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THE FLUORIDES OF URANIUM—III

KINETIC STUDIES OF THE FLUORINATION OF URANIUM TETRAFLUORIDE BY FLUORINE

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Abstract—The reaction between uranium tetrafluoride and fluorine has been studied between 265° and 348°C by following the change in weight of the solid phase, using a spring balance. Formation of uranium hexafluoride at the solid surface is accompanied by migration of fluorine ions into the UF_4 lattice. The rate of production of UF_6 is in agreement with the kinetics expected for reaction between a gas and a solid at a continuously diminishing spherical interface.

The rate of reaction depends on the temperature; no reaction is detectable below 220°C. Within the limits of experimental accuracy the Arrhenius equation relates the reaction-rate constant and the temperature of reaction: the activation energies determined for three preparations of UF_4 were 15·5, 19·1 and 19·9 kcal per mole.

A linear relationship is shown to exist between the reaction rate and partial pressure of fluorine, but within the range examined the reaction rate is not affected by the velocity of gaseous reactant past the solid. The rate of UF_6 production is dependent on an "effective" surface area of UF_4, rather than the surface area determined by gaseous adsorption.

URANIUM hexafluoride can be prepared by the reaction between uranium tetrafluoride and fluorine. Before this study was made, no fundamental data on the kinetics of the reaction were available, although it was believed(1) that uranium pentafluoride was an essential intermediate in the reaction:

$$2UF_4 + F_2 \rightarrow 2UF_5$$

$$2UF_5 + F_2 \rightarrow 2UF_6$$

The present work was undertaken to elucidate the kinetics and, if possible, the mechanism of reaction.

An extensive literature exists on solid–gas reactions in which the products are solids, e.g. the oxidation of metals. Kinetic studies in which the products of reaction are entirely gaseous have been much more limited. They include work on the carbon–water,(2–5) carbon–carbon dioxide(6,7) and carbon–oxygen systems.(8,9)

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The reaction taking place at surfaces may be considered as five separate processes, the slowest of which determines the rate of reaction.(10)

(1) Transport of the reacting gas to the surface.
(2) Chemisorption of the gas.
(3) Chemical reaction at the surface.
(4) Desorption of the reaction product.
(5) Transport of the reaction product away from the surface.

In general (1) and (5) are diffusion processes; since, under the experimental conditions, only small amounts of reaction products are formed, the boundary layer will not limit access of reacting gas to the outer surface. It is thus expected that (2), (3) and (4) are the rate-determining steps: they will depend on temperature. Amongst other factors, (2) will depend on the surface area available for adsorption. The reaction studied was believed to be a surface reaction, and these factors were therefore examined, although the possibility of reaction in the solid phase was also considered.

EXPERIMENTAL

A mixture of nitrogen and a large excess of fluorine was flowed over a thin layer, a few grains thick, of uranium tetrafluoride contained in an aluminium pan. The pan was suspended from the end of a calibrated beryllium–copper spring balance in a reactor tube heated by a vapour jacket. The reaction was followed by observing changes in the extension of the spring caused by changes in weight of the contents of the pan. Fig. 1 shows the apparatus used for the majority of the work.

Beryllium–copper spring balance

A typical spring used was 2·3 cm in diameter and consisted of 40 turns of wire of 0·0076 in. diameter. It was annealed at 320°C for 4 hr and stretched taut before use. The spring sensitivity determined by the addition of weights at the ends of the glass fibre, was 0·0177 g/cm.

The effect of the column temperature on the spring sensitivity was determined. There was a spring movement of 0·014 cm per °C (which would correspond to an apparent weight change of 0·4 per cent per °C) in the range 20–35°C, under typical experimental conditions. Consequently, to obtain maximum accuracy, the spring column was jacketed and water was circulated through the jacket from a thermostat.

The spring column was made with a constriction near the botton, as shown in Fig. 1. This was to reduce the effect of convection currents set up in the reactor tube. A glass weight was suspended from the end of the spring in the reactor and the temperature of the reactor raised and lowered. The spring reading was not altered in any appreciable amount by changes of the reactor tube temperature. The accuracy of weight measurement is set by the accuracy of the cathetometer reading at a weight of 10^{-4} g or 0·1 per cent of the original sample weight.

