uranyl acetate to coprecipitate with the desired double acetate.

The double acetates were prepared as follows (C.P. reagents were used without further purification): Uranyl acetate and alkaline earth acetate (in 2:1 molar ratio) were dissolved in a minimum volume of 4 *M* acetic acid at 80°. The solution was centrifuged while hot to remove traces of insoluble impurities, then cooled to 0°. If the double acetate did not precipitate on standing, the solution was allowed to evaporate at room temperature until precipitation did occur. The yellow crystals of double acetate were filtered, washed with cold 4 *M* acetic acid and dried at 60°. Analyses were made for alkaline earth metal and uranium. The magnesium and calcium uranyl acetates prepared in this manner were found to be hexahydrates, while the strontium and barium salts were obtained as dihydrates. The acetates were heated slowly in air to 700° to form the diuranates, which were also analyzed.

The color of the diuranates obtained in this manner are: magnesium, dull orange; calcium, light orange with a greenish tinge; strontium, orange; and barium, a bright orange.

Typical analytical results obtained are shown in Table I. Analyses were made gravimetrically by conventional methods. Uranium was separated as the peroxide, then precipitated with ammonia before ignition to U_3O_8. Magnesium was precipitated as magnesium ammonium phosphate and weighed as the pyrophosphate, calcium precipitated as the oxalate and ignited to the oxide, and strontium and barium precipitated and weighed as the sulfates.

II. Thermal Decomposition Studies

Apparatus.—The apparatus for studying the thermal decomposition of the diuranates (Fig. 1) consisted of a quartz reaction tube connected to a differential manometer through a standard taper $^7/_{25}$ joint sealed with apiezon W wax. The differential manometer (4-mm. i.d. precision bore tubing) could be closed or opened by raising or lowering the mercury level. It in turn was connected to a standard closed-end manometer and to a vacuum pump or a source of pure oxygen dried over phosphorus pentoxide. The volume of the reaction system (quartz tube and differential manometer to the calibration mark) was about three cc. The quartz tube was heated by a platinum-wound nickel block furnace, 10 cm. in length, mounted on a sliding carrier so the tube could be heated or cooled rapidly. The furnace was connected to a 110 v. a.c. line through a Temcometer temperature control and a Type 100 Q variac. Temperature measurements were made with a platinum–platinum, 10% rhodium thermocouple. The maximum temperature fluctuation observed during each Temcometer "cycle" at the highest working temperature (~1100°) was 3°. Temperature

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[1] Presented in part at the Fall, 1949, Meeting of the American Chemical Society.

[2] For data on this system see National Nuclear Energy Series, Div. VIII, Vol. 5, "The Chemistry of Uranium, Part I," McGraw-Hill Book Company, Inc., New York, N. Y., 1951, Chapter 11.

[3] J. Zehenter, *Monatsh.*, **21**, 243 (1900).

[4] B. Drenckmann, *Z. ges. Naturw.*, **17**, 149 (1861).

[5] J. Wertheim, *J. prakt. Chem.*, **29**, 225 (1843).

[6] A. v. Unruh, Dissert., Rostock, p. 12 (1909).

[7] V. Fischel, Dissert., Bern, pp. 20 (1889).

[8] A. Ditte, *Compt. rend.*, **95**, 990 (1882).

[9] J. J. Berzelius, *Pogg. Ann.*, **1**, 370 (1824).

[10] J. Wertheim, *J. prakt. Chem.*, **29**, 220 (1843).

[11] J. A. Arfvedson, *Pogg. Ann.*, **1**, 260 (1824).

[12] Biltz and Müller, *Z. anorg. Chem.*, **163**, 269 (1927).

TABLE I

ANALYSIS OF DOUBLE ACETATES AND DIURANATES[a]

Compounds	Magnesium, %		Calcium, %		Strontium, %		Barium, %	
Double acetates[b]	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
Uranium, %	46.35	46.42	46.00	45.71	46.42	46.77	44.30	44.59
Alkaline earth, %	2.36	2.37	3.89	3.84	8.54	8.61	12.82	12.86
U/Alk. earth ratio	2.01		1.99		2.00		1.99	
Diuranates								
Uranium, %	77.58	77.74	76.10	75.78	69.95	70.46	65.80	65.63
Alkaline earth, %	4.01	3.97	6.43	6.38	12.81	12.97	18.99	18.93
U/Alk. earth ratio	1.98		1.99		2.01		2.00	

[a] We are indebted to R. Telford of the Analytical Group for these results. [b] Calculated as the hexahydrates for magnesium and calcium, *i.e.*, $Mg(UO_2)_2(CH_3COO)_6 \cdot 6H_2O$, the dihydrates for strontium and barium, *i.e.*, $Sr(UO_2)_2(CH_3COO)_6 \cdot 2H_2O$.

variation along the length of the furnace was checked by sealing a second thermocouple inside the reaction tube and determining the temperature read as a function of the furnace position. The inner and outer thermocouples gave identical readings (±1°) over a 4-cm. length of the furnace at 1100°. In operation, the furnace was placed so that the diuranate sample was as nearly as possible in the center of this constant temperature region.

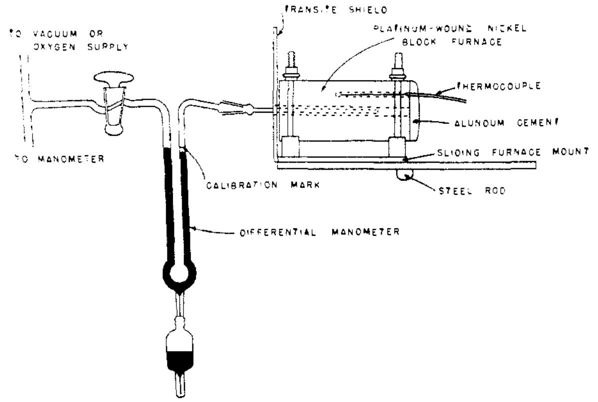

Fig. 1.—Apparatus for study of alkaline earth diuranates.

Since only a portion of the reaction system was heated to high temperature while the remainder was at, or near, room temperature, it was necessary to construct oxygen pressure calibration curves for each reaction tube employed. These curves were obtained by heating the system with various initial pressures of oxygen from room temperature to 1100°. It was then possible to convert oxygen equilibrium pressures at any temperature to a "corrected" pressure at 25°, and to calculate the composition of the solid in equilibrium with the oxygen. In none of the experiments was there any indication of a reaction between the oxygen in the system and equilibrium mercury vapor pressure (10^{-3} mm. at room temperature) from the differential manometer, so it was not deemed necessary to include a cold trap in the system.

