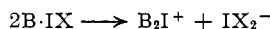
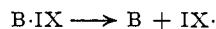


plex. On the other hand, the hindrance which one methyl group of the 2-picoline offers does not interfere sterically with the complex formation and since this amine is a stronger base than pyridine, correspondingly stronger complexes are formed with the iodine halides.

In a polar solvent, such as acetonitrile, the complexes undergo an ionic dissociation



while in non-polar carbon tetrachloride we have



This difference in the mode of dissociation of the polyhalogen complexes depending on the polarity of the solvent has been observed previously in the case of phosphorus polyhalides PCl_3I and PBr_3I .¹⁶

Acknowledgment.—The authors are indebted to the Research Corporation for the support of this work.

(16) A. I. Popov and E. H. Schmorff, *THIS JOURNAL*, **74**, 4672 (1952).

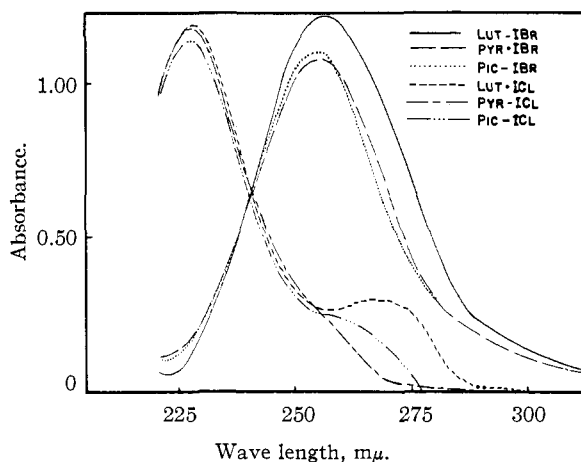


Fig. 2.—Absorption of ICl and IBr complexes in acetonitrile solutions; concn. $4 \times 10^{-5} M$.

IOWA CITY, IOWA

[CONTRIBUTION FROM HANFORD LABORATORIES OPERATION, GENERAL ELECTRIC CO.]

The Mechanism of Uranium Extraction by Tributyl Phosphate

BY H. T. HAHN

RECEIVED MARCH 21, 1957

Self-diffusion coefficients of uranium were measured by the capillary cell technique in concentrated aqueous solutions of uranyl nitrate and in hydrocarbon solutions of the uranyl nitrate-tributyl phosphate complex. The slowest diffusion rate observed was that of the complex in a solution of tributyl phosphate and Amsco 125-90W, a kerosene diluent. To determine whether the reaction was controlled by an interfacial barrier or by diffusion in the organic phase, the rate of extraction across a quiet interface was followed photometrically. It was found that the extraction initially proceeded by a combination of diffusion and convection, the convective force arising from the dissipation of reaction energy at the interface. The effect of an interfacial barrier was demonstrated by the addition of a surfactant to the system. The activation energy for diffusion of the uranyl nitrate-tributyl phosphate complex in Amsco was determined to be 5.68 kcal./mole.

Introduction

The rate-controlling step in the extraction of uranyl nitrate by tributyl phosphate may involve diffusion in either phase, complex formation, or elimination of water from the uranyl ion. In order to determine the importance of these factors it is then necessary to determine diffusion coefficients of uranium in concentrated aqueous solutions and in organic media. It is also necessary to follow, in detail, the transfer of uranium across the aqueous-organic interface. From a comparison of the extraction profiles based on the theoretical diffusion equation with experimentally observed profiles, conclusions may be drawn as to the mechanism of transfer.

Theoretical

Determination of the diffusion coefficients was made by the capillary cell method described elsewhere.¹ Briefly, the solution of Fick's equation for the case of diffusion from a capillary open at one end may be stated in terms of the fraction of activity remaining in a tube of length l , after time t

$$\gamma = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp[-(2n+1)^2 \pi^2 D t / 4l^2] \quad (1)$$

(1) J. S. Anderson and K. Saddington, *J. Chem. Soc.*, S80, S381 (1949).

The series is rapidly convergent and for values of $\gamma < 0.5$ may be represented by the first term with less than 0.2% error

$$D = [4l^2 / \pi^2 t] \ln(8 / \pi^2 \gamma) \quad (2)$$

Minimum error in D occurs when $\gamma = 0.32$. It was possible to use equation 2 in almost every case described in this paper.