It was found that the sensitivity of a spring did not change appreciably with time, and that the very small amount of corrosion of the spring which took place, due to diffusion of fluorine and uranium hexafluoride up the column, did not affect the accuracy of the experiments. The spring calibration was checked after every run and shown to be unchanged.

Uranium tetrafluoride

Three preparations of uranium tetrafluoride (UF_4) were used:

(i) A batch of tetrafluoride prepared by the hydrofluorination of uranium dioxide was used for most of the experimental studies. Thermogravimetry indicated that the water content was low ($<$0·2 per cent). Analysis, of which details are given below, showed that the material contained hexavalent uranium (4 per cent) and was low in fluorine content (22·8 per cent instead of the theoretical 24·2 per cent), indicating the presence of impurities such as uranium oxides and uranyl fluoride. The small amount of impurities does not affect the validity of the experiments, as possible weight changes of these impurities would be very small, of the order of the experimental accuracy.

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(10) S. Glasstone, K. J. Laidler and H. Eyring, *Theory of Rate Processes*. McGraw-Hill, New York (1941).

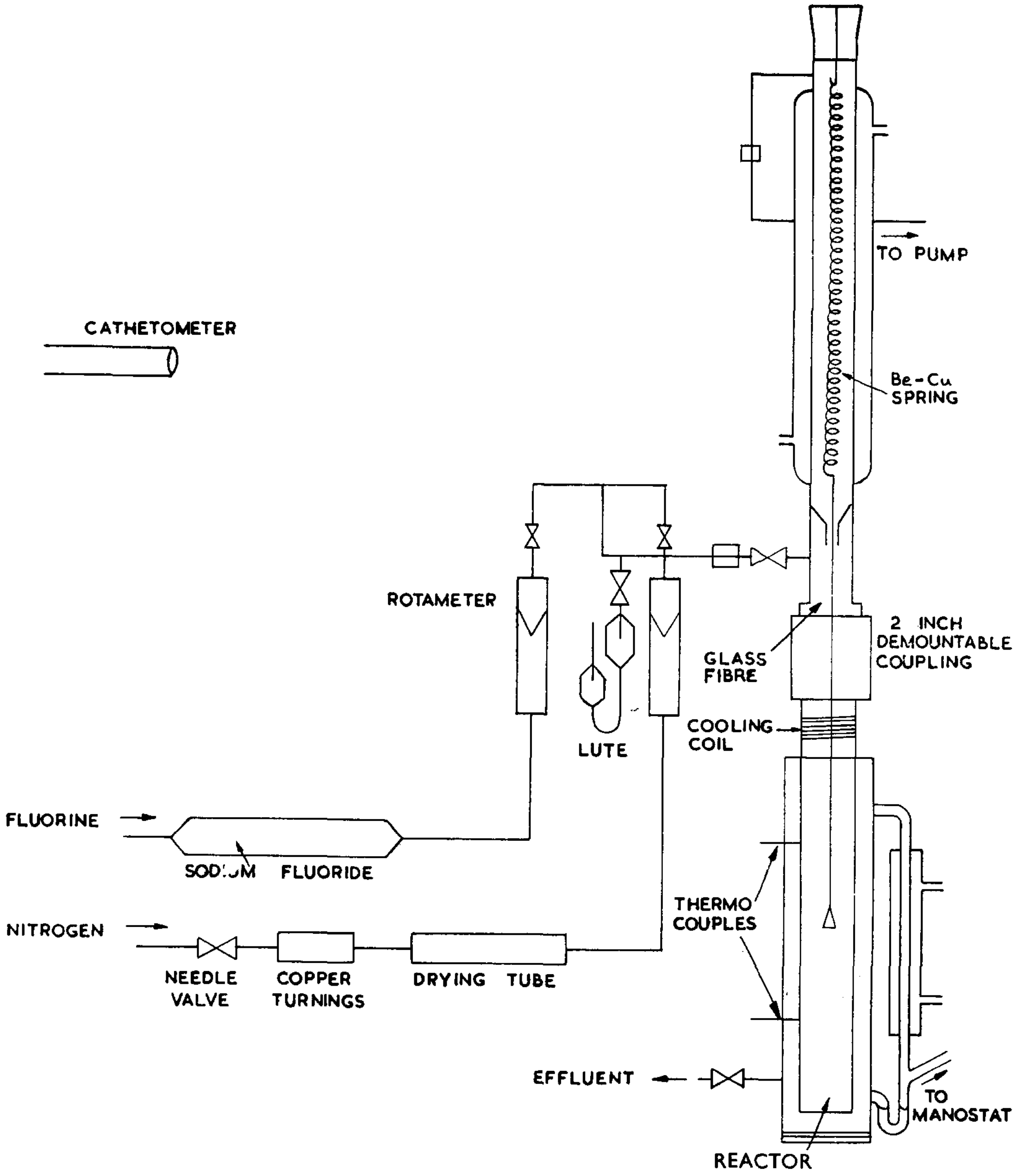

FIG. 1.—Apparatus for fluorination of uranium tetrafluoride.

(ii) Uranium tetrafluoride of large surface area was prepared by hydrating and dehydrating the tetrafluoride made by hydrofluorination. The hydrate $2UF_4{\cdot}5H_2O$ was produced by stirring material (i) in water at 20°C for five days. This hydrate was dehydrated at 270°C *in vacuo*. The product was found to be 98 per cent pure, the residual 2 per cent consisting of uranium dioxide and uranyl fluoride.

(iii) Uranium tetrafluoride of very small surface area was prepared by the sublimation of material (i) at 1000°C under high vacuum.

The surface areas of the different batches of material were determined by ethylene adsorption.(11)

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(11) L. A. WOOTEN and B. G. BROWN, *J. Amer. Chem. Soc.* **65**, 113 (1943).

All the uranium tetrafluoride used was ground in a mortar before being passed through a 150-mesh sieve into an aluminium pan of diameter 1 in. By direct sieving it was found that a uniform layer a few grains thick could be obtained. From the desired spring movement and thickness of the bed, the amount of uranium tetrafluoride used in a run was fixed between 70 and 85 mg.

Method of analysis of UF_4