Capillary depression errors in the differential manometer were avoided by lowering the mercury level slightly, then raising it to the calibration mark for each pressure reading. Pressures were read to the nearest 0.25 mm. in the range 0-5 mm., to 0.5 mm. at higher pressures. With a 100-mg. sample of calcium diuranate in a 3.00-ml. reaction system, a pressure of about 500 mm. of oxygen (25°) would be developed per atom of oxygen liberated from the molecule (*i.e.*, to CaU_2O_6). Thus changes in composition of 0.005 atom of oxygen could be measured without particular difficulty.

Procedure.—A sample of the diuranate (100-200 mg.) was weighed into the reaction tube which was then attached to the differential manometer. The system was evacuated, the mercury level raised to the calibration mark on the differential manometer, and the furnace slid into position. The temperature was slowly raised until decomposition of the diuranate began, as evidenced by the liberation of oxygen. Equilibrium pressures were obtained at a number of points up to 1100° (the maximum safe working temperature for our system). The temperature was maintained constant at each point until there was no measurable pressure increase for at least 30 minutes. The length of time required for the system to reach equilibrium in the experiments being discussed here generally varied from a few minutes to a number of hours depending upon the composition of the system under investigation. In a few cases when reversibility was being checked by determining the equilibrium pressure after a temperature decrease, several days were required for the equilibrium pressure to be achieved. The rate of oxygen uptake was apt to be particularly slow as the solid approached the diuranate composition in the regions where solid solutions were involved.

The end-point of a decomposition step could be determined when no further rise in equilibrium pressure was observed as the temperature was increased (with the exception of the small thermal expansion of the oxygen). Reversibility of the systems was checked by obtaining equilibrium pressures at several points with progressively lower temperatures. These pressures were in general found to coincide with the values obtained as the diuranate was being decomposed. In several instances a small amount of hysteresis was encountered in the composition range near a phase change. In these regions a small temperature decrease resulted in no measurable absorption of oxygen; however, a further small drop in temperature always caused equilibrium to be restored.

Results

Magnesium Diuranate-Oxygen System.—Decomposition of magnesium diuranate began at 850°. When the equilibrium pressures obtained in the 850-1100° temperature range were plotted in the conventional manner (log *p* *vs.* 1/*T*) they were found to fall along a straight line (Fig. 2, line I). The pressures obtained as the temperature was gradually decreased coincided with those plotted as line I. The end-point of the first decomposition step (not shown in Fig. 2) was found to be at $MgU_2O_{6.65}$. At this composition the rate of pressure increase in the system dropped sharply, and at $MgU_2O_{6.63}$ it stopped entirely. Temperature increase to 1100° caused no further change in composition of the solid. The exact composition of the solid product was checked by heating the diuranate to 850° in a vacuum, then measuring the oxygen required to reoxidize the product to its starting composition. In order to obtain more information about the magnesium diuranate decomposition, the procedure described above was repeated with a sample approximately one-half as large. Here, again, the equilibrium pressures fell along the same line until the solid composition reached $MgU_2O_{6.65}$. A third experiment was run starting with a positive pressure of oxygen in the system. No decomposition of the diuranate was noted until the decomposition pressure (as given by line I) reached that of the oxygen present in the system. From this point, until the solid composition reached $MgU_2O_{6.65}$, the pressures again followed line I.

In order to investigate any further decomposition in the magnesium diuranate system, a sample was heated to 850° in a vacuum for 30 minutes to convert it to $MgU_2O_{6.63}$. The differential manometer was then closed and the solid heated further. Above 950° a second decomposition step was observed as oxygen pressure built up in the system. The equilibrium pressures obtainable (to 1100°) again fell on a straight line when plotted as log *p* *vs.* 1/*T* (Fig. 2, line V). Since temperature limitations made it impossible to determine the end-point of this decomposition step directly,

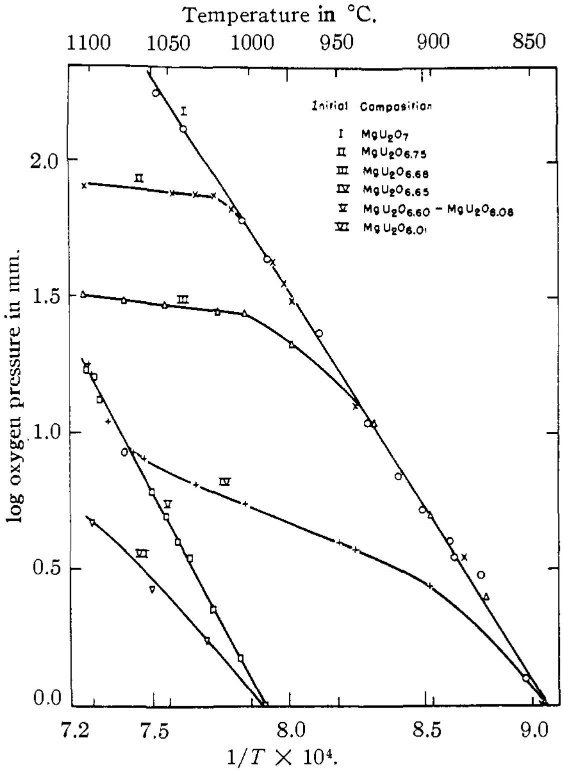

Fig. 2.—Thermal decomposition in magnesium diuranate system.