In those experiments in which the progress of extraction was determined as a function of both time and space coordinates, the experimental situation was one of free diffusion in two phases from an initially sharp interface, no changes in concentration being noted at either end of the cell. Let the organic phase be represented by the numeral II, and the aqueous phase by I. The equilibrium distribution between organic and aqueous phases E_A^0 is assumed to hold for all time at the interface plane $X = 0$. Initially $C = C_0$ for $X < 0$ and $C = 0$ for $X > 0$; alternatively stated, X is positive in the organic phase.

If only diffusion is involved in the transport between phases, Fick's Second Law may be applied to each phase

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2}$$

where $D = D_I$ for $X < 0$ and $D = D_{II}$ for $X > 0$

The general solution of this equation is given by Jost²

$$C/C_0 = 1 - \frac{E_A^0 \sqrt{D_{II}}}{E_A^0 \sqrt{D_{II}} + \sqrt{D_I}} [1 + \operatorname{erf}(x/2\sqrt{D_{II}t})],$$

for $X < 0$ (4)

$$C/C_0 = \frac{E_A^0 \sqrt{D_I}}{E_A^0 \sqrt{D_{II}} + \sqrt{D_I}} [1 - \operatorname{erf}(x/2\sqrt{D_{II}t})],$$

for $X > 0$ (5)

The constants C_0 , E_A^0 , D_I , and D_{II} are known. At a given time t , C is then determined as a function of distance x from the interface.

Experimental

Diffusion Coefficient Measurements.—In practice, a cell containing uranium-233 enriched solution was lowered by means of a hydraulic lift until the sealed end of the cell was partially submerged in a natural uranium solution of identical composition. The assembly, consisting of the lift, cell and beaker of natural uranium solution, was then placed in a Fisher "Iso-Temp" bath and maintained at the desired temperature ($\pm 0.01^\circ$) for 45 minutes to permit thermal equilibration. The cell was then submerged completely in the natural uranium solution, thereby initiating the diffusion period.

The capillary diffusion cells consisted of one-centimeter lengths of uniform bore capillary tubing sealed at one end. The shoulder of the open end was tapered and ground. Cell volumes were 4.46 and 4.57 microliters.

The stock solution of uranium-233 tracer was prepared from enriched uranium trioxide having a specific activity of 2.01×10^7 d./min./mg. uranium. The oxide was dissolved in dilute nitric acid, and the solution twice concentrated to a small volume. Distilled water was then added to form the stock solution. In experiments with natural uranium, this procedure produced a solution containing essentially no free acid, the pH being within 0.03 unit of a uranyl nitrate solution of the same concentration.

In those experiments involving tributyl phosphate in an organic diluent, 35 microliters of the stock solution was transferred by means of a calibrated pipet to a 100 microliter centrifuge cone. The water was removed over Drierite in a vacuum desiccator. After ten days, the cone was filled with the appropriate tributyl phosphate solution. Following dissolution of the uranyl nitrate, the solution was centrifuged to assure that no residual water of hydration remained suspended in the organic phase.

Bulk solutions were prepared in the usual manner. The tributyl phosphate was vacuum distilled, the product having a refractive index of n_D^{25} 1.4225. The kerosene diluent used was Amsco 125-90 W Odorless Mineral Spirits (hereafter referred to as Amsco) produced by the American Mineral Spirits Company. Before use the Amsco was washed with sodium carbonate.

The samples were mounted on discs and counted on an Alpha Simpson Proportional counter with a precision of $\pm 1\%$.

Extraction Profile Apparatus.—The apparatus used to determine the concentration of uranium as a function of time and space consisted of a vertical cell, and a traversing platform upon which was mounted a light source, collimating slit and photometer tube. The diffusion cell was patterned after that of Ogston.³ Instead of sliding Lucite panels, this cell was constructed of glass. Two stopcocks were used to close a 6 in. length of 25 mm. Pyrex tubing at top and bottom. Three additional stopcocks were attached to the cell at top, center and bottom. In order to achieve an aqueous contact angle approaching 90 degrees, the walls of the cell were treated with General Electric Silicone Fluid SF-99.

In operation the organic phase was admitted through the upper stopcock, the aqueous phase through the lower and both exited through the center. The junction of this side-arm with the main tube was narrowed to a slit to minimize

transfer into the side tube during the extraction. A sharp interface was created by allowing both phases to flow for at least five minutes. The entrance and exit cocks were then quickly closed, and the diffusion allowed to proceed.

