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RESEARCH ESTABLISHMENT

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LABORATORY STUDIES AND DEVELOPMENT OF A CATALYSED FLUOROX PROCESS FOR THE PRODUCTION OF UF_6

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ABSTRACT

Laboratory studies of a catalysed Fluorox process for the production of UF_6 are described. The rates of the reactions of UF_4 with oxygen, of UO_2F_2 with hydrogen and of UO_3 with hydrogen were greatly increased by the presence of small quantities of platinum and other metal catalysts, thus making it possible to carry out these reactions at economical rates at temperatures significantly lower than have been used by other workers. The rates of the catalysed reactions were studied as a function of temperature, catalyst concentration and the particle size of the reactants. The conditions for the preparation of the catalyst were studied to optimise catalytic activity, and

(continued)

methods for the recovery of the catalyst from the reaction mixture were also investigated. Preliminary studies in a bench-scale fluidised bed reactor have demonstrated the feasibility of using fluidised beds for the catalysed Fluorox process. The applications of these catalysed reactions to the commercial production of UF_6 are discussed.

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GENERAL INTRODUCTION

Uranium hexafluoride, the feed material for uranium isotope enrichment, is usually prepared by the reaction of UF_4 with elemental fluorine. The establishment of a fluorine plant is expensive, and the use of fluorine on such a large scale involves considerable toxicity and corrosion hazards. Thus the development of a commercial process for the production of UF_6 which does not require the use of fluorine at any stage would be desirable.

Two processes for achieving this aim have been proposed. The first of these involves the reaction of UCl_6 with HF according to reaction (1) (Rosen 1959)

$$UCl_6 + 6HF \rightarrow UF_6 + 6HCl \quad . \qquad \ldots(1)$$

This process suffers from the disadvantage that the UCl_6 starting material is rather unstable and is itself difficult to produce on a large scale. For these reasons, it seems unlikely that this process could ever be used commercially.

The other process, commonly called the Fluorox process, is based on the reaction of UF_4 with oxygen

$$2UF_4 + O_2 \xrightarrow{800^{\circ}C} UO_2F_2 + UF_6 \quad . \qquad \ldots(2)$$

The UO_2F_2 can be recycled to UF_4 by the reaction sequence

$$UO_2F_2 + H_2 \rightarrow UO_2 + 2HF \quad . \qquad \ldots(3)$$

and $$UO_2 + 4HF \rightarrow UF_4 + 2H_2O \quad . \qquad \ldots(4)$$

The oxidation reaction (reaction (2)) appears to have been discovered by Fried and Davidson in 1944 and has been the subject of several extensive studies (a bibliography of patents, reports and papers relating to the Fluorox process is included in Section D), including two pilot plant studies carried out at the Oak Ridge National Laboratory (Scott, Adams and Bresee 1960) and more recently by the South African Atomic Energy Commission (Geertsma, MacMillan, Paynter and Van Rensburg 1965).

The results of the ORNL study were, on the whole, quite optimistic. Using a 4 in. diameter Inconel fluidised bed, temperatures in the range 775 to 825°C and a bed consisting of approximately 10 per cent UF_4-90 per cent UO_2F_2, high yields of UF_6 were obtained and no significant problems with sintering and the formation of intermediate uranium fluorides were encountered. Similarly, the corrosion of the Inconel reactor appears to have been acceptable. It was noted, however, that if impure UF_4 feed material was used the corrosion of the reactor became catastrophic.

In contrast, the South African experience was much less favourable. Using a 4 in. diameter Inconel reactor, the South African investigators found

the corrosion of the reactor at 800°C to be severe and on occasions catastrophic. In addition, the UF_4 showed a tendency to sinter and a liquid phase consisting of various intermediate uranium fluorides was formed which prevented the proper operation of the fluidised bed. For these reasons, further developmental work appears to have been abandoned.

Economic assessments of the Fluorox process both at ORNL and South Africa suggested that the process had an advantage over conventional processes requiring elemental fluorine, particularly if the UF_6 plant was to be situated in a country which did not already possess an established fluorine generating capacity.

One of the major sources of difficulties with the Fluorox reaction (reaction (2)) is undoubtedly the high temperature (> 800°C) required to give acceptable rates of reaction. If the oxidation reaction in particular could be made to proceed economically at an appreciably lower temperature, the Fluorox process would present an attractive alternative process for the production of UF_6.

It has now been discovered that the rates of the reactions of UF_4 with O_2 and of UO_2F_2 with H_2 can be catalysed by the addition of small quantities of metal catalysts dispersed on a suitable support. With these catalysts economic rates of reaction could be obtained at temperatures near 600°C, at which temperature the corrosion and sintering problems would be much reduced. Following the discovery, a preliminary cost analysis showed that the catalytic Fluorox process would have an economic advantage over the conventional process requiring fluorine and consequently a comprehensive programme was undertaken to study various aspects of the process on a laboratory scale, with particular emphasis on the following:

(a) the rate of reaction of UF_4 with oxygen and of UO_2F_2 and UO_3 with hydrogen,

(b) the preparation and performance of the catalysts,

(c) the possibility of using impure feed materials,

(d) the recovery of the catalyst from the reaction mixture,

(e) the possibility of using a fluidised bed for carrying out the reactions.

The results obtained during the above investigations are summarised in this report in the following four sections:

Section A dealing with the measurements of the UF_4/O_2, UO_2F_2/H_2 and UO_3/H_2 reactions, under a variety of conditions,

Section B containing a detailed description on the preparation, testing

and recovery of the catalysts,
Section C describing the results obtained with the bench-scale fluidised bed reactor used to study the UF_4/O_2 reactions and
Section D discussing in general terms the results obtained in this study.

SECTION A

STUDIES OF THE RATES OF REACTION OF UF_4 WITH O_2, OF UO_2F_2 WITH H_2 AND OF UO_3 WITH H_2

A1. INTRODUCTION

Previous studies of the kinetics (Ferris 1959) and the thermodynamics (Kirlis et al. 1950, Ferris 1957) of the reaction of UF_4 with oxygen have yielded the following results:

(a) Although the reaction should be thermodynamically spontaneous at room temperature, the rate of formation of UF_6 is negligible at temperatures below approximately 740°C.

(b) The rate of the reaction is nearly first order with respect to the weight of UF_4, and one half order with respect to the oxygen partial pressure. The activation energy of the reaction was found to be 188.6 kJ mol^{-1}

(c) Several side reactions occur. These are:

(i) the sublimation of some of the UF_4 which is particularly noticeable at the higher temperatures (> 800°C) and

(ii) the formation of UF_5 according to the reaction

$$UF_4 + UF_6 \rightarrow 2UF_5 \qquad \ldots(5)$$

The subsequent fate of the UF_5 is not well understood. The free energy change for the reverse of reaction (5) passes through a minimum near 600°C, suggesting that at this temperature the UF_5 will dissociate to UF_4 and UF_6.

In contrast to the reaction between UF_4 and O_2, the reduction of UO_2F_2 by hydrogen has been the subject of only two preliminary studies (Kuhlman 1949, Ferris and Gardner 1959). These workers showed that, in general, the reaction proceeded rapidly at temperatures in the vicinity of 700°C, and observed that with sample sizes in the range 0.5 to 5.0 g the reaction rate was controlled by bed diffusion. No details regarding the mechanism of the reaction were obtained from these studies.

For a reaction such as reaction (2) it may be considered that the rate controlling step is the rate at which oxygen molecules dissociate into oxygen atoms. It is of interest to note that the free energy change for reaction (2) is -37.7 kJ mol^{-1} at 25°C (Kirlis et al. 1950), i.e. the reaction is thermodynamically spontaneous at room temperature. Further, the reaction of UF_4 with oxygen has been shown to display approximately a square root dependency on the oxygen partial pressure.

In view of these considerations an attempt was made to react UF_4 with ozone, in the hope that the ozone would dissociate into oxygen atoms which would in turn react with UF_4 at temperatures much below 800°C (Ekstrom and McLaren 1971). This experiment failed, no visible evolution of UF_6 being observed at temperatures up to 600°C. For these experiments the UF_4 had been

placed in a platinum boat and on removal of the boat from the furnace it was noticed that the UF_4 in the immediate vicinity of the walls of the platinum vessel had been converted to UO_2F_2. This observation suggested that platinum catalysed the reaction of UF_4 with oxygen. This conclusion was confirmed by mixing a platinum catalyst directly with UF_4 and exposing the mixture to dry oxygen gas at 600°C. Copious fumes of UF_6 were observed to leave the reactor, and the residue in the boat was analysed and found to be nearly pure UO_2F_2. Similar treatment of UF_4 not containing any catalyst did not result in the formation of any measurable quantities of UF_6 or UO_2F_2. It was then shown that the reduction of UO_2F_2 could also be catalysed by the presence of similar quantities of catalyst.