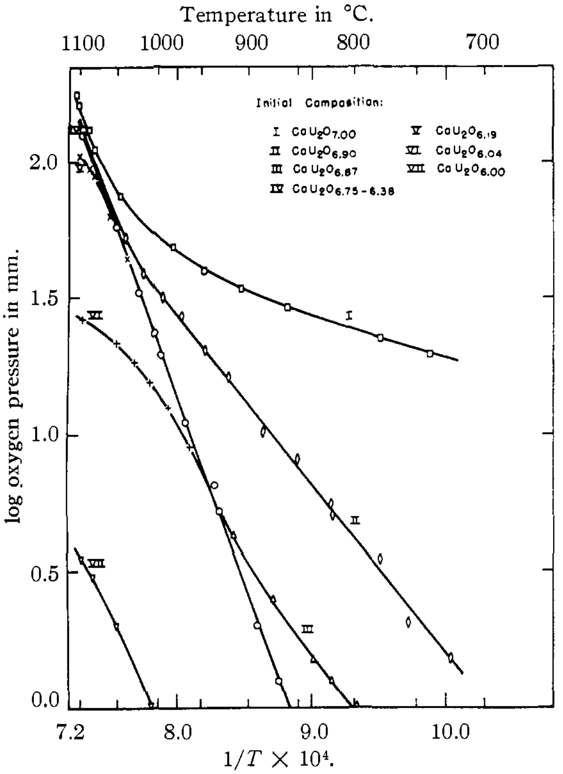

Fig. 3.—Thermal decomposition in calcium diuranate system.

the following procedure was utilized. The system was evacuated for 30 minutes at 1100°, cooled to room temperature, and an excess of dry oxygen added. The differential manometer was closed, the furnace (550°) slid into place, and the amount of oxygen required to reform the diuranate noted. Calculation showed the composition of the solid after heating at 1100° had been $MgU_2O_{5.84}$. This point did not appear to constitute the end of the second step of the decomposition, however, since the oxygen absorption took place in two well defined steps: an initial rapid reaction constituting only one-sixth of the total, followed by a second slower reaction. These rate phenomena will be discussed in greater detail below.

A more thorough study of the decomposition was made by again heating a sample at 1100° for 30 minutes while the system was being evacuated. Successive measured small amounts of oxygen were then added and equilibrium pressures obtained at various temperatures after each addition. The complete results obtained are plotted on Fig. 2 with the empirical composition of the starting material shown for each experiment.

Calcium Diuranate–Oxygen System.—Samples of calcium diuranate obtained by ignition of the double acetate at 700° always had a greenish tinge. The reason for this departure from the usual orange diuranate color became apparent when its decomposition was studied in the manner described above for magnesium diuranate. Heating an air-ignited (700°) calcium diuranate sample in an atmosphere of oxygen at 500° for a number of hours resulted in absorption of a small amount of oxygen and deepening of the sample's orange color.

Evolution of oxygen from calcium diuranate begins at about 150° in an evacuated system, at 500° under 200 mm. pressure. The oxygen evolved at 700° at 200 mm. pressure is small (less than 0.02 atom) but is sufficient to cause a perceptible color change.

The decomposition pattern of calcium diuranate was considerably different from that of the magnesium compound, but was also reversible. The data obtained are plotted in Fig. 3. The equilibrium pressure at any given temperature in the initial portion of the decomposition scheme (CaU_2O_7 to $CaU_2O_{6.84}$) was dependent upon the sample size, the volume of the system and the composition of the solid. Below 1000° samples having less than 6.84 atoms of oxygen per atom of uranium and more than 6.05 oxygen atoms showed identical equilibrium pressures which gave a straight line on a log p *vs.* $1/T$ plot. The constant pressure composition range was decreased somewhat at 1100°. Decrease in oxygen content below 6.05 atoms per molecule

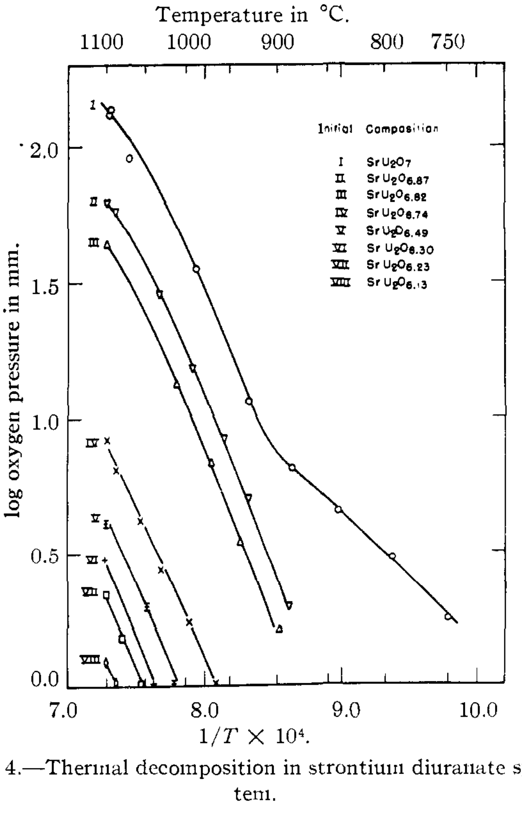

Fig. 4.—Thermal decomposition in strontium diuranate system.

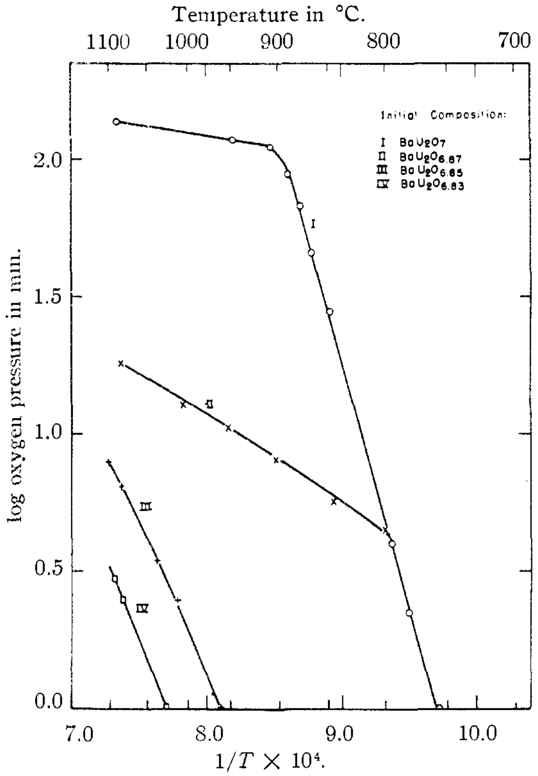

Fig. 5.—Thermal decomposition in barium diuranate system.

brought about a rapid lowering of equilibrium pressures at corresponding temperatures.