The total uranium content of a sample was determined using the standard method of solution in nitric acid, precipitation of ammonium diuranate and final ignition at 800–820°C to U_3O_8. The tetravalent uranium content was obtained by estimation with ceric sulphate: an excess of ceric sulphate solution was added to a weighed sample of UF_4, excess sulphuric acid added and the mixture heated to bring UF_4 into solution. On cooling, excess ceric sulphate was back-titrated against ferrous sulphate solution using N-phenylanthranilic acid as indicator. The fluorine content was determined by hydrolysis of a sample with sulphuric acid, steam distillation of the fluosilicic acid produced and estimation as lead chloro-fluoride.(12)

Fluorine supply

The fluorine was generated in an I.C.I. 60-amp electrolytic cell. The fluorine from the cell was flowed through towers packed with sodium fluoride pellets and through copper pipe to the apparatus on the bench. On the bench the fluorine was passed through a tube packed with sodium fluoride pellets and a Rotameter before entering the reactor. An overpressure-underpressure lute (see Fig 1) filled with Fluorolube (a fully fluorinated heavy oil) ensured that the cell would be subjected to only very slight suction or pressure. A Rotameter was unsatisfactory for the continuous measurement of fluorine flow rate, due to the high corrosion rate of the Rotameter tube and short-period fluctuations in the flow from the generating cell. Cell current was the most satisfactory and accurate measure of the average flow rate during a run; there was good agreement between the flow rate thus calculated and direct measurement with a new Rotameter (i.e. before the calibration was affected by corrosion).

The fluorine from the cell was found to be 98 per cent pure; no oxygen was detected.

Nitrogen supply

The nitrogen was the commercial material obtained in cylinders. The gas was passed through a purification train consisting of a heated silica tube packed with copper turnings at 650°C, and a drying tube containing calcium chloride and phosphorous pentoxide. The nitrogen flow rate was adjusted by a needle valve and measured with a Rotameter.

Heating the reactor

The reactor used for most of the runs was made of mild steel with the inside surface nickel plated. The reactor tube was surrounded by a vapour jacket in which mercury was boiled at a known pressure, measured by a mercury manometer and maintained by a Cartesian diver manostat. Different temperatures were obtained by varying the pressure in the vapour jacket. Two chromel–alumel thermocouples were soldered to the outside of the jacket approximately 25 cm apart; in the steady state the same temperature was registered by both thermocouples. The pan was suspended so as to move within this constant-temperature zone.

