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THE FLUORIDES OF URANIUM—IV

KINETIC STUDIES OF THE FLUORINATION OF URANIUM TETRAFLUORIDE BY CHLORINE TRIFLUORIDE

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Abstract—The reaction between uranium tetrafluoride and chlorine trifluoride has been studied between 17° and 193° C using the same basic technique as was used in an investigation of the uranium tetrafluoride-fluorine reaction. This consists essentially of following the change in weight of the solid phase using a spring balance.

The mechanism and kinetics of reaction were shown to be substantially the same for chlorine trifluoride as fluorine. The reaction rate passes through a maximum at 105°C, falls to a minimum at 148°C and then rises again. An explanation of this unusual behaviour is suggested.

In the regions $17-58^{\circ}$ C and $156-194^{\circ}$ 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 uranium tetrafluoride prepared by hydrofluorination were 5.6 and 3.4 kcal per mole respectively. A linear relationship is shown to exist near ambient temperature between the reaction rate and partial pressure of chlorine trifluoride. In the velocity range examined, gas velocity had no effect on the reaction rate.

URANIUM tetrafluoride can be converted to uranium hexafluoride using elemental fluorine or fluorine-containing compounds such as chlorine trifluoride and cobaltic trifluoride as fluorinating agent. A kinetic study of the uranium tetrafluoride–fluorine reaction, described in Part III,⁽¹⁾ suggests that the principal reaction is to form uranium hexafluoride, by a direct mechanism which is accompanied by diffusion of fluoride ions into the tetrafluoride, but which does not require the complete conversion of UF₄ to U₄F₁₇, U₂F₉ or UF₅ as a necessary intermediary step. A laboratory study had been performed elsewhere (G. EDWARDS, Imperial Chemical Industries, Ltd., Widnes), in which chlorine trifluoride vapour was passed over static beds of uranium tetrafluoride. This showed that the reaction rate was temperature-dependent, rising to a peak at 110°C, but falling in the region of 175°C to a trough, and increasing again thereafter up to 500°C.

It was thought desirable to investigate this unusual variation of reaction rate with temperature, using a technique which avoided the use of thick beds of solid material. This has been done using the same basic experimental method as that described previously.⁽¹⁾

The factors on which the rates of solid-gas reactions depend have been mentioned in Part III. In the present investigation the effect of temperature on reaction rate was examined in some detail. Also briefly examined were the effects of the concentration of gaseous reactant close to the solid surface and of gas velocity. The experimental

(1) Part III: V. Y. LABATON and K. D. B. JOHNSON, J. Inorg. Nucl. Chem. 10, 74 (1959).

conditions were such that diffusion was not the limiting factor determining the gas concentration at the solid surface, and the partial pressure was a measure of the effective concentration of gaseous reactant.

General

EXPERIMENTAL

A mixture of nitrogen and chlorine trifluoride in considerable excess 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 in a reactor tube heated by a vapour jacket. The reaction was followed by observing changes in weight of the contents of the pan.

The apparatus used was in the main identical with that described in Part III.⁽¹⁾ The source of chlorine trifluoride was a cylinder connected to a valve and a tube packed with sodium fluoride. Pressure gauges (Kelvin and Hughes, Ltd.) were included in the nitrogen and chlorine trifluoride lines after the Rotameters. All taps and glass tubing in the original apparatus in contact with undiluted chlorine trifluoride were replaced by metal valves (Paterson Engineering Co.) and copper tubing.

The following description omits details already given in Part III, and only emphasizes the important features of the experimental work, particularly where they differ from those of the fluorine study.

Uranium tetrafluoride

A batch of material prepared by the action of anhydrous hydrofluoric acid on uranium dioxide was used throughout. The water content was low (0.2 per cent); the hexavalent uranium (4 per cent) and low fluorine content (22.8 per cent instead of the theoretical 24.2 per cent) indicated the presence of small amounts of impurities, probably uranium oxides and uranyl fluoride. Possible weight changes of these impurities would be very small and of the order of the experimental accuracy.

The tetrafluoride was ground before use and sieved (150 mesh) directly into an aluminum pan, 1 in. in diameter. A uniform layer a few grains thick was so obtained. To obtain a convenient spring movement and thickness of bed, 65-85 mg of UF₄ were used in a run.