The system was calibrated with solutions of known uranium concentration in both phases either immediately preceding or immediately following each experiment. The duration of a scan was of the order of 20 minutes. Therefore, the elapsed time of an experiment was made long in comparison to the scanning time in order that the profile might have significance.

Preliminary experiments made use of the γ -emission of U-237 to follow the transport progress. The rays were collimated by a slit in a one inch thick lead shield and received by a scintillation center as the platform moved slowly up the length of the diffusion cell. This technique was incapable of high resolution because of poor collimation of the γ -rays and was abandoned in favor of the photometric method. In the latter, the traversing platform, containing a light source and photometer circuit, was attached to a threaded collar through which passed a drive shaft. A yoke at the upper end provided structural rigidity. The shaft was driven by a four r.p.m. Telechron motor geared down to one r.p.m. The vertical rate of travel for the scanning platform was one millimeter per minute, as determined by cathetometer measurements. The entire scanning assembly was fastened to a 25-pound lead brick and placed on a firm rubber pad. The bench was supported on rubber pads to further minimize vibration.

The light source, a Spencer microscope lamp containing a six volt bulb was attached to the traversing platform in position opposite to the photometer tube. The light source was air-cooled, a necessary precaution to prevent changes in the collimating slit width due to thermal expansion. The light beam was then passed successively through a heat absorbing glass filter and a Corning violet filter. The latter transmitted strongly in the range 350–480 μ with a maximum transmission at 405 μ . A $3/16$ " brass disc containing a $1/4$ mm. slit was attached to the front of the lamp, but thermally insulated from it by a polythene ring. The outer face of the disc was covered with black tape to reduce reflection. After passing through the cell the beam was collimated again by a $1/4$ mm. slit in black tape covering the face of the photometer tube.

The beam was received by an RCA 929 Photometer tube with maximum sensitivity at 510 μ . The choice of tube was based on size rather than sensitivity. Two 22.5 volt batteries were used as the tube voltage source with a load resistance of 300 megohms. The tube signal was fed to a Beckman pH meter for additional amplification and thence to a Leeds and Northrup Micromax recording potentiometer.

Results

Self-diffusion Coefficients.—Self-diffusion coefficients of uranium in uranyl nitrate solutions at 25° were determined to be 4.63×10^{-6} cm.²/sec. at 0.13 M ; 4.21×10^{-6} cm.²/sec. at 0.43 M ; and $3.51 \pm 0.03 \times 10^{-6}$ cm.²/sec. at 1.0 M . Plotting these values together with Saddington's value⁴ of 5.0×10^{-6} cm.²/sec. for uranium in 0.01 M uranyl perchlorate as a function of the square root of concentration shows departure from linearity only in the vicinity of one molar. This is in accord with the relatively large salting effect indicated for uranyl nitrate by the activity coefficient data of Robinson.⁵

Diffusion of the uranyl nitrate-tributyl phosphate complex in Amsco was found to be considerably slower than diffusion of the uranium species in aqueous media. For example, whereas experiments of one day duration in water were sufficient to reduce the cell activity to 32 to 45% of the orig-

(2) W. Jost, "Diffusion in Solids, Liquids and Gases," Academic Press, Inc., New York, N. Y., 1952, p. 68–69.

(3) C. A. Coulson, J. T. Cox, A. G. Ogston and J. S. Philpot, *Proc. Roy. Soc. (London)*, **A192**, 382 (1947).

(4) K. Saddington, "The Self-Diffusion of Uranium Ions in Solution," *AERE-C/R-626*, Dec. 1950.

(5) R. A. Robinson, J. M. Wilson and H. S. Ayling, *THIS JOURNAL*, **64**, 1469 (1942).

inal activity, in the organic phase studies, from 4 to 14 days were required.

Values of D , the self-diffusion coefficient, have been determined at 25° for 0.44 M uranium in 30% TBP-Amsco and 1 M uranium in 71% and 100% TBP solutions. These values were $1.27 \pm 0.01 \times 10^{-6}$ cm.²/sec. in 30% solution; $0.29 \pm 0.07 \times 10^{-6}$ cm.²/sec. in 71% solution; and $0.24 \pm 0.02 \times 10^{-6}$ cm.²/sec. in tributyl phosphate. The decrease in D with increase in volume per cent. tributyl phosphate and, hence, viscosity is marked. The product of D and viscosity for this range was found to be $3.8 \pm 0.2 \times 10^{-8}$ dyne.