The temperature registered by the Kent recorder (to which the thermocouples were connected) was constant throughout a run and differed less than -2°C from that predicted from the mercury vapour pressure registered by the manometer. Tests with a thermocouple suspended on the inside of the reactor showed that the temperature in the reactor was within 2°C of the temperature measured by the recorder, and usually the difference was much less than 2°C.

Direct electrical heating was used in preliminary experiments, but was unsatisfactory for accurate kinetic measurements because of variation in temperature along the length of the reactor.

A typical run

Except for three runs in which the initiation temperature was determined, a fixed temperature was used throughout a run.

In a typical run the beryllium–copper spring balance was first calibrated. The uranium tetrafluoride was then sieved into the pan and its weight determined. This weight was checked by the

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(12) R. BELCHER and J. C. TATLOW, *Analyst.* **76**, 583 (1951).

spring balance before the uranium tetrafluoride was vacuum degassed for 3 hr at a temperature close to that of the run. The temperature of the run was fixed, and after several minutes during which constancy of temperature was ensured, the apparatus was filled to atmospheric pressure with nitrogen. Meanwhile the fluorine cell was run at the desired current and the line from the cell to the apparatus flushed through with fluorine. Cathetometer readings were taken with the column under vacuum and filled with nitrogen. The buoyancy concentration is insignificant, but an apparent increase in weight of 0·2 per cent occurs when gas flow past the pan commences. This correction remains constant throughout the run. Fluorine was then allowed to flow through the reactor, the time of opening of the tap above the fluorine Rotameter being taken as the commencement of the experimental run. Further cathetometer readings were taken at intervals throughout the run. At the end of a run the apparatus was flushed out with nitrogen before being cooled and opened to the atmosphere.

DISCUSSION OF RESULTS

(a) *Initiation temperature*

No reaction detectable by the spring balance occurs in periods of several hours at temperatures up to 220°C, but the reaction rate is measurable at 230°C.

(b) *Kinetics of reaction*

During large scale production of uranium hexafluoride it is common experience that very little hexafluoride is formed until virtually complete conversion to pentafluoride has taken place, but the experimental results of the present study show that fluorination of individual uranium tetrafluoride particles does not take place in these two distinct steps. This is deduced from the kinetic data discussed below, the first-power dependence of the rate on fluorine pressure (discussed in (f)) and the absence of any large initial increases in weight of the contents of the pan. (Any initial weight increases were very small and if intermediate fluoride was formed it could only have been formed as a surface film). The rate of hexafluoride production decreases as the fluorination of an experimental batch proceeds.

The UF_6 production rate is in agreement with the kinetics expected for reaction between a gas and a solid at a spherical interface which is continuously diminishing due to reaction with the gas. In such a reaction the following relationship can be deduced:

If the initial mass of a solid particle $m_0 = \frac{4}{3}\pi r_0^3 \rho$, where r_0 = initial radius and ρ = bulk density, then the rate of reduction in mass at a given temperature is assumed to be proportional to the surface area of the particle,

i.e.
$$-\frac{dm}{dt} = K4\pi r^2 \tag{1}$$

where r is the radius of the particle at time t, and K is the constant for a given temperature, partial pressure of reactant gas, and chemical reaction.

The fraction of reaction C that has taken place in time t is given by

$$C = \frac{\text{reduction in mass of particle}}{\text{initial mass of particle}} = \frac{m_0 - m}{m_0} = 1 - \left(\frac{r}{r_0}\right)^3$$

whence equation (1) becomes $$\frac{dm}{dt} = -K4\pi r_0^2(1 - C)^{\frac{2}{3}}$$

$$\frac{dC}{dt} = \frac{1}{m_0}\frac{dm}{dt} = \frac{3K}{r_0\rho}(1 - C)^{\frac{2}{3}} = R(1 - C)^{\frac{2}{3}} \tag{2}$$

This expression is that given by ANDERSON⁽¹³⁾ for a gas–solid reaction governed by the Law of Interface Reaction; here R is a constant equal to $r_0\rho$. Integrating expression (2), we obtain

$$(1 - C)^{\frac{1}{3}} = 1 - R't \tag{3}$$

where

$$R' = \frac{K}{r_0\rho}$$

R' is a rate constant having the units of reciprocal time. When the quantity $(1 - C)^{\frac{1}{3}}$ is plotted against t the points lie on a straight line, in agreement with equation (3), except for small deviations for the first 10 per cent and last 10 per cent of the weight change at the beginning and end of the reaction. Deviation at the beginning of a run is explained by the experimental conditions used. The reactor is initially filled with nitrogen, and it takes approximately 5 min for the mixture in the reactor to become that fixed for the run. Consequently, the reaction rate at the beginning of the reaction is abnormally low. Deviation at the end of a run is discussed below.