Chlorine trifluoride

The chlorine trifluoride used was taken directly from a cylinder obtained commercially. It is known that hydrogen fluoride is the chief impurity present, and this was removed by passing the gas stream through a tube packed with dry sodium fluoride pellets. The flow rate was measured directly with a Rotameter, which functioned satisfactorily for several runs before replacement, provided that air and nitrogen which might contain trace impurities were excluded. Back-diffusion of nitrogen was reduced to a minimum by maintaining the pressure of chlorine trifluoride slightly in excess of the nitrogen pressure. The minimum flow, adopted for the majority of the runs, was such that chlorine trifluoride was in a six-fold excess at the highest reaction-rate.

Heating the reactor

The reactor was surrounded by a vapour jacket in which different materials were boiled under atmospheric and reduced pressure. In order to cover the temperature range examined, chloroform, *n*-amyl methyl ketone and naphthalene were used in the vapour jacket. In the steady state, the same temperature was registered by the two thermocouples which were soldered to the outside of the jacket, about 25 cm apart. The pan was suspended so as to move within the constant-temperature zone.

A typical run

In a typical run the beryllium-copper spring was calibrated before use. The weight of pan and uranium tetrafluoride was determined on an analytical balance and checked by the spring balance. The uranium tetrafluoride was vacuum-degassed for three hours at a temperature close to that of the run. When the temperature of the run had been fixed, the apparatus was filled to atmospheric pressure with dry nitrogen, except for the chlorine trifluoride supply system. The time at which chlorine trifluoride flow began was taken as the commencement of a run, although it was apparent from extrapolation of the reaction-rate curve that the chlorind trifluoride took several minutes to reach the uranium tetrafluoride.

In runs at low temperatures, the change in weight of the contents of the pan was followed by cathetometer readings taken at intervals throughout the run. In high-temperature runs, when reaction was complete in a few minutes, the cathetometer was replaced by a telescope containing a graticule. The fluorination was then followed by noting the times at which the "pointer" on the spring, moving down the field of vision, passed the fixed marks of the graticule.

This, incidentally, suggests a possible technique of general application to fast gas-solid reactions, a ciné-camera being used to record the field of view in the telescope.

At the end of a run the apparatus was flushed out with nitrogen, and finally the whole apparatus as far as the cylinder valve was evacuated.

DISCUSSION OF RESULTS

(a) Initiation temperature

The reaction rate was measurable at room temperature.

(b) Kinetics of reaction

At temperatures above 150° C the solid material undergoing fluorination did not increase in weight at all. At lower temperatures the weight increase was always less than that required for complete conversion of UF₄ to U₄F₁₇. Volatile uranium hexafluoride therefore begins to form before conversion of tetrafluoride to a higher fluoride is complete (see Fig. 2).

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. For such a reaction the following relationship can be deduced:

$$(1-C)^{1/3} = 1 - R't$$

where C is the fraction of the total reaction completed in time t,

R' is a rate constant having the units of reciprocal time.

When the quantity $(1 - C)^{1/3}$ is plotted against *t*, the points lie on a straight line in agreement with the equation, except for small deviations for the first 10 per cent and last 5 per cent of the weight change at the beginning and end of the reaction, respectively. Deviation at the beginning of the reaction is explained by the experimental conditions, 1-2 min being required for the proportions of the gaseous mixture in the reactor to become those fixed for the run; the reaction rate at the beginning of the reaction is thus abnormally low The end deviation can be explained by a consideration of the mechanism of reaction.⁽¹⁾

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

(c) Effect of chlorine trifluoride concentration

In all the runs at elevated temperatures, the partial pressure of chlorine trifluoride was maintained at 39 mm and the total gas flow rate at 158 cm³/min. In two runs at ambient temperature the partial pressure was varied, the total flow of gas being kept approximately constant. Table 1 summarizes the effect of this variation.

The results obtained indicate an approximately linear relationship between



TABLE 1.—EFFECT OF CHLORINE TRIFLUORIDE CONCENTRATION ON RATE CONSTANT FOR UF₄ prepared by hydrofluorination

Partial pressure of ClF ₃ (mm Hg)	Temperature (°C)	<i>R'</i> (min ⁻¹)	$10^3 R'/P_{CIF_3}$ (mm ⁻¹ min ⁻¹)	
57	17.5	0.114	2.00	
39	17.5	0.071*	1.82	
74	21.0	0.142	1.91	
39	21.0	0.075*	1.92	

*Interpolated values from Fig. 3.

reaction rate and partial pressure of chlorine trifluoride within the narrow temperature and pressure range examined.