Strontium and Barium Diuranates.—These compounds were studied following the procedures outlined above for the magnesium and calcium diuranates. The equilibrium pressures for these systems are plotted on Figs. 4 and 5. The lowest oxygen content obtained with the strontium compound by evacuating at 1100° was $SrU_2O_{5.89}$. Equilibrium pressures were attained very slowly for the most part, and the values were consequently not as reproducible as those obtained with the magnesium and calcium diuranates. The equilibrium pressures obtained along the curved line portions of the decomposition scheme were again dependent upon sample size and system volume and the pressures shown are therefore correct only for the sample size to volume ratio used in the particular experiment shown.

Perhaps the most interesting feature of this system is the fact that solid containing less than 6.2 atoms of oxygen per molecule will absorb oxygen at temperatures as low as 0° until its composition reaches $\sim SrU_2O_{6.2}$.

Barium diuranate was the only one of the four compounds investigated which did not lose at least one atom of oxygen per molecule on being heated to 1100° in a vacuum. The lowest oxygen content obtained corresponded to the formula $BaU_2O_{6.51}$ (1125° in a vacuum). The initial decomposition step ending at $BaU_2O_{6.86}$ follows a straight line log p *vs.* $1/T$ plot, but at corresponding temperatures compounds containing less than 6.86 oxygen atoms per molecule exhibited progressively smaller decomposition pressures with decrease in oxygen content.

III. Discussion

Interpretation of Equilibrium Pressure Data.[13]—The results obtained above can be readily interpreted by a straightforward application of the Gibbs phase rule. Defining C in the phase rule expression $F = C - P + 2$ as the smallest number of chemical constituents necessary to specify the composition of every physically distinct phase, then the number of phases P present at any time can be deduced from the experimentally observed degrees of freedom, F, found for the system.

The data on the magnesium diuranate–oxygen system represented graphically (Fig. 2) may also be expressed as isotherms on a pressure–composition plot as shown by Fig. 6. From these graphs it is evident that a univariant system is under consideration in the regions MgU_2O_7–$MgU_2O_{6.65}$ (step I) and $MgU_2O_{6.63}$–$MgU_2O_{6.03}$ (step II); if the temperature is set arbitrarily, the pressure in the system is also fixed. By definition, the number of phases present in such a system must be one more than the number of components. Assuming that there are two components, *e.g.*, MgU_2O_7 and O_2 for step I and $MgU_2O_{6.63}$ and O_2 for step II, three phases are present (gaseous oxygen, MgU_2O_7 and $MgU_2O_{6.65}$ for step I and O_2, $MgU_2O_{6.63}$ and $MgU_2O_{6.03}$ for step II). The remainder of the composition is divariant, and must, therefore, have but one solid phase.[14]

The calcium diuranate decomposition isotherms on a pressure–composition plot (Fig. 7) indicate two regions of solid solution, $CaU_2O_7 \rightarrow CaU_2O_{6.84}$ and $CaU_2O_{6.05} \rightarrow CaU_2O_{5.95}$, with solid in the intervening region consisting of the phases $CaU_2O_{6.84}$ and $CaU_2O_{6.05}$. At 1100° the extent of the solid solution region is noticeably increased so its lower limit reaches $CaU_2O_{6.75}$.

The extensive solid solution range in the strontium diuranate–oxygen system (Fig. 8) probably accounts for the extremely slow attainment of equilibrium and poor reproducibility. The regions $SrU_2O_7 \rightarrow SrU_2O_{6.6}$ and $SrU_2O_{6.4} \rightarrow SrU_2O_{5.95}$ can be classed as solid solutions with some certainty. However, we feel that at present there are insufficient data to determine definitely whether or not a diphasic system exists in the intervening region at 1050–1100° where a measurable decomposition pressure is found.

As pointed out by Anderson,[15] and illustrated by the calcium diuranate system, the mutual solubility of solid phases increases with temperature. At a

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[13] As pointed out by J. S. Anderson (*Ann. Reports*, **43**, 109 (1946)), correct interpretation of equilibria in oxide systems hinges on the absence of "active" states due to solids which are imperfectly crystallized or have a high surface energy due to their state of subdivision. G. Tammann (*Z. anorg. Chem.*, **149**, 67 (1925)) showed that diffusion and recrystallization become appreciable at 0.5 × absolute melting point. Since the diuranates studied here decompose before melting, this property could not be determined. However, a sample of $BaU_2O_{6.86}$ ignited to 1400° in air showed evidence of fusion with decomposition. As an approximation it can be assumed that the melting points of the alkaline earth diuranates fall in the same temperature range. This observation coupled with evidence of crystal growth from X-ray studies on ignited samples indicate that one can assume true equilibria are under investigation (with the possible exception of the low temperature equilibria involved in the calcium diuranate system).

[14] Interpretation of the magnesium diuranate system is complicated by crystallographic data indicating that the solid actually consists of two phases, *i.e.*, $MgU_2O_7 = \frac{1}{2}MgUO_4 \cdot MgU_3O_{10}$. This fact does not materially alter interpretation of the decomposition scheme as far as the regions of solid solubility and insolubility are concerned, but it does present problems requiring further investigation in order to completely understand the system. Preliminary data indicate that the reaction involved in step I is the loss of oxygen by the MgU_3O_{10} phase. The product, $MgU_3O_{9.80}$, forms a solid solution with $MgUO_4$ to give a monophasic solid with the composition $MgU_2O_{6.65}$ when the reaction is complete. A more detailed investigation of the problem is underway and will be reported later. Where the term magnesium diuranate is used in this paper, it should be borne in mind that reference is being made to $MgUO_4 \cdot MgU_3O_{10}$. Present data indicate that the magnesium compound is the only one of the four diuranates to exhibit this diphasic structure.

[15] J. S. Anderson, *Proc. Roy. Soc. London*, **A185**, 77 (1946).