A2. EXPERIMENTAL

The UF_4 used in this study was made by reducing UO_3, derived from ammonium diuranate (ADU), in hydrogen at 500°C followed by hydrofluorination with anhydrous HF at 550°C. A typical analysis of the UF_4 product is shown in Table A1. Nearly all of the work was carried out using the -60 +120 BSS size fraction, for which the surface area was in the range 1-2 $m^2\ g^{-1}$ (Table A2).

The crude UF_4 was prepared from a uranyl sulphate solution by the ADU route. Typically 500 g of pure UO_3 was dissolved in the appropriate quantity of sulphuric acid, and sufficient ammonium sulphate and water added such that the final solution was approximately 1M UO_2^{++} and 1.5M $(NH_4)_2\ SO_4$. The required quantities of impurities were than added in the form of sulphates, the solution warmed to 50°C and the uranium precipitated with ammonia at pH 7.5. The ADU was filtered, dried at 120°C, calcined at 350°C, reduced to UO_2 at 500°C and the latter converted to UF_4 by reaction with anhydrous HF at 500°C.

Uranyl fluoride was obtained by the reaction of UO_3 with anhydrous HF at 500°C. The UO_3 was obtained by thermal decomposition of ADU in a fluidised bed at 350°C. The UO_3 prepared in this manner had a high surface area and was highly reactive and this is reflected in the high surface areas of the UO_2F_2 prepared from it (Table A2).

Two forms of UO_3 were used as the starting material for the study of the rates of reduction of UO_3 by hydrogen. The first was the highly reactive form derived from ADU described above, the second was prepared by thermal denitration of concentrated uranyl nitrate solution. This latter form was a very hard, unreactive material with a surface area an order of magnitude lower than that of the ADU-derived material (Table A2).

TABLE A1

TYPICAL ANALYSIS OF UF_4 USED IN THE PRESENT WORK

Impurity	ppm (Based on UF_4)
Fe	100
Al	10
Cu	20
Mo	1
V	None
Na	200
Cr	None
Pb	None
Mn	< 1
Mg	<50
Zn	None
Cd	<0.5
Co	20
Si	20
U(VI)	≈1%

TABLE A2

SUMMARY OF SURFACE AREAS OF UF_4, UO_2F_2 AND UO_3 USED IN THE PRESENT WORK

Material *	Origin	Surface Area $m^2\ g^{-1}$
UO_2F_2	From ADU	8.3
UO_3	From ADU	14.7
UO_3	Denitrator	1.4
UF_4	From ADU	1.90

* All samples were -60 + 120 BSS

The platinum catalyst used in the present work was, unless otherwise indicated, a commercial catalyst (Matthey Garrett) and consisted of 5 wt.% Pt on γ-Al_2O_3. The material had a surface area of approximately 180 m^2 g^{-1} and was a very fine powder, 50% of the particles being less than 5 μm diameter. The preparation of other catalysts used in this work is described in detail in Table B1.

The initial experiments were carried out in a conventional horizontal tube furnace. The oxygen gas was dried by passage through two consecutive traps filled with an activated molecular sieve (Type 5A).

The rate studies for the reaction of UF_4 with O_2 were carried out using a Cahn thermobalance. The sample, typically 20-50 mg of UF_4, was placed in a small nickel boat, approximately 10 mm in diameter, usually as a layer approximately 1 mm deep on the bottom of the boat. Preliminary experiments showed that the rate of reaction was independent of sample size in the range 50-150 mg, and independent of oxygen flow rate in the range 3.3 to 16.7 cm^3 s^{-1}. The oxygen gas used was of Medical Dry grade (CIG Ltd.) and was further dried by passing through three consecutive drying columns (1 m long, 50 mm diameter) filled with activated molecular sieve (Type 5A).

The rates of reduction of UO_2F_2 and UO_3 by hydrogen were also measured with the above apparatus, using samples of 50-60 mg. The rates were found to be independent of hydrogen flow rate in the range 3.3 to 16.7 cm^3 s^{-1}.

A3. RESULTS

A3.1 The Reaction of Uranium Tetrafluoride with Oxygen

A3.1.1 Preliminary results

Prior to the measurement of the rates of reaction, a series of exploratory experiments were carried out using the tube furnace. These gave the following results:

(a) In the presence of the catalyst, the oxidation reaction started at approximately 550°C and proceeded quite rapidly in the range 600-640°C.

(b) The concentration of catalyst (5 wt.% of platinum on γ-alumina) required was in the range 0.1 to 1.0 wt.%.

(c) The yields of UO_2F_2 (Table A3) were quantitative within the experimental error, while the yields of UF_6 were generally in the range 40-50% of theoretical. However, it is notoriously difficult to collect quantitatively, small quantities of UF_6, so that the poor yields were not altogether surprising. Small scale batch fluidised bed studies have recently given UF_6 yields of the order of

TABLE A3

YIELDS OF UF_6 AND UO_2F_2 FROM REACTION OF UF_4 WITH O_2 IN THE PRESENCE OF 1 wt.% OF CATALYST AT 610°C

Weight of UF_4 at Start (g)	Weight of UO_2F_2 at Completion of Reaction (g)	% Theoretical Yield of UO_2F_2	Weight of UF_6 Collected (g)	% Theoretical Yield of UF_6
6.67	3.05	93.2	1.81	48.3
4.20	2.03	99.0	1.01	42.5
4.00	1.85	94.3	0.78	34.8

70% of theoretical, using a bed consisting of 20% UF_4, 80% UO_2F_2, 1% catalyst and temperatures of 640°C. (Section C).

(d) The catalyst could be recycled from UF_4 to UO_2F_2 and back to UF_4 at least five times without showing any apparent loss of activity. This observation is of importance for the development of a fully integrated continuous process.

A3.1.2 Rate studies on the reaction of uranium tetrafluoride with oxygen

Figure A1 shows the effect of catalyst concentration on the reaction rate of UF_4 with oxygen. As expected, the rate of reaction in the presence of the catalyst was very much higher than in its absence. Typically, in the presence of 1 wt.% of catalyst, the reaction was complete in 15 minutes at 640°C, while only some 10% of the UF_4 reacted under these conditions in the absence of any catalyst.

An interesting aspect arising from the present work is illustrated in Figure A2, which shows the rate curves obtained from UF_4 placed respectively on a platinum and on a gold boat, no catalyst being present in either sample of UF_4. The UF_4 placed on the platinum surface reacted considerably faster than that on the gold surface, thus again illustrating the marked catalytic effect on platinum.

Contrary to previous work at this temperature on the reaction of UF_4 with O_2 (Ferris 1959), we find (Figure A3) that the catalysed reaction does not follow a first order rate with respect to the weight of UF_4. The deviation is probably due to the formation of some UF_5, according to the reaction

$$UF_4 + UF_6 \rightarrow 2UF_5 \qquad \ldots(6)$$

which leads to a weight loss greater than that predicted. Comparison of the

present work with that of Ferris also shows that, in the presence of the catalyst, the rate of reaction at 640°C is considerably faster than the uncatalysed rate measured by him at 815°C. However, it should be noted that our uncatalysed rate at 640°C is also slightly faster than his at the same temperature, this observation probably being a reflection of the fact that the surface area of the UF_4 used in the present study is considerably higher than that used by Ferris.

The effect of temperature on the rate of reaction of UF_4 containing various concentrations of catalyst with oxygen is shown in Figures A4 to A6. From these data, activation energies of 96.4 kJ mol^{-1} were determined (Figure A7), the rates of reaction being obtained from initial slopes of the rate curves. It should be noted that the activation energies of the catalysed and uncatalysed reaction are the same within our experimental error.

A3.1.3 Recycling of UF_4 and catalyst

One of the important requirements for the process presently under investigation is the ability of the catalyst to remain active during the reaction sequence:

$$\begin{aligned} 2UF_4 + O_2 &\rightarrow UO_2F_2 + UF_6 \\ &\downarrow H_2 \\ UO_2 + 2HF \\ &\downarrow 4HF \\ UF_4 + 2H_2O \\ &\downarrow O_2 \\ &\text{etc.} \end{aligned} \qquad \ldots(7)$$

Preliminary experiments (A3.1.1) had shown that this was indeed the case, no obvious loss in catalyst activity being observed after five recycles. These experiments were repeated, and the rate of reaction of UF_4 with oxygen measured after each recycle. After each recycle, the catalyst concentration in the UF_4 would be approximately 2%, since one half of the UF_4 is converted to UF_6 and thus to maintain the catalyst concentration constant in the UF_4, it was necessary to dilute the recycled UF_4 with an equal weight of UF_4 which did not contain any catalyst.