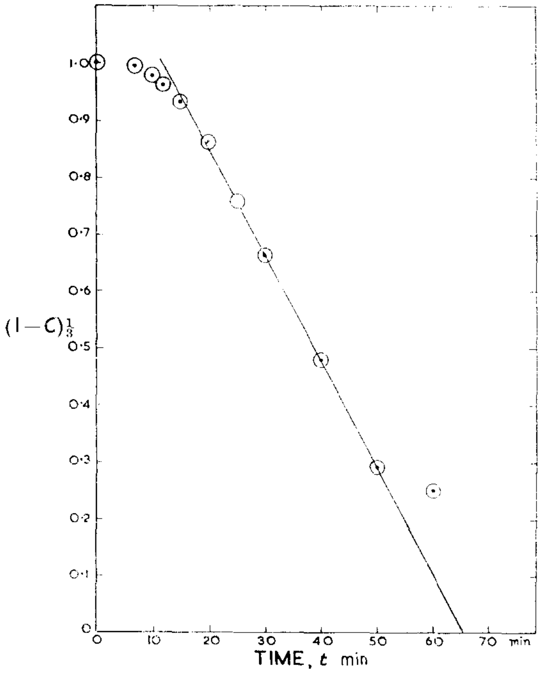

FIG. 2.—Plot of $(1 - C)^{\frac{1}{3}}$ against time at 300°C. C is fraction of the total reaction completed in time t.

Fig. 2 is the plot of $(1 - C)^{\frac{1}{3}}$ against t for a typical run, and Fig. 3 the uranium hexafluoride production curve based on weight loss of uranium tetrafluoride for the same run.

Attempts to fit the experimental observations to alternative mathematical models give less satisfactory agreement.

⁽¹³⁾ J. S. ANDERSON, *Bull. Soc. Chim.* **20**, 781 (1953).

(c) *Mechanism of reaction*

In several runs when the reaction was stopped before completion it was noted that the material remaining in the aluminium pan was grey or black in colour. Closer examination showed a dark skin around the uranium tetrafluoride particles. Analysis of the residue for tetravalent uranium content confirmed an uptake of fluorine. It follows that, in addition to the principal reaction producing uranium hexafluoride, fluoride ions simultaneously diffuse into the tetrafluoride lattice. A general picture of the reaction can now be drawn.

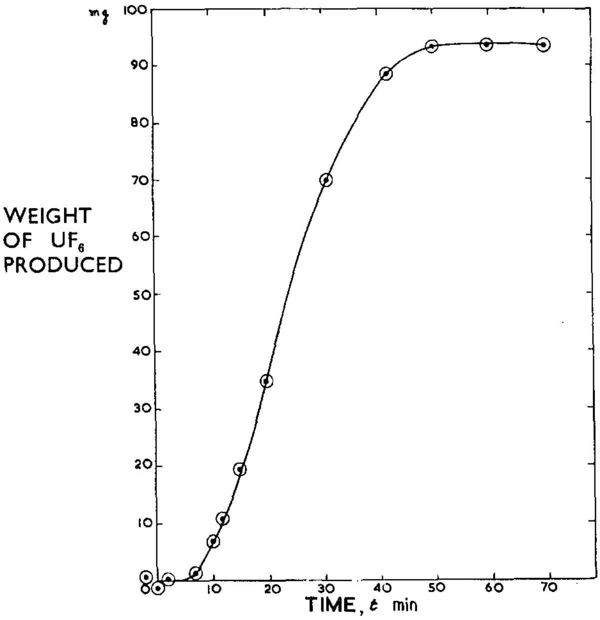

FIG. 3.—Rate of UF_6 production at 300°C. Initial weight of UF_4 (prepared from UO_2 and HF) 83 mg. Partial pressure of fluorine 220 mm.