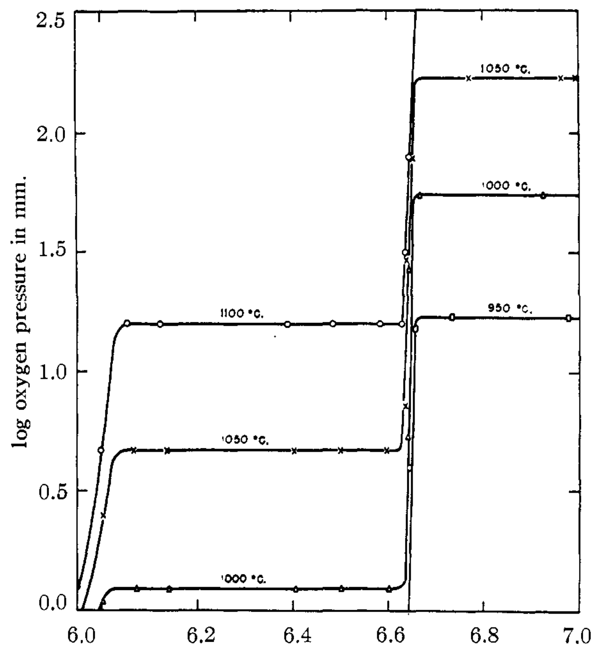

Fig. 6.—Magnesium diuranate decomposition isotherms.

critical temperature the diphasic region vanishes and the solid becomes monophasic over the entire composition range (*i.e.*, SrU_2O_7 to $SrU_2O_{5.9}$). The shape of the 1100° isotherm closely resembles that of a system at or very near its critical temperature. A careful investigation with the assistance of X-ray techniques of the region in question with samples heated at 800-1100° will be necessary to clear up this point.

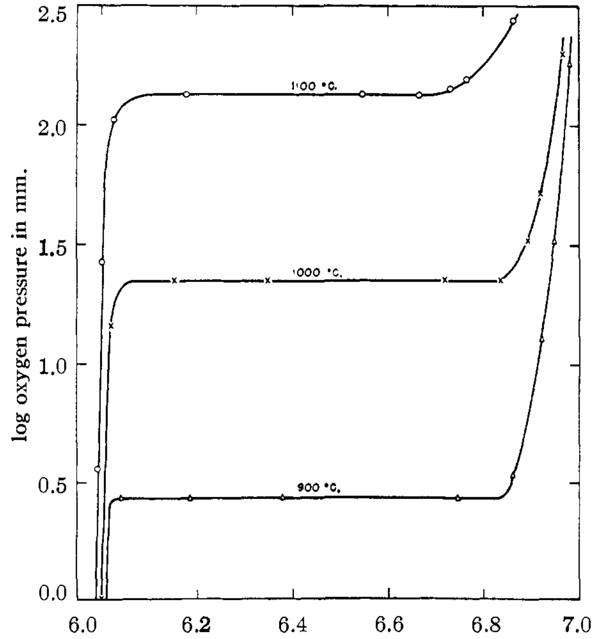

Fig. 7.—Calcium diuranate decomposition isotherms.

The barium diuranate–oxygen system has not been represented by isotherms since the greater stability of barium diuranate gave rise to measurable pressures over only a very small composition range. From Fig. 5 it is evident that a solid diphasic region extends from BaU_2O_7 to $BaU_2O_{6.86}$, with the remainder consisting of a solid solution.

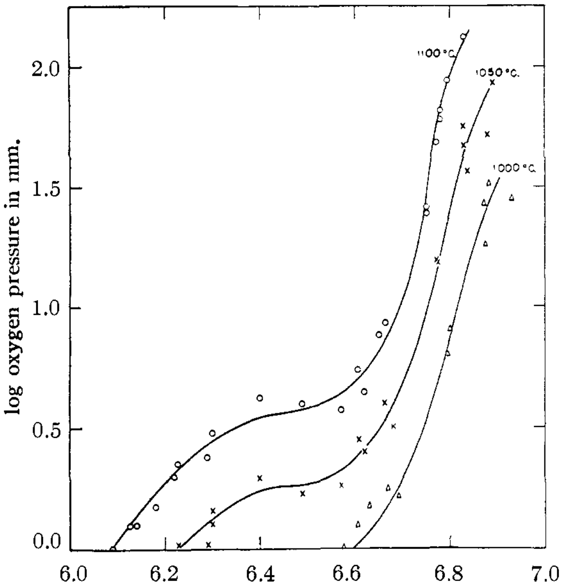

Fig. 8.—Strontium diuranate decomposition isotherms.

Crystal Structures in Alkaline Earth Diuranate Systems.—The crystal structure results reported here are not complete, but they do indicate a definite relationship between the uranium–oxygen system and the metal diuranate–oxygen systems. The structures of the diuranates themselves were all found to be complex, and only the magnesium compound has been investigated to any extent; it consists of two solid phases, $MgUO_4$ and MgU_3O_{10}. Samples in the magnesium diuranate system with the empirical formulas $MgU_2O_{6.04}$ and $MgU_2O_{5.90}$ were also investigated. These were found to have fluorite structures similar to uranium dioxide, but with a smaller unit cell. The actual cell measurements (as determined by the Cohen Method) are 5.281 Å. for $MgU_2O_{6.04}$ and 5.292 Å. for $MgU_2O_{5.90}$, as compared with 5.458 Å. for UO_2. It should be noted that as in the uranium oxide system, removal of oxygen from MgU_2O_6 actually serves to increase the cell dimensions. The expansion due to the decrease in ionic valence of uranium evidently more than balances the shrinking tendency due to loss of oxygen. The MgU_2O_6 structure can be interpreted as a uranium dioxide (fluorite) lattice with every third uranium atom replaced by magnesium. The relatively smaller size of the unit cell can be ascribed to the smaller magnesium ion and to the existence of uranium in the pentavalent state rather than the tetravalency it exhibits in UO_2. Calcium and strontium compounds having the formula MU_2O_6 also exhibit the fluorite structure with the unit cell size increasing with the size of the alkaline earth atom, *i.e.*, CaU_2O_6, 5.379 Å. and SrU_2O_6, 5.452 Å. Densities of the solids calculated from these X-ray data are: MgU_2O_6, 8.97 g./cc., CaU_2O_6, 8.71 g./cc., and SrU_2O_6, 9.07 g./cc.