The results obtained (Table A4) show that there is no measurable change in the activity of the catalyst after each recycle.

TABLE A4

EFFECT OF CATALYST RECYCLING ON THE RATE OF REACTION OF UF_4 WITH OXYGEN*

Sample	Time Required for 50% Reaction (min.)
Original	4.0
1st Recycle	3.5
2nd Recycle	3.5
3rd Recycle	3.6
4th Recycle	3.8

* 640°C, 1 wt.% of catalyst, UF_4 -60 + 120 BSS

A3.1.4 Experiments with pelletised UF_4

During the early stages of this work it was thought that some difficulty may be experienced in operating a fluidised bed containing the very finely divided catalyst. Two approaches to overcome this problem were examined

(i) An attempt, discussed in detail in Section B, was made to develop a coarse particle size catalyst and

(ii) The rates of reaction of pelletised mixtures of UF_4 and catalyst were studied.

The pellets were made by mixing UF_4 (-120 BSS) and catalyst (1 wt.%, -300 BSS) and compressing the mixture into pellets approximately 6.4 mm diameter and 3.8 mm high, using a pressure of 400 MN m^{-2}. The pellets weighed approximately 0.5 g and had a density of 1.1 g cm^{-3}.

As shown in Figure A8, these pellets reacted with oxygen relatively slowly, presumably because the diffusion of oxygen into the pellet and the diffusion of UF_6 out of the pellet were relatively slow. This conclusion was confirmed by the results illustrated in Figure A9 which shows that if the above pellets were crushed and sieved into various size fractions, reaction with oxygen was very rapid.

After the pellets of UF_4 had been completely converted to UO_2F_2 it was noticed that their mechanical strength was still quite good although their weight had decreased by nearly 50%. An attempt was made to measure the rate of reduction of the pellet (now UO_2F_2) in hydrogen, however the rate was extremely rapid, the reaction being complete in less than 3 minutes at 650°C. The pellet was then reconverted to UF_4 by treatment with anhydrous HF at 600°C. No difficulty was experienced with this conversion, the integrity of the

pellet was maintained despite the decrease in the density of the pellet to 0.4 g cm^{-1}.

A3.1.5 Effect of UF_4 particle size

Figure A10 summarises the rate curves of three ranges of UF_4 particle size used with the commercial catalyst. The results indicate that there was little difference in reactivity in the -150 and -60 + 150 BSS sizes, while the +60 BSS fraction was observed to react considerably slower.

A3.1.6 Studies using various types of UF_4

To obtain some understanding of the effect on the reaction rate of the properties of the UF_4, the rates of reaction of several different types of UF_4 were measured in the presence and absence of catalyst, but under otherwise identical conditions. The properties of the various types of UF_4 used, and the results obtained from these experiments are summarised in Table A5. The catalytic effect was observed in all four cases, although as expected, the rate of reaction was clearly a function of both the surface area and particle size of the UF_4.

A3.1.7 Studies using impure UF_4

This work was undertaken to test the feasibility of using an Allied Chemical type of process (in which impure feed materials are used and the UF_6 product is distilled in a final stage to achieve nuclear purity) in conjunction with the Fluorox reaction. Accordingly an attempt was made to convert yellow cake directly in UF_4 by treatment with hydrogen and anhydrous HF at 500°C, but this attempt failed due to the complete sintering of the sample. A sample of yellow cake was then dissolved in nitric acid, and the uranium reprecipitated with ammonia at pH 7.5 and 50°C. The sample was filtered, washed, dried at 120°C, and converted to UO_3 and UF_4 by the method described in Section B. The impurity levels found in this material are summarised in Table A6 under columns 3 and 4. The analysis for the other samples of synthetic crude UF_4 are shown under columns headed 'sample 1' and 'sample 2'.

It is clear from these results that (with the exception of $SO_4^{=}$ and Si) there is little if any decontamination from the impurities during the conversion of the UO_3 to UF_4. However, the results show that the catalytic effect of platinium was in no way diminished by these large concentrations of impurities in the UF_4.

TABLE A5

SUMMARY OF PROPERTIES AND REACTIVITY OF VARIOUS TYPES OF UF_4 (1)

Source of UF_4	Surface Area ($m^2\ g^{-1}$)	Particle Size* (μm)	Time for 50% Reaction (minutes)	
			With 1 wt.% Catalyst	No Catalyst
Ex ADU (2)	1.90	~90	6.0	50
MERCK (3)	2.29	~30	3.0	38
French (4)	1.88	~ 5	5.5	44
RIC (5)	0.32	> 1	9.0	Slow > 60

(1) All rates measured at 640°C.

(2) Same as that used in the previous work.

(3) Merck, nuclear purity material.

(4) Material obtained from French Atomic Energy Commission, very fine powder.

(5) Material obtained from Research Inorganic Chemical Corp., Sun Valley, Calif., USA. It was a very fine, dark green, almost crystalline sample.

* The particle sizes were estimated from microscopic measurements.

TABLE A6

SUMMARY OF IMPURITY LEVELS AND REACTION RATES OF VARIOUS SAMPLES OF UF_4*

(Unless otherwise shown results are in ppm on a uranium basis)

Impurity	High Purity UF_4#	FROM YELLOW CAKE		SAMPLE 1		SAMPLE 2	
		UO_3	UF_4	UO_3	UF_4	UO_3	UF_4
SO_4 n.d.**	n.d.	n.d.	n.d.	9.4%	0.23%	1.48%	0.68%
Fe	100	1000	1000	5300	4400	32000	32000
Al	10	70	100	3200	5200	1800	5100
Cu	20	20	20	780	830	3900	3800
Mo	1	2	3	240	240	2100	2300
V	n.d.	10	n.d.	250	190	400	450
Na	200	200	400	45	100	115	500
Cr	n.d.	200	150	220	320	1850	1800
Pb	n.d.	-	-	360	350	340	340
Mn	1	35	45	520	480	3100	3100
Mg	50	150	150	66	70	2100	2500
Zn	n.d.	10	10	930	860	1800	1800
Cd	0.5	0.5	0.5	290	240	1800	1300
Co	20	-	-	340	320	2000	2000
Si	20	1000	20	n.d.	n.d.	n.d.	n.d.
Time required for 50% reaction, using 1 wt.% of catalyst	6.2 mins.		6 mins.		4 mins.		6 mins.
Time required for 50% reaction in the absence of catalyst	40 mins.		40 mins.		25 mins.		35 mins.

High purity UF_4 is same material as used for the rate experiments. (-60 + 120 BSS)

* Reaction temperature: 640°C.

** n.d. = not detected

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A3.1.8 Other catalysts

In addition to platinum a wide range of other metals and metal oxides were tested as possible catalysts for the oxidation of UF_4 with a view to finding an alternative and possibly cheaper catalyst. Table A7 lists the compounds examined and their catalytic activity. The reaction curves of the best alternative catalysts are also shown in Figure A11. The results indicate that with the possible exception of ruthenium, platinum is by far the best catalyst for the oxidation reaction. It should be stressed however that comparisons between the performance of different catalysts can be misleading. The studies with platinum catalysts have shown the wide range of activities possible for this metal dependent on its dispersion, support, temperature of reduction, etc. (Section B). In an effort to minimise such variations, the same support was used in each case with the same conditions for reduction of the supported metal, acid or salt. However it is possible that, for example, the conditions for producing a highly dispersed ruthenium catalyst could be different from those to produce a platinum catalyst having the same degree of dispersion.

A series of mixed transition metal catalysts were also examined. No mixture was found whose activity exceeded that of the platinum catalyst alone (Table A8) and only with mixtures of ruthenium and palladium was any increase in catalytic activity observed above that for one metal on its own. The activities found for these mixtures were still, however, less than that of the platinum catalyst.

A3.1.9 Attempts to detect $UO_{0.5}F_4$

In their study of the reaction of UF_4 with oxygen, Kirlis et al. (1950) isolated a compound from the reaction which they claimed was $UO_{0.5}F_4$ or U_2OF_8. We attempted to repeat this work using the apparatus shown in Figure A12. It was thought that any U_2OF_8 formed by the reaction of oxygen with UF_4 would be swept from the boat and condensed on the cold finger, from which it could be removed in a dry box at the completion of the experiment and analysed.