Above the initiation temperature fluorine is adsorbed on to the surface of a uranium tetrafluoride particle and migrates into the crystal lattice, giving a non-stoicheiometric compound of variable composition richest in fluorine at the surface. Uranium hexafluoride is desorbed from the particle surface so long as the partial pressure of UF_6 in the surrounding atmosphere is less than the dissociation pressure of UF_6 for the intermediate fluoride at the surface. As reaction continues, the particle diminishes in size due to this mechanism of reaction, and the inward diffusion of fluoride ions continues so that the concentration at the centre of a particle tends to become that at the surface, the latter being determined by the partial pressure of fluorine and uranium hexafluoride at the surface.

It is stated above that there is a deviation from the expected kinetics as the fluorination nears completion. This is thought to be the result of the progressive migration of ions into the uranium tetrafluoride lattice. As reaction nears completion the concentration of fluorine at the particle centre approaches that at the surface. Whereas for the majority of the fluorination a particle consists essentially of uranium tetrafluoride with a fluorine-enriched outer surface, near the completion of reaction a phase change may occur because of the high fluorine concentration, so that the particle becomes one of an intermediate uranium fluoride. Experiments have shown that the rate of fluorination of an intermediate fluoride made from the same UF_4 by combination with UF_6 is less than that of uranium tetrafluoride under the same conditions.

TABLE 1.—FLUORINATION OF INTERMEDIATE URANIUM FLUORIDES

UF_4 used in intermediate preparation	Intermediate fluoride subjected to F_2	Intermediate fluoride produced by F_2 uptake	Temperature of fluorination (°C)	Reaction rate constant R'	Reaction rate constant R′ calculated for UF_4
Dehydrated	$UF_{4.52}$	$UF_{4.52}$	300	0·00770	0·0185
Dehydrated	$UF_{4.28}$	$UF_{4.57}$	300	0·00530	0·0185
Hydrofluorinated	$UF_{4.23}$	$UF_{4.32}$	303	0·00476	0·0212
Hydrofluorinated	$UF_{4.19}$	$UF_{4.52}$	300	0·00435	0·0196

Intermediate fluorides were prepared from uranium tetrafluoride by the action of uranium hexafluoride at 300°C and 42 mm pressure. The apparatus was that used throughout the work (fluorination studies previously described), with the addition of a source of uranium hexafluoride. In Table 1 the experimental results are summarized and a comparison is made with the fluorination of uranium tetrafluoride. The last column in Table 1 was calculated for the fluorination of uranium tetrafluoride, assuming the dependence of fluorination rate on fluorine pressure (see section (f)).

The results show that intermediate fluorides with a composition in the region of U_4F_{17} are fluorinated up to U_2F_9 with fluorine at 300°C. Further fluorination gives UF_6. The rate of fluorination of U_2F_9 and other intermediate fluorides in this composition range is less than that of the fluorination of uranium tetrafluoride under the same conditions; the ratio of the reaction rate constants is approximately 1 : 4.

It is not possible to decide whether this change in reaction rate constant is due to a change of reaction mechanism which takes place with intermediate fluorides, or to particle growth occurring during preparation of the intermediate fluoride from the tetrafluoride (see section (e)).

In many early experiments with tray reactors, intermediate fluorides were obtained in quantity as reaction products during the fluorination of uranium tetrafluoride with fluorine. Such results are now thought to be caused by using thick layers of tetrafluoride: the concentration of fluorine is less in the lower parts of the tray, whilst the concentration of uranium hexafluoride may be high, with the consequent absorption of UF_6 and production of intermediate fluorides.

(d) *Effect of temperature*

The constant R' was determined at different temperatures using the same fluorine: nitrogen ratio and total gas flow for each type of uranium tetrafluoride. Plots of ln R' against T^{-1}, where T is in °K, were straight lines, showing that the Arrhenius relationship between the reaction-rate constant and temperature holds for this reaction.