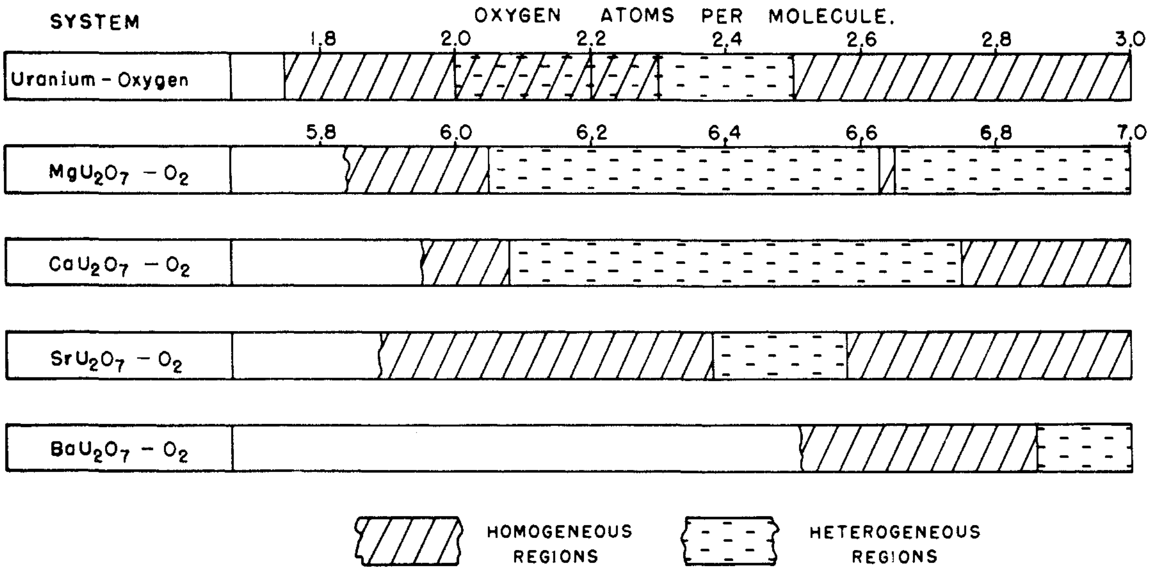

Fig. 9.—Comparison of phase relationships.

Combination of the information obtained from X-ray studies and tensimetric methods indicates that two types of solid solution are encountered in the MgU_2O_6 region. Zintl and Croatto[16] found that defect structures based on the fluorite lattice are due to an excess of anions with incomplete occupation of their lattice positions, and with the cation lattice being substantially perfect in each instance. On this basis $MgU_2O_{6.04}$ is considered to have interstitial oxygens and $MgU_2O_{5.84}$ to have vacant oxygen sites.

Comparison of Phase Relationship and Thermal Stability of Diuranate Systems with the Uranium Oxide System.—The data obtained on the phase relationships of the alkaline earth diuranates have been summarized in Fig. 9. For purposes of comparison, the uranium–oxygen system has also been included. Data on the latter system were taken for the most part from "The Chemistry of Uranium"[2]; the region $UO_{2.0}$ to $UO_{2.3}$ is shown as either monophasic or diphasic as a result of the work of Alberman and Anderson.[17] They showed that the region $UO_{2.0}$–$UO_{2.2}$ is monophasic at low temperatures, but disproportionation to $UO_{2.0}$ and $UO_{2.2}$ occurs at high temperatures. The same holds true for the $UO_{2.2}$–$UO_{2.3}$ region which disproportionates to $UO_{2.2}$ and the U_3O_8 phase.

It is evident that the extent of solid solution regions in the diuranates increases with increasing size of the alkaline earth involved, and that, in general, stability of the diuranate increases in the same way.

The isobaric decompositions of the alkaline earth diuranates have been plotted on Fig. 10, for purposes of comparison with Biltz and Müller's[12] data on the uranium oxide system. Direct comparison of the thermal stabilities in these systems is difficult since loss of one gram atom of oxygen from UO_3 involves a decrease in uranium valence from six to four, while a similar loss in the diuranate systems gives a product containing pentavalent uranium. On the other hand, crystallographic data have shown that the products, MU_2O_6 and UO_2, have similar structures, and phase studies also show a great similarity in this region.

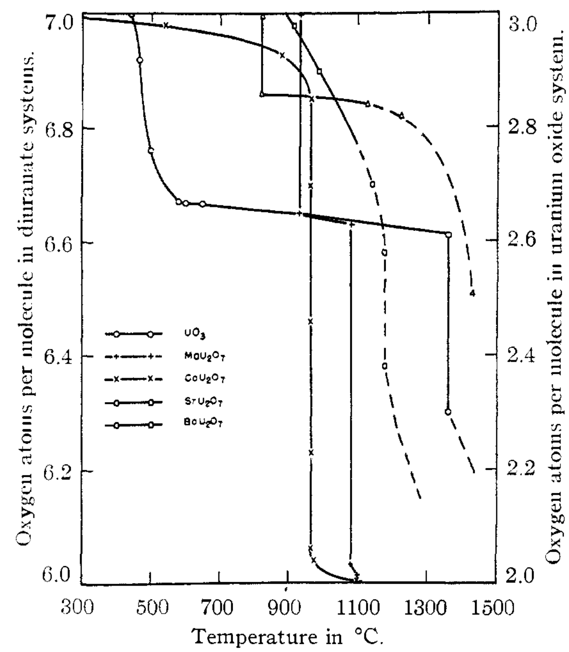

Fig. 10.—Isobaric decomposition in uranium oxide and alkaline earth diuranate systems (10 mm. isobar).

In general, presence of alkaline earth metal ions stabilizes the hexavalency of the uranium (with the exception of a very small amount of reduction in the calcium diuranate system). There is, however, no structure in these diuranate systems corresponding to U_3O_8 as in the uranium–oxygen system. $MgU_2O_{6.65}$ might be considered an exception to this rule, but its stability range is much less than that of U_3O_8.

Thermodynamic Calculations.—The heats of reaction, free energy changes and entropy changes can be calculated by the conventional methods for the univariant portions of the diuranate decom-

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(16) Zintl and Croatto, *Z. anorg. Chem.*, **242**, 96 (1936).

(17) K. B. Alberman and J. S. Anderson, *J. Chem. Soc.*, S303 (1949).

positions from the data given above. By referring to Fig. 4 it would appear as if the ΔH given for only a small portion of the strontium diuranate system can be used with fair accuracy as an average value for the entire SrU_2O_7 to SrU_2O_6 region.