The reaction was carried out under a variety of experimental conditions: temperature, gas flow rate, pressure and UF_4 particle size. A white material whose appearance resembled that described by Kirlis et al. (1950) was usually deposited on the cold finger, but X-ray diffraction analysis invariably showed this to be UF_5 or a mixture of UF_5, UF_4 and UO_2F_2.

A3.2 The Reaction of UO_2F_2 and UO_3 with Hydrogen

A3.2.1 The reduction of UO_2F_2

The effect of platinum catalyst concentration on the rate of reduction

TABLE A7

COMPARISON OF THE ACTIVITY OF VARIOUS CATALYSTS IN PROMOTING THE RATE OF OXIDATION OF UF_4

Catalyst Concentration (wt %)	Catalyst (-300 B.S.S.)	Catalyst Number (a)	$t_{\frac{1}{2}}$ (b) mins
1	5% Pt on γ-Al_2O_3	1	5
1	5% Ru on γ-Al_2O_3	12	8
1	5% Rh on γ-Al_2O_3	13	20
1	5% Ir on γ-Al_2O_3	14	20
1	5% Pd on γ-Al_2O_3	10	33
1	5% Os on γ-Al_2O_3	15	27
1	5% Au on γ-Al_2O_3	16	33
10	5% Au on γ-Al_2O_3	16	28
10	5% Ag on γ-Al_2O_3	17	50
10	Co_3O_4 unsupported	18	10
1	Co_3O_4 unsupported	18	29
10	5% CuO on γ-Al_2O_3	22	50
1	V_2O_5 unsupported	23	50
10	MnO_2 unsupported	20	50
1	Fe_2O_3 unsupported	25	50
1	ZrO_2 unsupported	24	(c)
1	La_2O_3 unsupported	30	(c)
1	HfO_2 unsupported	31	(c)
1	Cr_2O_3 unsupported	32	(c)
1	MoO_3 unsupported	24	(c)
1	WO_3 unsupported	26	(c)
1	ZnO unsupported	33	(c)
1	CdO unsupported	24	(c)
1	NiO unsupported	27	(c)

(a) See Section B, Table B1

(b) $t_{\frac{1}{2}}$ = time taken for 50% of the UF_4 to react

(c) no catalysis, absorbs UF_6

TABLE A8

COMPARISON OF THE ACTIVITY OF SOME MIXED METAL CATALYSTS IN PROMOTING THE RATE OF OXIDATION OF UF_4

Catalyst	$t_{\frac{1}{2}}$ mins
2.5% Pt + 2.5% Au on boehmite -300 BSS	7 *
4% Ir + 1% Pt " " " "	8 *
4% Ru + 1% Au " " " "	20 *
4% Ir + 1% Au " " " "	25 *
4% Ir + 1% Ag " " " "	25 *
2.5% Pd + 2.5% Au " " " "	28 *
1% Ru + 4% Pd " " " "	25
2.5% Ru + 2.5% Pd " " " "	12
0.5% Pt + 4% Pd " " " "	8 *

* No increase in reactivity over that of the most active component alone.

of UO_2F_2 to UO_2 by hydrogen is shown in Figure A13 and the stoichiometry of the reaction according to the equation

$$UO_2F_2 + H_2 \rightarrow UO_2 + 2HF \qquad \ldots(8)$$

was confirmed by the data summarised in Table A9. The rate of reduction of UO_2F_2 was greatly enhanced by the catalyst (Figure A13), the effect being clearly noticeable at catalyst concentrations as low as 0.1 wt %.

The rate curves in the presence of the catalyst show an unusual form, indicating the occurrence of a fast initial reaction, followed by a region in which the reaction rate was much slower. This effect was particularly noticeable at the lower catalyst concentrations (Figure A13) and the lower temperatures (Figure A14), but was not observed in samples which did not contain any catalyst (Figure A15). It was also noticeable that a catalyst concentration in excess of approximately 1 wt % did not produce any further enhancement of the rate of reduction.

From the preceding results it was possible to obtain an estimate of the activation energy of the reaction in the absence and presence of the catalyst. While the rate of the uncatalysed reaction can be taken as the slope of the reaction curve, the measurement of the rate of the catalysed reaction was

TABLE A9

CALCULATED AND OBSERVED WEIGHT CHANGES IN THE REDUCTION OF UO_2F_2 WITH HYDROGEN

Weight of UO_2F_2 (mg)	Observed Weight Change (mg)	Calculated Weight Change* (mg)
150	18.6	18.5
100	12.2	12.3
50	6.1	6.2

* calculated according to the reaction $UO_2F_2 + H_2 \rightarrow UO_2 + 2HF$

more difficult because of the obvious differences in the initial and subsequent rates. For the purposes of determining the activation energy of the catalysed reaction, it was decided to use the rate at 50% reaction. As shown in Figure A16, the activation energies of the uncatalysed and catalysed reactions are, within our experimental error, the same at 109 ± 8 kJ mol^{-1}.

Examination of the effect of catalyst particle size, using the catalysts whose preparation is described in Section B, shows (Figure A17) that there was surprisingly little variation in the reaction rate with change in catalyst particle size. This result implies that the active species formed on the catalyst surface can migrate quite large distances before reacting with UO_2F_2.

The effect of UO_2F_2 particle size in the presence of 1 wt % of catalyst is shown in Figure A18. As expected, the coarser UO_2F_2 particles reacted considerably more slowly than the finer ones.

The effectiveness of a series of catalysts containing metals other than platinum in promoting the rate of reduction of UO_2F_2 is illustrated in Figure A19 and summarised in Table A10. In contrast to the UF_4- O_2 reaction, the reduction was effectively catalysed by a wide variety of different catalysts including silver, nickel and copper oxides. It should be noted however, that the determination of a true relative catalytic activity scale is very difficult as the particle size surface area, dispersion and support coverage of the various catalysts would have to be carefully controlled and known. As these factors were not studied any conclusion regarding the relative efficiency of the various catalysts tested must be treated with caution.

TABLE A10

COMPARISON OF THE EFFECTIVENESS OF VARIOUS CATALYSTS IN PROMOTING THE RATE OF REDUCTION OF UO_2F_2 AND UO_3

Catalyst	(a) Catalyst Number	Time Required for 50% Reaction	
		(b) $UO_2F_2 \rightarrow UO_2$	(c) $UO_3 \rightarrow UO_2$
None	-	25.0	10.0
Pt	1	7.0	1.5
Ru	12	5.5	3.0
Pd	10	6.0	2.0
Rh	13	5.0	1.8
Ir	14	6.5	3.4
Au	16	15.0	8.5
Ag	17	2.5	5.0
CuO	21	2.5	10.0
CuO (supported)	22	9.0	10.0
Co_3O_4	18	19.0	9.0
Pt black	6	1.0	1.0
Pt black (supported)	7	10.0	1.0
$PtO_2.xH_2O$	8	6.5	1.5
PdO_2	11	5.5	2.0
Ni_3O_4	28	2.5	2.0

(a) The catalyst number refers to the catalysts listed in Table B1.

(b) UO_2F_2, -60 + 120 BSS, 600°C

(c) UO_3, denitrator derived, -120 + 150 BSS, 550°C

For all catalysed rates, the catalyst concentration is 1 wt %.

A3.2.2 The reduction of UO_3

The results illustrated in Figure A20 clearly show that the reduction of UO_3 prepared by denitration can be catalysed by platinum, the catalytic effect being most pronounced in the finer samples. The particle size effect was not unexpected, since the material was very dense, hard and not very reactive. The grinding of this material presumably breaks the outer shell of the particles and facilitates the access of the gas to their interior, as well as improving the contact between the catalyst and the UO_3.

The effect of temperature on the rate of the catalysed and uncatalysed reactions was determined and the initial rates used to determine the activation energies. The results obtained (Figure A21) show that for this system also, the activation energies for the catalysed and uncatalysed reactions are the same at 126 kJ mol^{-1}.

The reduction of the UO_3 prepared by denitration can be catalysed by a wide variety of metals (Table A10), as can UO_2F_2. Again, too much emphasis should not be placed on the relative efficiency of the different catalysts, the difficulties in obtaining meaningful comparisons discussed above were compounded in the case of UO_3 by the difficulty in obtaining good mixing between the UO_3 and the catalyst. This problem is caused by the high density of the UO_3 (tap density ~ 5 g cm^{-3}) compared to the catalyst (tap density ~ 1.2 1.2 g cm^{-3}) and results in the floating of the catalyst on the UO_3.