(d) Effect of gas velocity

In several runs the total flow rate of gas was varied, the partial pressure of chlorine trifluoride being kept constant. The effect of this variation is shown in Table 2, in

Total flow rate (cm ³ /min)	Reaction rate constant R' (min ⁻¹)	Temperature of reaction (°C)	Rate constant at 20°C R' ₂₀ (min ⁻¹)	Gas velocity (cm/min)
99	0.0719	18.5	0.0781	4.9
126	0.0877	23.0	0.0751	6.3
158	0.0780	20.0	0.0780	7.9
172	0.1205	29.0	0.0762	8.6

Table 2.—Effect of gas flow rate on rate constant (partial pressure of $ClF_3 = 39$ mm)

which the gas velocity has been estimated from the flow rate and dimensions of the apparatus. Since the runs were carried out at different temperatures, a "corrected" reaction rate constant R'_{20} has been calculated from the Arrhenius plot for each flow rate.

It is clear that, in the velocity range 5-8.8 cm/min, gas velocity has little or no



FIG. 3.—Plot of reaction-rate constant R' against temperature.

effect on the reaction rate; variations in the reaction rate constant due to change of gas velocity are within the experimental error.

(e) Effect of temperature

The reaction-rate constant, R', was determined at different temperatures using the same partial pressure of chlorine trifluoride (39 mm Hg) and the same total gas flow-rate (158 cm³/min). Fig. 3 is a plot of R' against temperature. The reaction rate passes through a maximum at 105°C, falls to a minimum at 148°C and then rises again.

In considering the kinetics of the solid-gas reaction and in particular the variation of rate with temperature, three models were considered. In the first model, the initial uranium tetrafluoride particle is assumed to form during fluorination a layer or skin of intermediate fluoride UF_{4+x}, in which 0 < x < 1 with x greatest at the surface and initially zero at the centre of the particle. It is believed that x can have values between 0 and 0.25, or can be 0.5 or 1.0, corresponding with solid solutions between UF₄ and U₄F₁₇, and with U₂F₉ or UF₅, respectively. There is no evidence for the existence of a continuous range of non-stoicheiometric intermediate fluorides above U_4F_{17} . The value of x is known (from X-ray crystallographic studies of the residual solid just before complete conversion to hexafluoride) to rise above zero at the centre in the later stages of reaction. The second model assumes a layer or skin of a distinct stoicheiometric intermediate fluoride, U_4F_{17} , U_2F_9 or UF_5 , with a sharp boundary between the phases. The third model assumes that during fluorination the particle has distinct but irregular sections of uranium tetrafluoride and intermediate fluoride, the latter growing from one or two nucleation sites. From the evidence presented in Part III and this paper, the first model is believed to represent the facts most closely. Models analogous to these have been discussed for oxidation of uranium dioxide.(2,3)

In the present case the picture is complicated compared with the oxide system by the facts that uranium hexafluoride—the final fluorination state—is volatile, and a back-reaction of hexafluoride with lower fluorides is possible. All or any of the following steps may occur:

- (i) diffusion of ClF_3 to the solid surface.
- (ii) adsorption of ClF_3 on the surface.
- (iii) chemical reaction $UF_4 \rightarrow UF_6$.
- (iv) chemical reaction $UF_4 \rightarrow UF_{4+x}$.
- (v) chemical reaction $UF_{4+x} \rightarrow UF_6$.
- (vi) desorption of UF_6 .
- (vii) diffusion of UF_6 away from the surface.
- (viii) recombination of UF₆ with UF_{4+x} at the surface.

At the lowest temperatures studied, physical adsorption of ClF_3 would be expected to occur on the surface. No data are available for the adsorption of chlorine trifluoride on uranium tetrafluoride, but for many systems a monolayer is obtained when the ratio of the partial pressure to the saturation vapour pressure is about 0·1. This occurs at 5°C under the present conditions. At higher temperatures the surface coverage would be partial and tending toward a linear (Langmuir type) adsorption isotherm, consistent with the observation that reaction rates near the ambient temperature have first-order dependance on the partial pressure of chlorine trifluoride. At still higher temperatures, in particular at temperatures above the critical temperature of chlorine trifluoride (150°C), extensive physical adsorption becomes impossible The fall in reaction rate constant at temperatures between 100°C and 150°C may be qualitatively ascribed to the transition from physical adsorption to chemisorption of

⁽²⁾ S. ARONSON, R. B. ROOF, JR. and J. BELLE, J. Chem. Phys. 27, 137 (1957).