The results obtained are compared (Table II) with those calculated for the uranium–oxygen system.[18]

TABLE II

THERMODYNAMIC PROPERTIES OF ALKALINE EARTH DIURANATES AND URANIUM OXIDE SYSTEMS

Reaction	ΔH, kcal./mole O_2	ΔH, kcal./g.a. O	ΔF^0_{1273} kcal./g.a. O	ΔS^0_{1273}, e.u.
$MgU_2O_{7.00} \rightarrow MgU_2O_{6.65}$	72.6	36.3	3.3	25.9
$MgU_2O_{6.63} \rightarrow MgU_2O_{6.03}$	87.4	43.7	8.1	27.9
$CaU_2O_{6.84} \rightarrow CaU_2O_{6.05}$	62.7	31.3	4.5	21.1
$SrU_2O_{6.58} \rightarrow SrU_2O_{6.38}$	53.6	26.8	8.4	14.5
$BaU_2O_{7.00} \rightarrow BaU_2O_{6.86}$	82.6	41.3	− 1.2	33.4
$UO_{3.00} \rightarrow UO_{2.67}$	35.0	17.5	−10.0	21.6
$UO_{2.67} \rightarrow UO_{2.62}$	60.0	30.0	− 0.6	24.0
$UO_{2.62} \rightarrow UO_{2.25}$	81.0	40.5	15.0	20.0
$UO_{2.25} \rightarrow UO_{2.00}$	96.0	48.0	25.6	17.6
$UO_{2.67} \rightarrow UO_{2.00}$	84.0	42.0	17.2	19.5

IV. Oxidation of Decomposition Products to the Diuranates

Theory.—The general types of heterogeneous solid–gas reaction which may be encountered are (a) the phase-boundary controlled reaction, and (b) the diffusion controlled reaction. Combinations of these mechanisms are to be expected, and are probably encountered in the majority of cases. If the two solid phases, reactant and product, do not tend to form solid solutions, *i.e.*, do not show stability over an appreciable composition range, the kinetics will be phase-boundary controlled. The reaction rate at constant temperature and pressure will be dependent upon the total surface area of solid reactant. The rate at which the thickness of the layer of oxidized product increases will be a linear function of time, assuming that the product does not affect the availability of oxygen to the reactant surface.

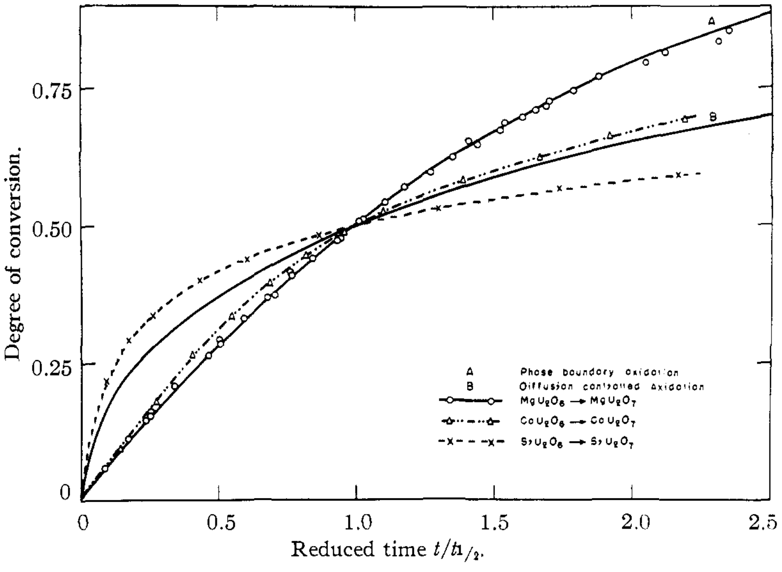

Fig. 11.—Oxidation to the diuranates.

An expression for the extent of oxidation as a function of time may be obtained by modification of an equation developed by Jander[19] in his investigation of reactions in the solid state: $kt = [1 - (1 - c)^{1/3}]^2$. The equation applies to a system in which the product layer does affect the rate of diffusion of reactant to the unreacted solid.

The phase-boundary controlled equation for the case when diffusion of gas is not hindered by the product layer becomes

$$kt = 1 - (1 - c)^{1/3}$$

where c is the degree of conversion at time t. The reaction rate curve is plotted (Fig. 11, curve A) as the degree of conversion against the reduced time, $t/t_{1/2}$, thus permitting a direct comparison of results obtained at more than one temperature.

If, on the other hand, extensive regions of solid solution are encountered, the reaction does not take place at a surface, but extends through a finite depth. A composition gradient is set up with the greatest degree of oxidation at the surface, and the least at the center of the particle. The kinetics have been shown to be analogous to the flow of heat into a solid sphere,[20] the equation being

$$c = 1 - \frac{6}{\pi^2} \sum_{1}^{\infty} \frac{1}{n^2} e^{-\pi^2 n^2 Dt/r^2}$$

where D is the diffusion coefficient of oxygen in the particle of radius r, and $n = 1, 2, 3, \ldots$. The theoretical rate curve is shown by curve B of Fig. 11.

Experimental

The fact that decomposition products of the alkaline earth diuranates can be reoxidized to the diuranates has been discussed, but no mention has been made of the reaction mechanisms involved in this process. We have carried out a number of experiments which serve to give at least a qualitative picture of the reaction mechanism involved in oxidation and which lend confirmation to the phase relationships deduced from the equilibrium measurements.

The oxidation reactions investigated were carried out in the same system used in studying the thermal decomposition of the diuranates. The method used was to admit an excess of oxygen to the reaction system at room temperature; the furnace, preheated to the desired temperature, was then slid into place, and the absorption of oxygen measured by the pressure change in the system. This technique has two obvious difficulties which make the results useful only for semi-quantitative purposes: First, several minutes are required to obtain thermal equilibrium. Inaccuracy from this source can be minimized by disregarding the initial portion of the oxidation time, and by selecting a reaction temperature such that only a small fraction of the total oxidation takes place before thermal equilibrium is attained. Secondly, the reaction is necessarily not carried out at constant pressure. Addition of a large excess of oxygen serves to minimize this error.

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[18] L. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, USAEC-MDDC1543 (1945).

[19] For Jander's derivation, see *Z. anorg. Chem.*, **163**, 7 (1927).

[20] B. Serin and R. T. Ellickson, *J. Chem. Phys.*, **9**, 742 (1941).