In contrast to the UO_3 prepared by denitration, the UO_3 derived from ADU was not catalysed by platinum or any other catalyst found to be effective for the reduction of UO_2F_2. (Figure A22). The ADU-derived UO_3 was a high surface area, low density (tap density ~ 2 g cm^{-3}) material, the appearance of which was quite different from that prepared by denitration, and its rate of reduction was very much faster. Despite these differences however, the activation energy of the reduction was the same for UO_3 prepared by both methods (Figure A21).

A4. DISCUSSION OF RESULTS

The results described in the previous pages show conclusively that gas-solid reactions can be catalysed by the addition of a solid catalyst. Since the solid substrate (in our case either UF_4, UO_2F_2, or UO_3), is only physically mixed with a relatively small amount of solid catalyst, it seems highly improbable that the substrate molecules, or some species derived from the substrate is adsorbed onto the catalyst and that the reaction between the substrate and the gas occurs on the catalyst surface. Rather, we believe that the gas, either hydrogen or oxygen, is adsorbed onto the catalyst, is

dissociated into atoms or converted to some other active form on the catalyst surface, and that these leave the catalyst surface and exist in the gas phase for a sufficient length of time to diffuse to and react with the substrate.

It is of interest to note that a number of rather similar observations to those described here have been reported in the literature over the past few years, although their potential significance does not appear to have been fully realised. These reports (Khoobiar, 1964; Benson et al. 1966; Sancier 1971; for a summary and discussion of this and other work, see also Il'chenko 1972) have been concerned with the observation that the rate of reduction of various metal oxides such as Fe_2O_3, NiO, and WO_3 can be increased by the addition of catalysts such as platinum. These studies only give a description of the phenomenon and have not provided any insight into the origin and mechanism of the effect. It should be pointed out however that despite the immense amount of research carried out in the field of catalysis in general, the understanding of the processes and reactions which occur on catalyst surfaces under conditions of monolayer and, in particular, multilayer coverage of the catalyst by the adsorbed gas, is almost nonexistent. This lack of understanding can be traced directly to the very severe experimental difficulties encountered in attempting to study such systems.

It seems probable that, for the reduction reactions discussed in this report, the active species formed on the catalyst surface are hydrogen atoms. In the case of the oxidation reaction, the formation of excited oxygen molecules, particularly the first excited singlet state ($^1\Delta$) with an energy of approximately 96.4 kJ above the ground state cannot be excluded, particularly since there is some indication that this species can be formed on a platinum surface (Kearns 1960). The formation of excited hydrogen molecules is improbable since the first excited state of hydrogen lies some 1089 kJ above the ground state (Herzberg 1961).

The formation of oxygen and hydrogen atoms on a platinum surface, and their subsequent desorption from the surface has been well established (Brennan and Fletcher 1959, 1960; Brennan 1963). These studies have been confined to low gas pressures (10^{-2}-10^{-6} mmHg) and high temperatures (>1200 K) but we conclude that these results are not applicable to the experimental conditions at present under discussion. This conclusion is based on two observations, the first and most conclusive being that the activation energies for the catalysed oxidation of UF_4 (~96.4 kJ mol^{-1}), for the catalysed reduction of UO_2F_2 (~115.2 kJ mol^{-1}) and the catalysed reduction of UO_3

(~125.7 kJ mol^{-1}) are less than the activation energies measured for the dissociation of oxygen on platinum (257.7 kJ mol^{-1}), and the dissociation of hydrogen on platinum (214.1 kJ mol^{-1}; Brennan and Fletcher 1960).

The second observation is less conclusive, but may be illustrated as follows. The rate of atomisation of hydrogen on platinum was found (Brennan and Fletcher 1959) to be given by the expression:

$$Va = \left[1.3 \times 10^{25} \left[P_{mm}\right]^{\frac{1}{2}} \exp(-51{,}100/RT)\right] \text{atoms } s^{-1} cm^{-2}. \qquad ...(9)$$

Assuming that the above expression is valid at 650°C and at pressures of the order of one atmosphere it can be readily shown that the rate of formation of hydrogen atoms is approximately 1×10^{15} atoms $min^{-1} cm^{-2}$.

In the case of the catalysed reduction of UO_2F_2 we find that in the presence of 1 wt % of catalyst (surface areas ~100 m^2 g^{-1}), 60 mg of UO_2F_2 was reduced in 4 minutes. Assuming that each molecule of UO_2F_2 requires 2 atoms of hydrogen, we find that 2×10^{20} hydrogen atoms were required in 4 minutes. Now the sample contained 0.6 mg of the catalyst whose surface area was ~100 m^2 g^{-1} and hence only $[1 \times 10^{15} \times 100 \times 10^4 \times 0.6 \times 10^{-3} \times 4] = 2.4 \times 10^{18}$ hydrogen atoms are predicted to be formed on the catalyst surface during that time. A similar calculation was made for the oxidation reaction and gave a similar result. While this calculation is clearly only a crude approximation, it would nevertheless suggest that the results obtained for the rate of atomisation of hydrogen and oxygen at high temperatures and low pressures cannot be extrapolated to the present situation of low temperatures and high pressures, particularly when it is considered that it is highly unlikely that all of the hydrogen or oxygen atoms formed on the catalyst will react with the UO_2F_2 or UF_4.

One of the most intriguing results obtained during this investigation is that the activation energies of the catalysed and uncatalysed reactions are the same for all three systems studied. At first sight, this result would tend to disprove our initial hypothesis that the rate of reaction between UF_4 and oxygen is controlled by the rate of dissociation of oxygen into atoms.

When comparing the effectiveness of a series of different catalysts in promoting the rate of a common reaction, it is the usual practice to obtain the Arrhenius plots for each catalyst and to compare the values of the pre-exponential factor (A) and the activation energy (E_A) for the different catalysts. As discussed in detail by Bond (1962), there are three main cases of the relationship between the pre-exponential factor and the activation

energy. These are

(a) both A and E_A are varied (Figure A23a)

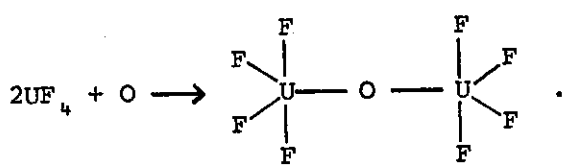
(b) A is constant; but E_A is varied (Figure A23b)

and (c) A is varied, but E_A is constant (Figure A23c)

Of these alternatives, case (c) is of particular relevance to the present situation, and is believed to occur in situations where the entropy of adsorption of the reactants onto the catalyst surface is important while the heat of adsorption is irrelevant or constant. These conditions are believed to arise at full surface coverage, which can be expected under the experimental conditions used in the present study. An alternative way of interpreting the present results is to regard both the substrate and catalyst as surfaces for the adsorption and dissociation of hydrogen or oxygen molecules, for which the heat of adsorption of the gases is much the same, but for which the entropy of adsorption is different, being small in the case of the substrate, but large in the case of the catalyst. This interpretation would seemingly require that the activation energies for the reduction of both UO_2F_2 and UO_3 be the same, and in fact they are observed to be quite similar, being ~115.2 kJ mol^{-1} for the UO_2F_2 and ~125.7 kJ mol^{-1} for the UO_3 reduction respectively.

On this basis, the inability to catalyse the reduction of the ADU-derived UO_3 is attributed to peculiarities in the surface properties of the material which results in the entropy of adsorption of hydrogen for this material being either the same or much greater than that for the adsorption of hydrogen onto platinum. In support of this interpretation, recent experiments have shown that if the ADU-derived UO_3 is heated to high temperatures (>~800°C), platinum will catalyse the reduction of the product (now U_3O_8). This treatment reduced the surface area of the material from approximately 14 m^2g^{-1} to 4 m^2g^{-1}.