The self-diffusion coefficient of tributyl phosphate in 30% TBP-Amsco has been determined in this Laboratory⁶ to be 4.3×10^{-6} cm.²/sec. The value of 1.27×10^{-6} cm.²/sec. for the uranium complex in 30% TBP-Amsco is, therefore, the slowest diffusion step found in this system.

Attempts were made to determine the coefficient for this complex in carbon tetrachloride. However, an extremely rapid exodus of the activity from the cell resulted, e.g., 98% in 20 minutes. The same phenomenon also was observed here in the zirconium(IV) nitrate-tributyl phosphate system⁷ in which careful immersion and immediate removal of the cell resulted in 15-75% loss of activity. A small part of the increased diffusivity may be ascribed to lower viscosity. The major portion is perhaps due to a high sensitivity to very small concentration gradients.

The Activation Energy for Diffusion of the Uranyl Nitrate-Tributyl Phosphate Complex.—The activation energy for diffusion of the uranyl nitrate-tributyl phosphate complex in Amsco was determined from measured diffusion coefficients at 25, 30 and 35°. Coefficient values obtained were $1.27 \pm 0.01 \times 10^{-6}$ cm.²/sec. at 25°; $1.47 \pm 0.02 \times 10^{-6}$ cm.²/sec. at 30°; and $1.79 \pm 0.04 \times 10^{-6}$ cm.²/sec. at 35°. When plotted against the reciprocal of temperature a least squares treatment gives

$$E = 5.68 \text{ kcal./mole}$$

for 0.44 M uranyl nitrate-tributyl phosphate complex in 30% TBP-Amsco solution.

No other values for activation energies determined by this method in non-aqueous systems have been found. However, Krauss and Spinks⁸ have observed the diffusivity of $H_2PO_4^-$ ion in aqueous solution. They found that the activation energy increased from 4.3 kcal. at infinite dilution to 5.4 kcal./mole at 0.93 M .

Gradient Profiles.—Previous experiments with uranium-237 had indicated that turbulence prevailed in the interfacial region during the early stages of transfer. The net result was that the uranium front moved out from the initially sharp interface several millimeters into the organic phase during the first 15 minutes.

The same initially rapid movement of the front was observable photometrically. After 15 minutes, concentrations of 0.2 to 0.35 M uranium were noted 1 mm. from the interface, while the advanc-

ing edge of the uranium band was 4 mm. from it. On the basis of equations 4 and 5, this edge should have been within 1.5 mm. at this time. Beyond indicating that an excessive transfer was taking place, no quantitative interpretation of the data for short time intervals is possible since even in the early stages 10 to 15 minutes was required for a scan.

Experimental data for the transfer of uranium from 1.03 M uranyl nitrate into 30% TBP-Amsco are presented in Figs. 1 and 2 for time intervals of

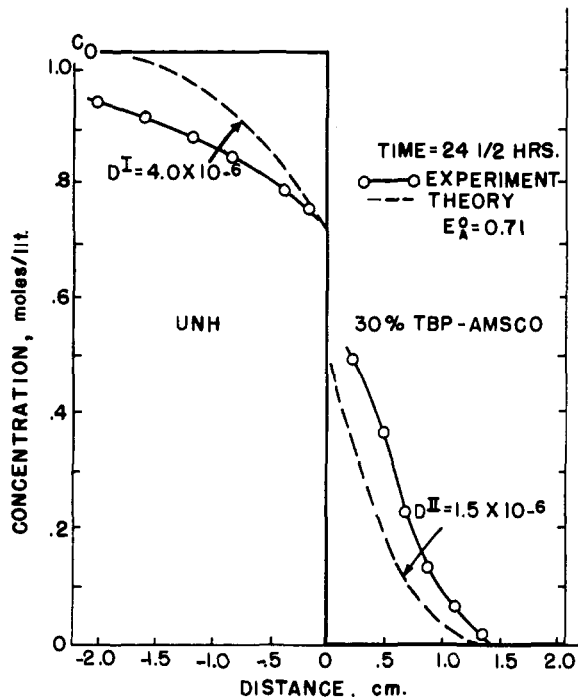


Fig. 1.—Uranium extraction profile after one day.