⁽³⁾ K. B. ALBERMAN and J. S. ANDERSON, J. Chem. Soc. S.303 (1949).

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chlorine trifluoride. The desorption of chlorine trifluoride is assumed to have a greater effect on the reaction rate than the increase in kinetic energy of the molecules. It has not been possible to interpret this hypothesis mathematically.

A more likely explanation of the effect of temperature on rate constant lies not in step (ii) above but in steps (iv) and (v)—the reactions to form UF_{4+x} and its subsequent fluorination to UF_6 . The activation energies for diffusion processes in gases are generally very small, and it is known that gaseous diffusion rates vary with the square of the absolute temperature, whereas the rate of fluorination varies exponentially with the temperature. It is therefore highly improbable that stages (i) or (vii) are rate-controlling. The fluorination with fluorine to form uranium



FIG. 4.--Arrhenius plot for region 16-60°C.

hexafluoride occurs at measurable rates only at temperatures above 220°C. At this and higher temperatures intermediate fluorides with $x \ge 0.25$ are not stable if the partial pressure of uranium hexafluoride is less than 0.02 mm Hg.⁽⁴⁾ In the work described in Part III stoicheiometric intermediate fluorides, viz. U_4F_{17} etc., are not expected to be stable during the early stages of fluorination because of the conditions obtaining. At the lower temperatures at which chlorine trifluoride reacts, intermediate fluorides with $x \ge 0.25$ are more easily formed. At temperatures below 100°C, the migration of fluoride ion through the UF₄ lattice is very slow, and plays a relatively unimportant part. At temperatures above 100°C the incorporation of additional fluoride ions in a surface layer can probably begin. Other work at this laboratory on the reaction of UF₆ with UF₄ has shown that penetration of fluoride ion throughout the grain is temperature and pressure dependent, and from the results one would only expect very slow penetration with low UF_6 pressures below 100°C. It is known⁽¹⁾ that the fluorination of intermediate fluorides is slower (by about a factor of 4) than the fluorination of the tetrafluoride, for reasons probably not connected with grain size or surface area. The lower rate constants between 100° and 150°C can therefore be ascribed to the lower reaction rate of chlorine trifluoride with a UF_{4+x} surface than with a UF₄ surface. Production of UF₆ by steps (iii) and (v)

(4) P. AGRON. U.S.A.E.C. Report AECD 1878 (declassified 1948).

and formation of intermediate fluoride, step (iv), are both expected to depend on the surface area of the particles undergoing fluorination, and in fact the $(1 - C)^{1/3}$ relationship as expected is followed throughout the temperature range. At temperatures above 150°C the reaction passes into a range where intermediate fluorides are not stable and therefore do not form.

This explanation accords with the observations that initial weight increases occurred in the present experiments only at temperatures below 150°C. The data obtained in the present experiments do not enable a distinction to be drawn between this explanation and one based on formation of UF₆ and its subsequent recombination with the solid by step (vii) above, but in a flowing system the necessary steady-state local concentrations of uranium hexafluoride vapour seem unlikely to arise.

Fig. 4 shows the variation of $\ln R'$ with temperature plotted to follow the Arrhenius relationship, in the range 15–58°. The apparent activation energy in this range is 5.6 kcal per mole. A similar plot in the range 156–194°C shows the Arrhenius relationship to hold, and the deduced energy of activation is 3.4 kcal per mole.

(f) Comparison with fluorination by fluorine

A comparison of the results obtained in this study and those obtained previously for the uranium tetrafluoride-fluorine reaction⁽¹⁾ shows that fluorination with chlorine trifluoride proceeds at a much lower temperature than that with fluorine. The activation energy is also much lower, that for the uranium tetrafluoride-fluorine reaction being 19·1 kcal per mole for the same solid material. The relative magnitude of the reaction rates with fluorine and chlorine trifluoride was obtained by extrapolation of the plot in Fig. 3 to 265°C. The reaction-rate constants were compared, correcting for the difference in partial pressure of the runs: the fluorination by chlorine trifluoride is 160 times faster than that by fluorine (at 265°C). It is probable, however, that the difference between the reaction rates would be smaller at higher temperatures, as the reaction rate with fluorine increases rapidly with temperature, whereas that with chlorine trifluoride shows a less rapid increase in the region above 170° C.

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