The details of the mechanism of the reaction of UF_4 with oxygen, either as atoms or excited molecules, are as obscure as the origin of the catalytic effect of platinum and, as pointed out previously (Kirlis et al., 1950) it is difficult to conceive how molecular oxygen can insert itself into the UF_4 lattice. If the present hypothesis that the reaction involves atomic oxygen is correct, it is plausible that the first step in the conversion is the reaction



...(10)

The U_2OF_8 must then thermally decompose to UF_6 and UO_2F_2 as suggested by

Kirlis et al. (1950),

$$2U_2OF_8 \longrightarrow 2UF_4 + UF_6 + UO_2F_2 \quad \ldots(11)$$

or may react with another oxygen atom according to the reaction:

$$U_2OF_8 + O \longrightarrow UF_6 + UO_2F_2 \quad . \quad \ldots(12)$$

Kirlis et al. claimed to have observed the formation of the compound $UO_{0.5}F_4$ at temperatures in the vicinity of 800°C, thus implying that the rate of decomposition of the intermediate is relatively slow at this temperature. However, to account for the present results, it must be postulated that the rate of decomposition of the intermediate is rapid even at temperatures as low as 640°C, since in the presence of catalyst we observe the reaction of UF_6 with oxygen to be 50% complete in 5-6 minutes.

Figure A24 lists, in periodic table order, those elements examined as potential catalysts. Only elements in the shaded area were found to be active catalysts. Those outside the shaded area did not catalyse the oxidation and in many instances absorbed the product, UF_6, of the non-catalysed reaction, giving rise to apparently long reaction times.

This data allows the following catalytic activity series to be stated:

$$Pt \approx Ru > Co_3O_4 > Ir \approx Rh \approx Os \approx Au > Pd > Ag \quad .$$

Not surprisingly, the catalyst activity series for this reaction is unlike any previously reported. In most catalysed oxidations, the reaction involves adsorption on the catalyst of both oxygen and the reactant with the catalyst activity being a function of the heats of chemisorption of oxygen and electronic factors, such as d-character of the metals, which influence the adsorption of the reactants. However, in the catalysed oxidation of UF_4 we are concerned with the surface reaction of only one reactant, oxygen, to produce an activated species which desorbs and reacts with UF_4. It is well known that the dissociation of molecular oxygen occurs at the surface of many transition metals and metal oxides. Attempts to measure the effectiveness of various catalysts in promoting this dissociation have been made by measuring the rate of exchange between oxygen-16 and oxygen-18 in the presence of different catalysts. The relative efficiency of various catalysts in promoting this exchange is claimed (Boreskov, 1964) to be

$$Pt > Co_3O_4 > Ag > MnO_2 > CuO > NiO \quad .$$

Of these catalysts, only Pt and Co_3O_4 showed any catalytic activity in our case, but no comparable data for the exchange of oxygen on Pd, Ru, Rh and Ir could be found. While these considerations suggest that at least two of the catalysts found to be effective in the present conditions are known to be good catalysts for the exchange of oxygen, it is obvious that other factors,

such as the ease with which atomic oxygen can desorb from a catalyst surface, are probably equally important. The only available data on the desorption refer to conditions of high temperature and very low pressure and, as discussed previously, appear to have little relevance to data obtained under the present experimental conditions.

It is evident that surface properties also play an important role in determining the activity of the catalysts. These include not only metal crystallite size, state of dispersion and catalyst surface area, as discussed previously, but possibly geometric factors such as lattice spacings and the arrangement of atoms in the exposed crystal planes. More data is required before the mechanism of the reaction can be fully interpreted.

In contrast to the oxidation reaction, the reduction of UO_2F_2 and UO_3 is catalysed by a wide variety of different metals and metal oxides. Again the relative order of the effectiveness of these catalysts cannot be correlated with any of their physical properties, emphasising once again the uniqueness of the present system.

The reaction curves obtained in nearly all of the systems studied do not obey any simply rate law. In the case of the oxidation of UF_4 this effect is probably at least in part due to the formation of some UF_5 by a side reaction. However it is also clear that the distribution of the catalyst in the substrate is not homogeneous in the sense that all UF_4, UO_2F_2 and UO_3 particles are not in the immediate vicinity of a catalyst particle. This effect is illustrated in Figure A25, which is a photograph of a catalyst/UF_4 mixture after exposure to oxygen at 640^0C for three minutes. The preferential reaction of the UF_4 around the catalyst particles can be clearly seen, and it would be expected that under conditions in which the catalyst particles do not move, the topographical selectivity of the reaction would be reflected in the rate curves.