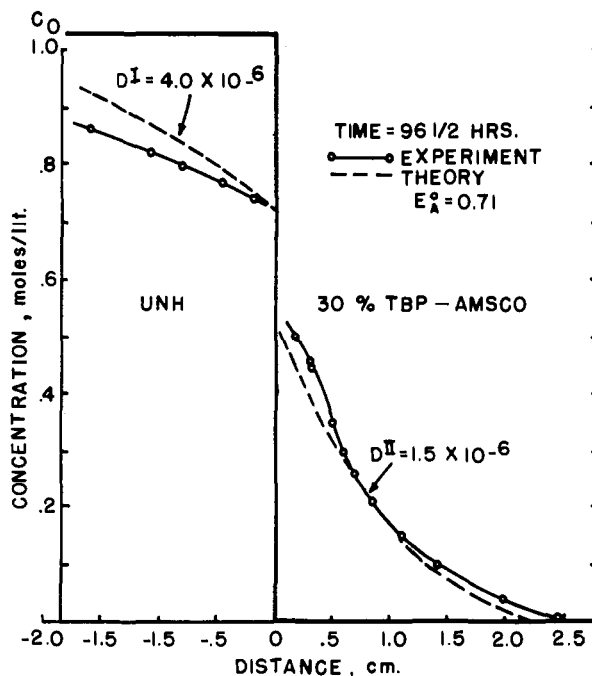


Fig. 2.—Uranium extraction profile after four days.

(6) W. F. Johnson and R. L. Dillon, HW-29086 (Sept. 1, 1953).

(7) J. C. Sheppard, private communication.

(8) C. J. Krauss and J. W. T. Spinks, *Can. J. Chem.*, **32**, 71 (1954).

24.5 and 96.5 hours. Although single points have been chosen in plotting the data, the curve obtained experimentally is a continuous one. It was not possible to obtain reliable readings closer than one millimeter to the interface since, due to the transfer, the density of the organic phase is increased locally resulting in a small meniscus.

The theoretical curves are based on a distribution coefficient of 0.71. The diffusion coefficient in the aqueous phase varies from 3.5×10^{-6} at 1 *M* to 5×10^{-6} cm.²/sec. at 0.01 *M*. In the cases of interest here, the concentration ranges are only 0.7 to 1.0 *M* uranyl nitrate, and a constant value of $D_I = 4 \times 10^{-6}$ cm.²/sec. was used to simplify the calculation. The variation of *D* with concentration in 30% TBP-Amsco has not been determined. However, at 0.44 *M* uranium $D_{II} = 1.27 \times 10^{-6}$ cm.²/sec., and if the constancy of the product of diffusion coefficient and viscosity holds, the diffusion coefficient would have a value of 2×10^{-6} at infinite dilution. Therefore, a value of 1.5×10^{-6} cm.²/sec. for D_{II} was chosen to test equations 4 and 5.

The assumption of invariance of *D* introduces relatively small errors in this case. For example, the concentration on the organic side of the interface represents the maximum achieved in that phase. The error due to the assumption of constant diffusion coefficient is, therefore, greatest at $x = 0$. After 24.5 hours the concentration at this point is calculated to be 0.51 *M* using $D = 1.50 \times 10^{-6}$ cm.²/sec.; using $D = 1.27 \times 10^{-6}$ cm.²/sec., *C* is found to be 0.52 *M*. The deviation is, therefore, -0.01 *M*. In the dilute region *D* probably approaches 2×10^{-6} cm.²/sec. After 24.5 hours at $x = 1.0$ cm., *C* is calculated as 0.03 *M* using the value of 1.5×10^{-6} cm.²/sec.; if $D = 2 \times 10^{-6}$ cm.²/sec., *C* = 0.045 *M* or a deviation of 0.015 *M*. Similarly, the deviations in the aqueous phase are of the order of 0.01 *M*.