Figs. 4, 5 and 6 are Arrhenius plots fitted by the method of least squares for the three types of tetrafluoride used. There is a considerable spread in the experimentally

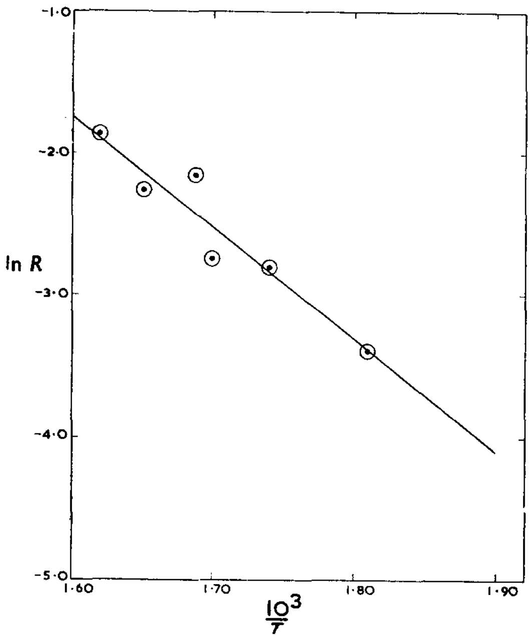

FIG. 4.—Arrhenius plot for UF_4 prepared by dehydration of $2UF_4 \cdot 5H_2O$.

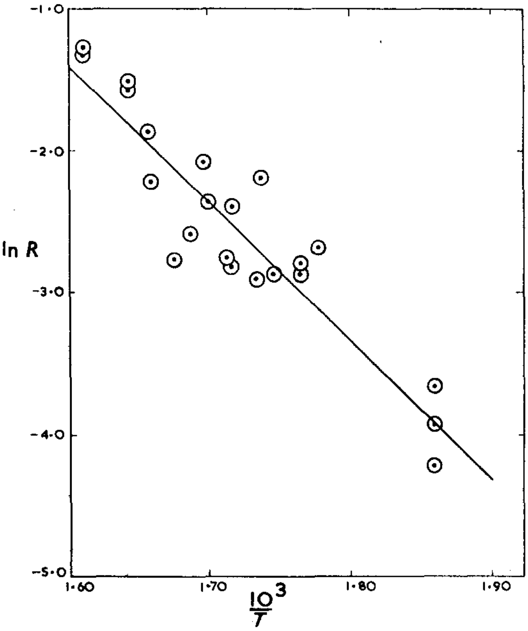

FIG. 5.—Arrhenius plot for UF_4 prepared from UO_2 and HF.

determined points, but a statistical survey of the results showed the degree of correlation in the case of uranium tetrafluoride prepared by direct hydrofluorination (with which the largest scatter was obtained) to be high, viz. —0·885. The spread of results is not surprising when one considers the non-reproducible nature of particulate solid materials. In the present work the very high heat of reaction makes temperature control at the solid surface uncertain and is probably the principal cause of experimental scatter.

Values of R' were deduced from smoothed Arrhenius plots, and the activation energy of the reaction was deduced and is given in Table 2.

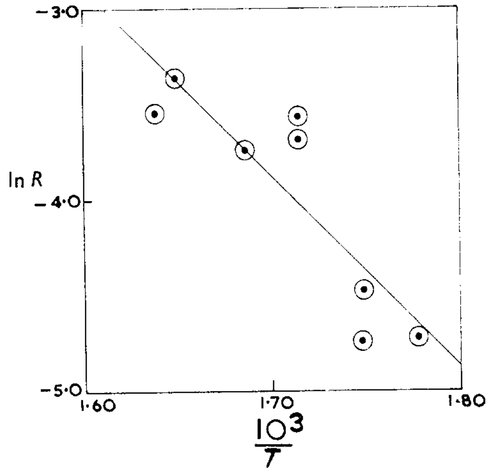

FIG. 6.—Arrhenius plot for UF_4 prepared by sublimation.

The difference in activation energy between the three materials is not large but is significant. There is an increase in activation energy with increasing degree of crystal perfection, as shown by the highest diffraction angle in a Debye–Scherrer photograph, and increased temperature of preparation.

(e) *Effect of particle size*

The constant R' of equation (3) includes r_0, the initial radius of the particle, so that a comparison of R' at the same temperature and partial pressure of fluorine for the different types of uranium tetrafluoride should show the dependence of reaction rate on the initial particle size of material. This comparison is made in Table 3.