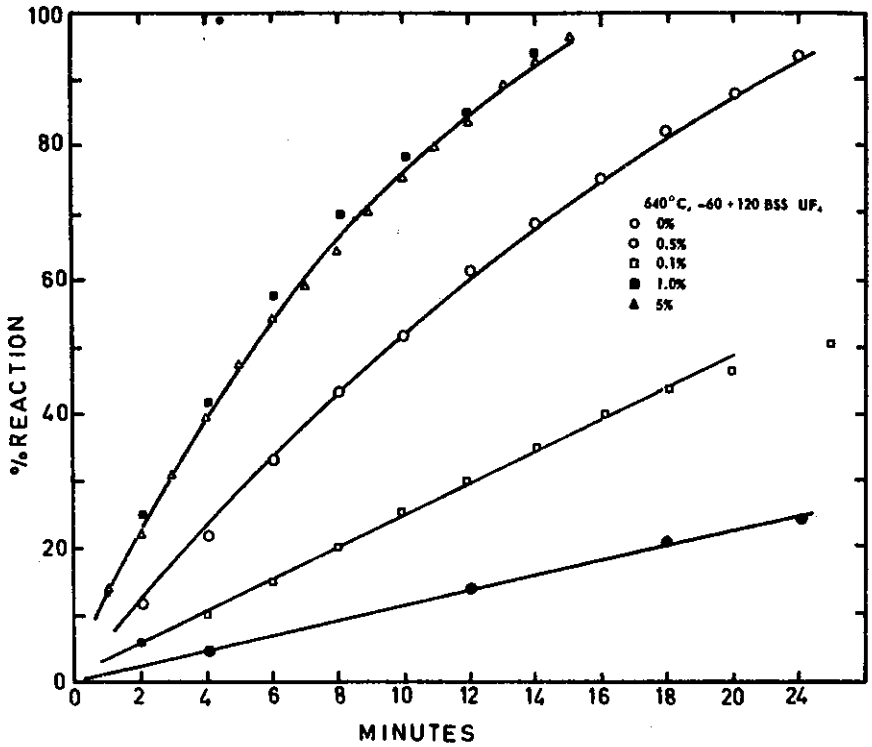


FIGURE A1. EFFECT OF CATALYST CONCENTRATION ON THE REACTION RATE OF UF_4 WITH OXYGEN

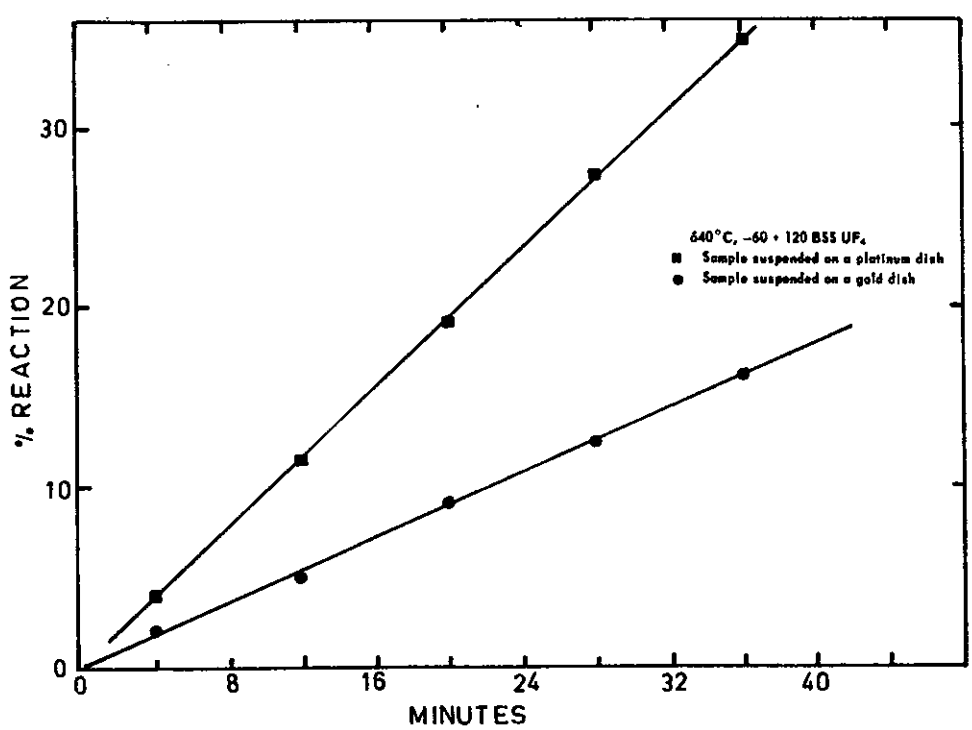


FIGURE A2. COMPARISON OF THE REACTION RATE OF UF_4 WITH OXYGEN

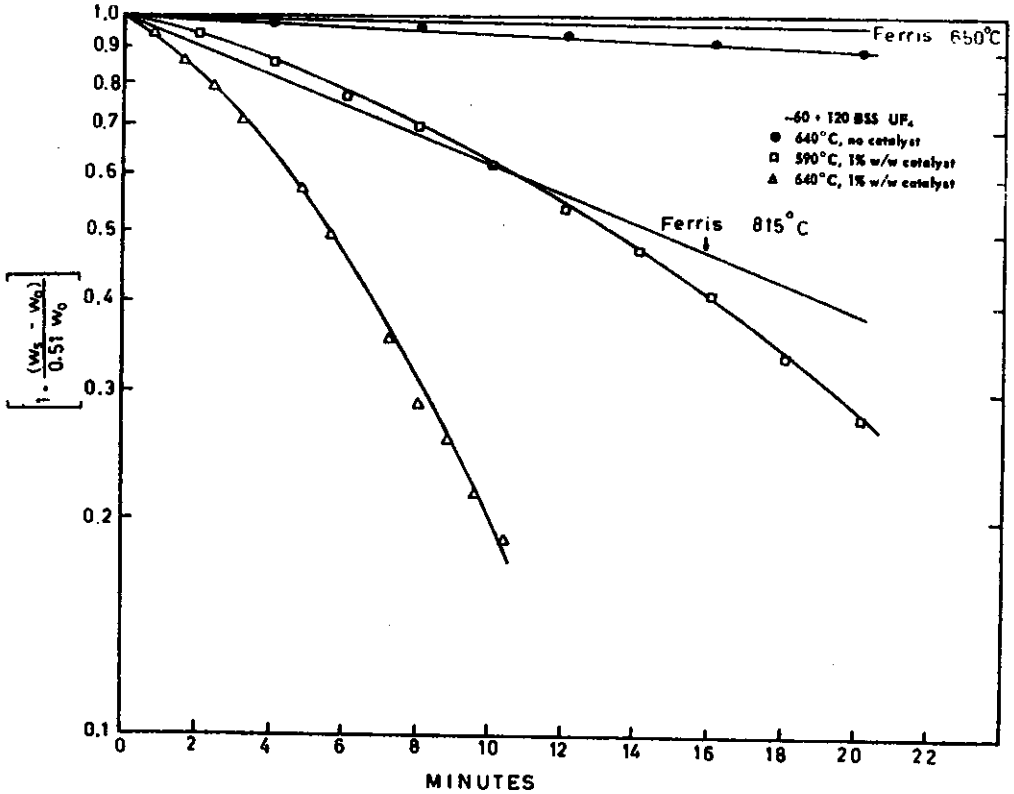


FIGURE A3. COMPARISON OF THE RESULTS OF THE PRESENT WORK AND THAT DESCRIBED BY FERRIS PLOTTED ACCORDING TO FIRST ORDER KINETICS.