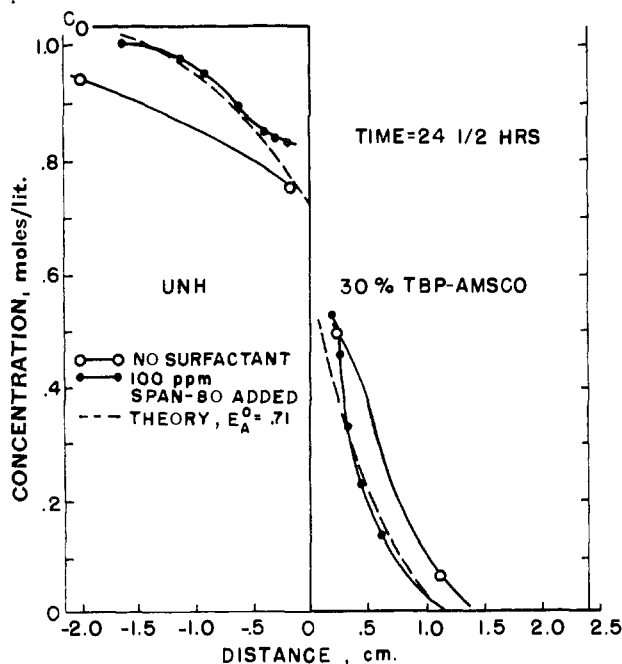


Fig. 3.—The effect of added surfactant.

The retardation of extraction by the presence of surface active agents presents an excellent means of determining whether the scanning method used is capable of observing an interfacial barrier.

After preliminary addition of 100 p.p.m. of the surface active Span 80 (Sorbitan monooleate) to the aqueous phase, the transfer was allowed to proceed under conditions identical to those previously described. The uranium profile with and without surfactant is compared in Fig. 3. The higher uranium concentration on the aqueous side is quite evident in the former curve.

In other experiments it was found by integration of the area beneath the profiles that in the range 15 to 60% tributyl phosphate the amount of uranium extracted per day was proportional to the initial tributyl phosphate concentration. This observation resulted from an increased E_A^0 and decreased organic phase diffusion coefficient as the tributyl phosphate concentration was increased. The net result was a fortuitous counterbalancing of the fractional coefficient in equation 5.

Discussion

From Fig. 1 it is seen that after one day an amount of uranium has been extracted in excess of that predictable solely from diffusion. This excess enters during the early stages of transfer and is presumably the result of convection in the interfacial region. The convective force must arise from a relatively rapid release of energy, probably the energy of complex formation. The latter effect would be greatest initially when the concentration of free tributyl phosphate close to the interface was at a maximum. After four days the initial excess has largely disappeared because of diffusion further into the organic phase and a somewhat reduced rate of extraction.

The mechanism of extraction could conceivably be limited by any of the following steps: (1) an interfacial barrier; (2) complex formation; (3) elimination of water; (4) diffusion in the aqueous phase; (5) diffusion in the organic phase.

The first step may be eliminated since no uranium excesses were noted on the aqueous side of the interface. Such excess was shown to exist when an artificial barrier was introduced. Complex formation is relatively rapid, as evidenced by the interfacial turbulence and speed of the initial extraction. A slow elimination of water may be regarded as a special case of the barrier mechanism, since it would require alignment of complex molecules at the interface.

The rate of extraction is initially greater than the slowest diffusive process. However, the system approaches organic phase control in later stages. It would be desirable to incorporate the convective effect into a mathematical formulation for each phase such as

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} - V \frac{\partial C}{\partial X} \quad (6)$$

The implicit assumption of a limitless convective force is not in accord with experimental fact, and it is, therefore, necessary to restrict the force to the interfacial region. Relating the effect to either the

rate of complex formation or the energy release did not produce differential equations capable of solution. The alternative is to introduce an arbitrary step function to describe the force solely in the vicinity of the interface.

Since this work was completed in early 1954, Lewis has published⁹ results obtained with stirring in essentially the same system. No interfacial barrier was observed initially. However, a barrier did appear in later stages of the extraction. The latter fact in no way contradicts the present work.

(9) J. B. Lewis, *Nature*, **178**, 274 (1956).

It is quite reasonable that the eddy diffusion coefficients be larger than those for molecular diffusion with the interfacial barrier providing a resistance intermediate to these extremes. The lack of an immediate barrier in the stirred system suggests that even here the energy of reaction is sufficiently great to prevent its formation.

Acknowledgment.—The author is indebted to the Laboratory Analytical group under E. W. Christopherson for analyses, and to Dr. L. L. Burger for helpful discussion.