Results and Discussion

Oxidation of $MgU_2O_{5.84}$.—The oxidation of $MgU_2O_{5.84}$ was found to consist of two steps: (a) a low temperature oxidation at 200–300° which gave a product with oxygen composition slightly above MgU_2O_6, and (b) a second step requiring 525–550° for a conveniently measurable reaction rate. The final product of the principal oxidation step is the diuranate, with no evidence being found for the formation of an intermediate phase corresponding to $MgU_2O_{6.65}$. At these temperatures the oxidation rate was dependent upon the oxygen pressure only at very low gas pressures. Oxidation of $MgU_2O_{6.65}$ required heating at 700°, confirming the conclusion that this compound is not involved in the oxidation of MgU_2O_6 to the diuranate.

The two steps in the oxidation of $MgU_2O_{5.84}$ to MgU_2O_7 were found to follow different mechanisms. The initial step was diffusion controlled as would be expected on the basis of previous data which had shown the existence of a solid solution in this composition range ($MgU_2O_{5.84}$ to $MgU_2O_{6.04}$). The experimentally determined curve for this step is not shown on Fig. 11, but it was found to follow closely the curve shown for the strontium diuranate system. The second step followed the phase-boundary controlled reaction curve (Fig. 11, curve A) over the entire range plotted. The experimental points obtained on three separate oxidations at 550 and 575° are plotted along the theoretical curve A. The results indicate that the MgU_2O_6 to MgU_2O_7 oxidation involves little, if any, solid solution, and that the diffusion of oxygen through oxidized product is not a rate-determining factor.

Oxidation of $CaU_2O_{5.95}$.—The oxidation of $CaU_2O_{5.95}$ followed a pattern somewhat similar to that of the corresponding magnesium compound in that two steps were again evident. The low temperature oxidation process gave a product containing slightly more than six oxygen atoms per calcium atom. The second oxidation step to the diuranate took place in the same temperature range as the corresponding magnesium compound reaction.

The first portion of this second step of the oxidation curve followed the theoretical phase-boundary controlled reaction curve fairly well, but the latter portions more nearly resembled the diffusion controlled oxidation. These observations can be explained by the thermal decomposition data which show a diphasic region to $\sim CaU_2O_{6.85}$ and solid solution extending from this point to the diuranate. Oxidation to the diuranate apparently takes place by consecutive reactions, the phase-boundary reaction predominating in the initial portions, and giving way to the diffusion controlled process in the later stages.

Oxidation of $SrU_2O_{5.89}$.—Partial oxidation was observed at temperatures as low as 0°. At room temperature the oxidation rate fell essentially to zero as the composition reached $SrU_2O_{6.2}$. Heating caused further reaction, with complete oxidation requiring several hours at 550°.

As was expected from the phase diagram, the curve for the rate of oxidation of the strontium compound is much more like curve B (diffusion controlled) than like curve A (phase-boundary). The deviation between the experimental curve and curve B may be due to the formation of the intermediate oxide indicated by the thermal decomposition data.

Acknowledgment.—We are indebted to Dr. W. H. Zachariasen of the University of Chicago, to Dr. Stanley Siegel of the Chemistry Division, and to Dr. M. H. Mueller of the Metallurgy Division of Argonne National Laboratory for the X-ray data and their interpretation. We also wish to thank Dr. Norman R. Davidson of the California Institute of Technology for carefully reading the manuscript and for making a number of valuable suggestions and comments.

CHICAGO, ILLINOIS RECEIVED SEPTEMBER 4, 1951

[CONTRIBUTION FROM THE RADIO CORPORATION OF AMERICA, RCA LABORATORIES]

High-silica Fluosilicic Acids: Specific Reactions and the Equilibrium with Silica

BY S. MILTON THOMSEN

High-silica fluosilicic acids have escaped general recognition. They are readily prepared with any desired amount of "extra" silica up to 18% more than the composition represented by the formula H_2SiF_6. They show characteristic reactions with sodium salts and with fluorides, and these reactions are convenient for detecting and estimating the extra silica. They attack glass. They react with hydrated silica, and an equilibrium constant for this reaction has been approximately evaluated.

Introduction.—Analyses on samples of fluosilicic acid, reported[1] in 1936, showed the silica component to be present in proportions larger than required by the formula H_2SiF_6. Solutions prepared by dissolving hydrated silica in commercial fluosilicic acid have been used to produce low reflection films on glass, both by a vapor process,[2] and by a liquid bath[3] process.

This paper reports (1) preparation of high-silica fluosilicic acids (HSF acids) of predetermined compositions; (2) data on two previously reported[4] specific reactions of HSF acids; and (3) data on the equilibrium between silica and fluosilicic acid.

Terminology.—In this paper, the term fluosilicic acid is extended to apply to any homogeneous liquid reaction product of silica, hydrogen fluoride and water. All such products constitute the three-component fluosilicic acid system.

Two numbers are required to specify the composition of a fluosilicic acid. Used for this purpose are the concentration, denoted by C, and the silica number, denoted by S. Thus, C is the concentration of the hydrogen fluoride component, expressed as moles of H_2SiF_6 per liter, and S is the number of moles of silica component present for each 6 moles of hydrogen fluoride component. Both C and S are computed from data obtained by acidimetric titration.

Fluosilicic acid *of composition corresponding to the formula* H_2SiF_6, has $S = 1$. The HSF acids have $S > 1$, and the low-silica fluosilicic acids have $S < 1$. At the lower extreme is hydrofluoric acid, a degenerate fluosilicic acid with $S = 0$; at the upper extreme are the silica-saturated fluosilicic acids, having S approximately 1.18, but varying with C.

The silica component present in low-silica fluosilicic acids, and in an acid of $S = 1$, is termed primary silica. The HSF acids contain, in addition to such primary silica, a secondary silica component with its own characteristic chemical behavior.

Because the composition of silica-saturated fluosilicic acids approach closely that of $H_2SiF_6 \cdot SiF_4$ (fluodisilicic acid) for which $S = 1.2$, the secondary silica will be considered to be present in this form. The equation for the reaction of silica to form an HSF acid is then

$$4H^+ + 5SiF_6^= + SiO_2 \longrightarrow 3[SiF_6 \cdot SiF_4]^= + 2H_2O \quad (1)$$

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(1) Ivan Tannanaev, *J. Gen. Chem. U. S. S. R.*, **6**, 1430 (1936).

(2) F. H. Nicoll, *RCA Review*, **X**, 440 (1949).

(3) S. M. Thomsen, *ibid.*, **XII**, 143 (1951).

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