TABLE 2.—EXPERIMENTALLY-DETERMINED ACTIVATION ENERGIES OF THE THREE PREPARATIONS OF URANIUM TETRAFLUORIDE

Type of UF_4	Temperature of preparation (°C)	θ_{max} in Debye-Scherrer photograph	Activation energy (kcal/mole)
Dehydrated	270	58°	15·5
Prepared by hydrofluorination	400	74°	19·1
Sublimed	1000	90°	19·9

In the above table, S_0 is the surface area of sublimed material and R_0 the reaction rate constant for this material. Particle size is taken as the reciprocal of surface area, in m^2/g, for comparison purposes.

The surface areas of the three types of uranium tetrafluoride were determined by ethylene adsorption, using the B.E.T. method.

TABLE 3.—EFFECT OF INITIAL PARTICLE SIZE ON RATE OF UF_6 PRODUCTION

Temperature of fluorination (°C)	Material	Temperature of preparation (°C)	Surface area, S (m^2/g)	$\frac{S_0}{S}$	R' (min)$^{-1}$	$\frac{R'}{R'}$	$\frac{R'}{S}$ (g/m^2 min)
280	Sublimed	1000	0·021	1	0·0024	1	0·1123
280	Hydro-fluorinated	400	0·93	0·023	0·0113	0·21	0·0122
280	Dehydrated	270	2·02	0·010	0·0107	0·22	0·0051
320	Sublimed	1000	0·021	1	0·0080	1	0·3810
320	Hydro-fluorinated	400	0·93	0·023	0·0290	0·27	0·0312
320	Dehydrated	270	2·02	0·010	0·0341	0·23	0·0169

It is apparent, that the rate of uranium hexafluoride production is not directly proportional to the initial surface area as determined by gaseous adsorption. This area includes the area of channels and pores in the solid material. One might expect a surface area measured by reaction rate with fluorine not to include those pores which fluorine would only reach with difficulty by diffusion, and from which desorption of uranium hexafluoride would be slow. The sublimed uranium tetrafluoride is highly crystalline and would not be expected to be very porous, whereas the poor crystallinity of the dehydrated and hydrofluorinated materials implies a highly porous surface. These considerations satisfactorily explain the determined rates of reaction: the poorly crystalline material reacts with fluorine at a lower rate than that predicted from the surface area determined by adsorption.

Thus, although the rate of uranium hexafluoride production depends on the surface area of the tetrafluoride used, other factors, such as porosity of the material, modify the results predicted from surface areas measured by adsorption. It is therefore not sound to base predictions of reaction rate on such measurements if the temperature of preparation of the types of tetrafluoride are different; particle sizes based on Stokes' diameter measurement are more likely to be useful.

(f) *Effect of fluorine concentration*

Most of the runs were carried out with the same partial pressure of fluorine (220 mm) and total flow rate (140 cm^3/min). In several runs, however, the partial pressure of fluorine was varied, the total flow of gas being kept approximately constant. Table 4 summarizes the effect of varying the partial pressure of fluorine:—

TABLE 4.—EFFECT OF FLUORINE CONCENTRATION ON RATE CONSTANT AT 308°C FOR UF_4 PREPARED BY HYDROFLUORINATION

$F_2 : N_2$ ratio	Partial pressure (p_{F_2}) of fluorine (mm Hg)	R' (min^{-1})	$100 \times R'/p_{F_2}$
∞	760	0·0877	0·0115
1 : 1	380	0·0383	0·0105
1 : 2·5	220	0·0245*	0·0111
1 : 10	70	0·005	0·007

* Interpolated value.

There is an approximately linear relationship between reaction rate and partial pressure of fluorine for the range of partial pressures up to 760 mm.

(g) *Effect of gas velocity*

Two runs were made in which the partial pressure of fluorine was kept constant, but the total flow rate of gas was varied. The effect of this variation is shown in Table 5.

TABLE 5.—EFFECT OF GAS FLOW RATE ON RATE CONSTANT AT 311°C AND PARTIAL PRESSURE OF FLUORINE OF 220 mm (UF_4 PREPARED BY HYDROFLUORINATION)

Gas velocity (cm/min)	Total flow rate (cm^3/min)	R' (min^{-1})
12	240	0·0227
7	140	0·0265*
2·4	48	0·0217

* Interpolated value.

It is evident that the velocity of the gas has no effect on the rate of uranium hexafluoride production. It should be noted that, even with the smallest flow rate, a large excess of fluorine is present.

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