RICHLAND, WASHINGTON

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Preparation of Tungsten Carbide

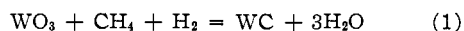
BY ARTHUR E. NEWKIRK AND IFIGENIA ALIFERIS

RECEIVED APRIL 11, 1957

The tungsten carbide, WC, may be prepared by heating tungstic acid, a blue oxide of tungsten or ammonium paratungstate in a mixture of hydrogen and methane at 850 to 1000°. The effects of time, temperature and methane concentration are given. With tungstic acid, the reduction to tungsten metal is shown to be complete before carburization begins.

As a part of a general investigation of reactions forming tungsten carbide, the reactions of tungstic acid, a blue oxide of tungsten and of ammonium paratungstate with a gaseous mixture of hydrogen and methane were examined. The only reference to these specific reactions is by Hilpert and Ornstein¹ who reported they succeeded one time in preparing tungsten carbide by heating tungsten trioxide at 1000° in a 1:1 mixture of methane and hydrogen. In general, the rate of carbon formation was so rapid at this temperature that a reasonably pure product could not be obtained, and it was necessary to use lower temperatures. No details of such experiments were reported. There are numerous references to the carburization of metallic tungsten by carbon or carburizing gases and of the formation of tungsten carbides by reaction of tungsten oxides with carbon.²

The tungsten trioxide-hydrogen-methane reaction was first tried in this Laboratory by E. H. Winslow and E. L. Brady³ who showed that tungsten carbide could be obtained in quantitative yield by heating tungsten oxide between 2 and 5 hours at 1000° in hydrogen containing 0.85% methane by volume. The gas composition was selected as containing slightly less methane than that which would deposit carbon, 0.95% at this temperature.⁴ Using the data of Kubaschewski and Evans⁵ it can be shown that the free energy of the over-all reaction



(1) S. Hilpert and M. Ornstein, *Ber.*, **46**, 1669 (1913).

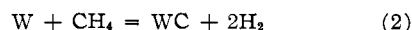
(2) P. Schwarzkopf and R. Kieffer, "Refractory Hard Metals," The Macmillan Co., New York, N. Y., 1953, Ch. 13.

(3) E. H. Winslow and E. L. Brady, private communication.

(4) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Series 3, Table 3, 1947.

(5) O. Kubaschewski and E. L. Evans, "Metallurgical Thermochemistry," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

is favorable to the formation of tungsten carbide under these conditions, and that the equilibrium pressure of methane for the reaction



is less than that for the decomposition of methane to carbon and hydrogen. The effect of time, temperature and methane concentration were therefore studied for reactions similar to the one shown in eq. 1.

Experimental

Materials.—Tungsten compounds were obtained from the Lamp Wire and Phosphors Department of the General Electric Company and their tungsten content determined by measuring the loss in weight after firing in hydrogen for three hours at 1000°. In each case the product gave an X-ray diffraction pattern showing only the presence of elemental tungsten. Tungstic acid, residue weight 74.06%, theory for H_2WO_4 73.59%, for WO_3 79.30%; ammonium paratungstate, residue weight 70.50%, theory for $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 5\text{H}_2\text{O}$, 70.43%; blue oxide residue weight 79.35%, theory for WO_3 79.30%, for $\text{W}_{20}\text{O}_{58}$ 79.85%. The ammonium paratungstate gave variable results until samples were equilibrated and weighed in a room at constant temperature and humidity. This material was also difficult to handle due to static charges. The difficulty was overcome by holding the active element of a "Static master" brush near the boat while loading it into the quartz tube.

Laboratory line hydrogen was passed through a "Deoxo" unit and a liquid nitrogen trap to obtain hydrogen with a dew point below -100° . Commercial methane was used directly from a cylinder.

Apparatus and Procedure.—The hydrogen and methane were separately metered to a mixing bulb provided with a fritted filter on the outlet. This led to the inlet of a quartz combustion tube 2 cm. dia. by 75 cm. long which was heated by an electric furnace over a 55 cm. length. Semi-cylindrical boats of fused quartz or nickel were used. For the parallel boat runs, a special boat was made which held two quartz liners each having a quarter-circle cross section. In this way both tungsten and the oxide could be exposed under the same conditions. The temperature was measured by a chromel-alumel thermocouple in a quartz well centered above the sample. The outlet of the combustion tube was drawn to a jet. Samples were inserted through the inlet end which had been fitted with a ground joint for the purpose.