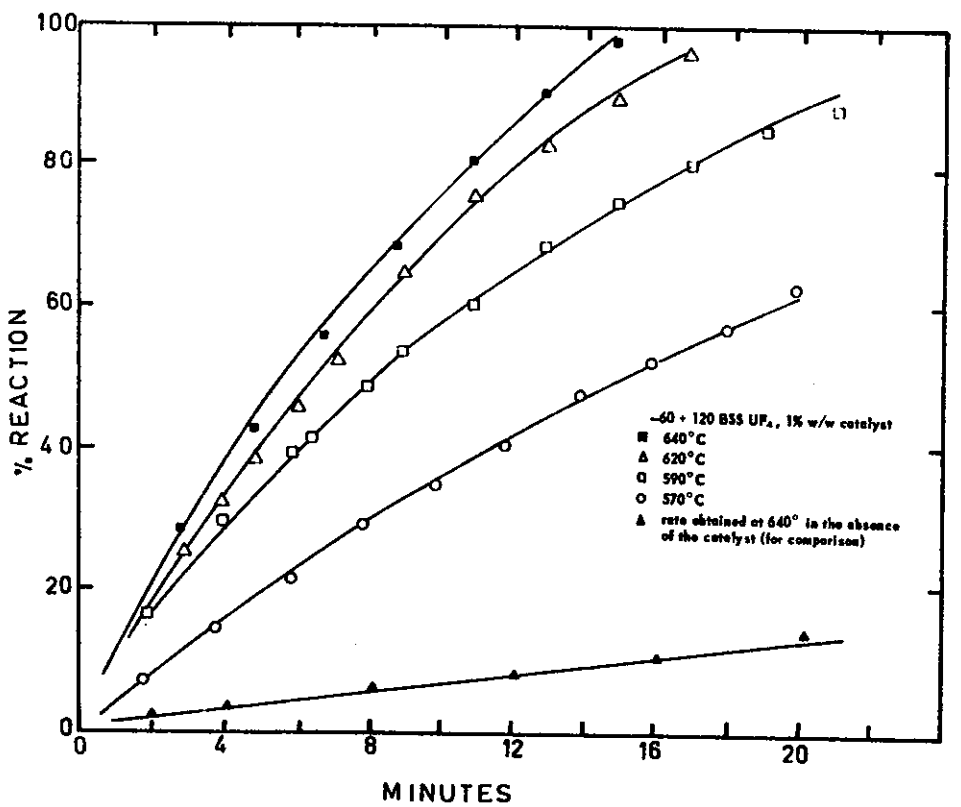


FIGURE A4. EFFECT OF TEMPERATURE ON THE RATE OF REACTION OF UF_4 WITH OXYGEN

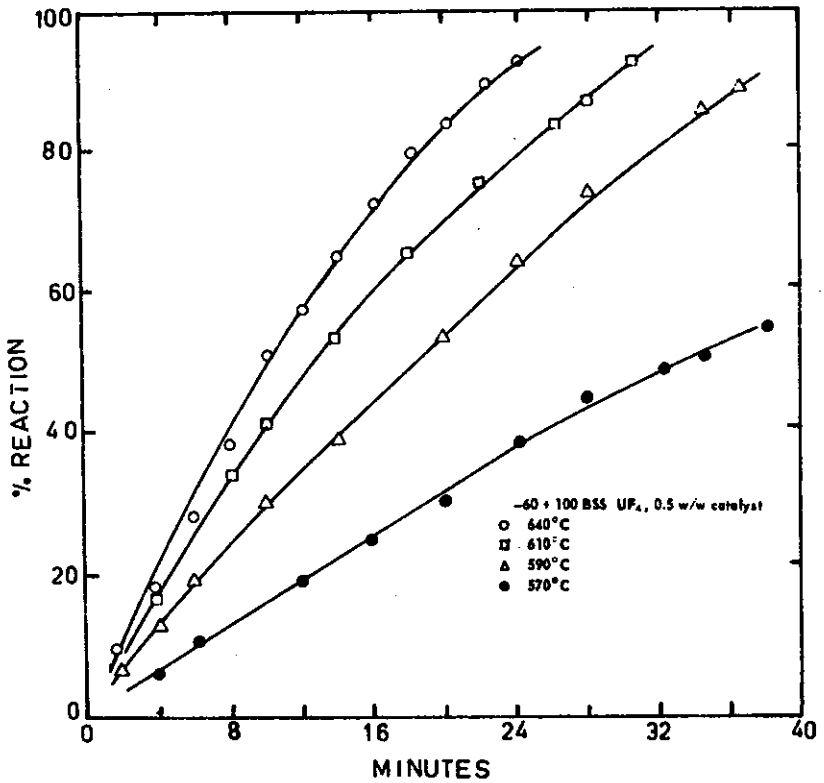


FIGURE A5. EFFECT OF TEMPERATURE ON THE RATE OF REACTION OF UF_4 WITH OXYGEN

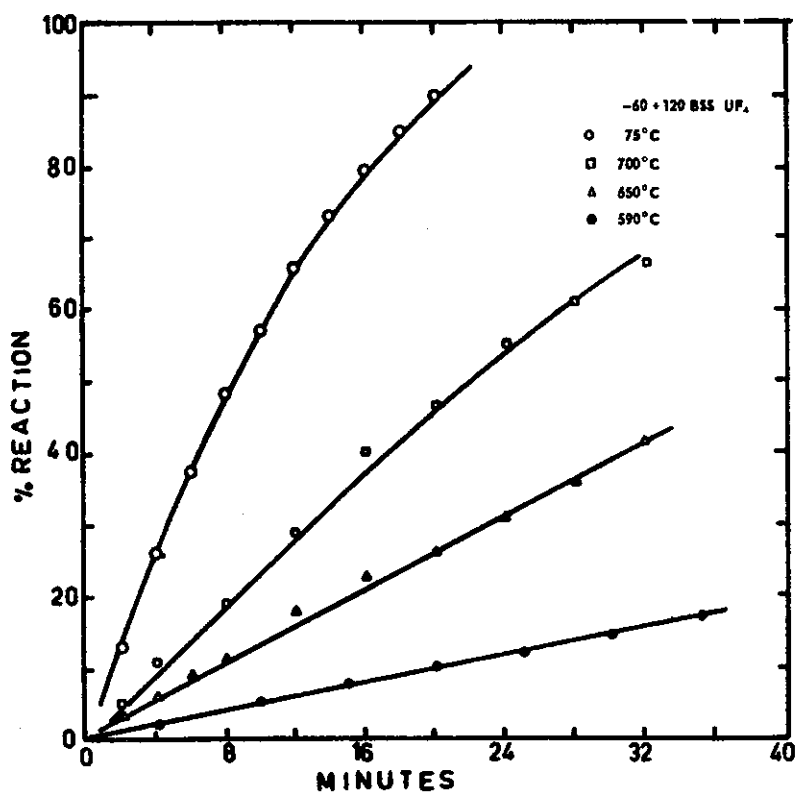


FIGURE A6. EFFECT OF TEMPERATURE ON THE RATE OF REACTION OF UF_4 WITH OXYGEN IN THE ABSENCE OF CATALYST

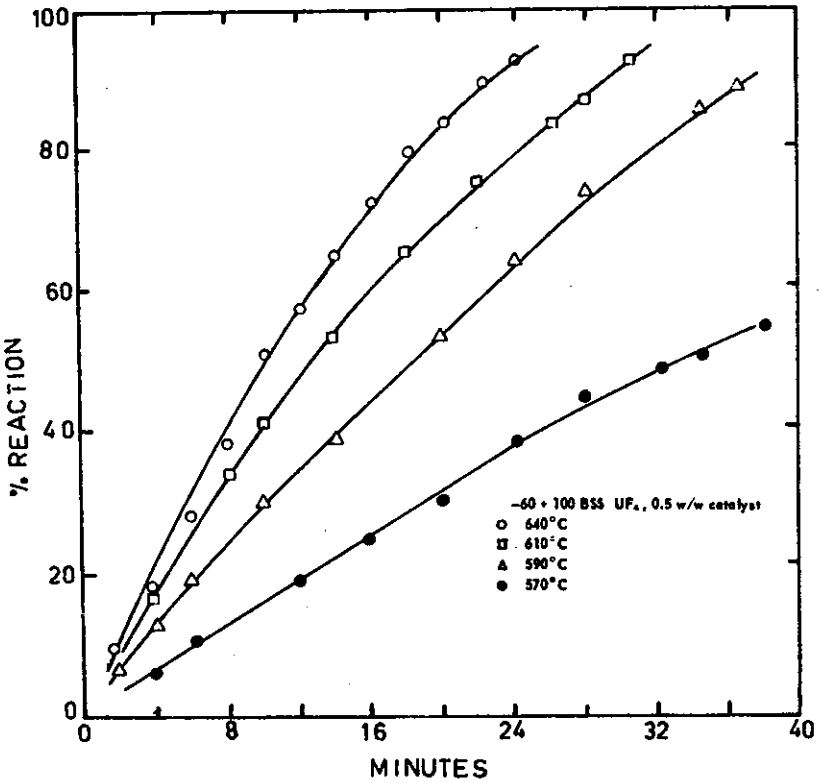


FIGURE A5. EFFECT OF TEMPERATURE ON THE RATE OF REACTION OF UF_4 WITH OXYGEN

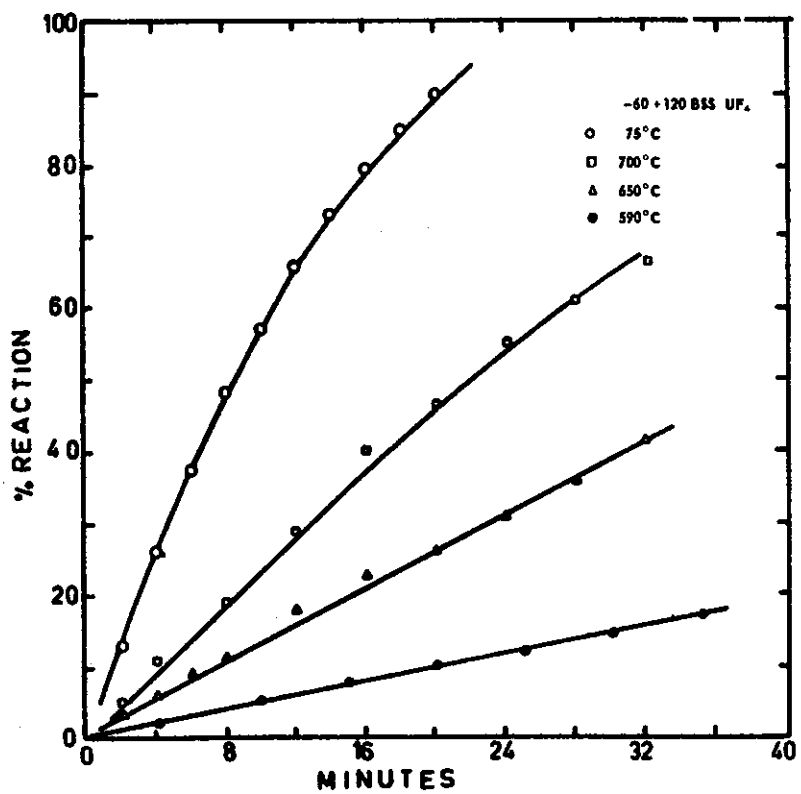


FIGURE A6. EFFECT OF TEMPERATURE ON THE RATE OF REACTION OF UF_4 WITH OXYGEN IN THE ABSENCE OF CATALYST

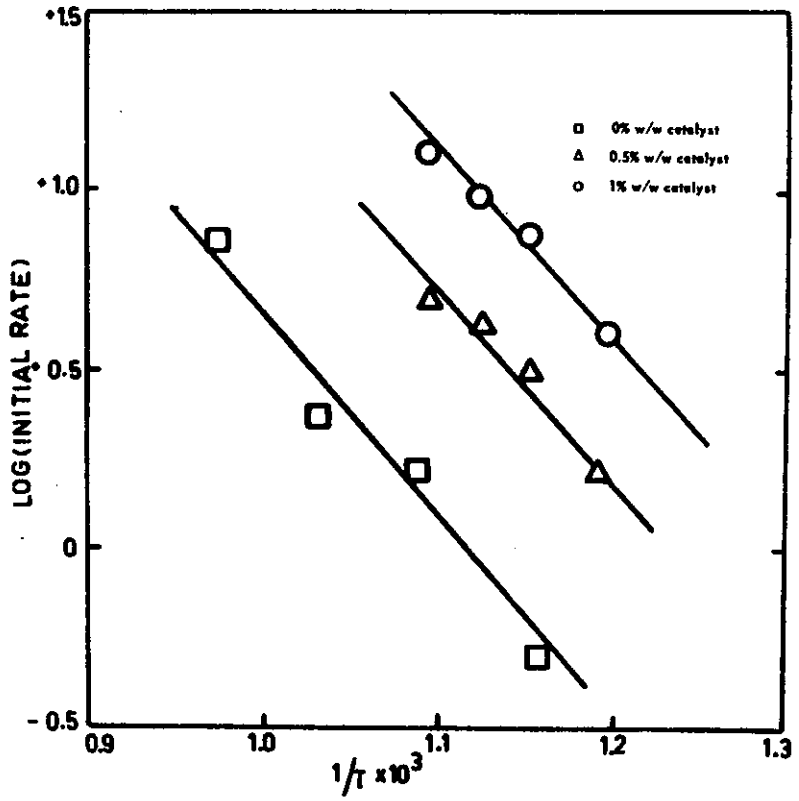


FIGURE A7. ARRHENIUS PLOTS OF THE INITIAL RATES FOR THE REACTION OF UF_4 WITH OXYGEN AT VARIOUS CATALYST CONCENTRATIONS

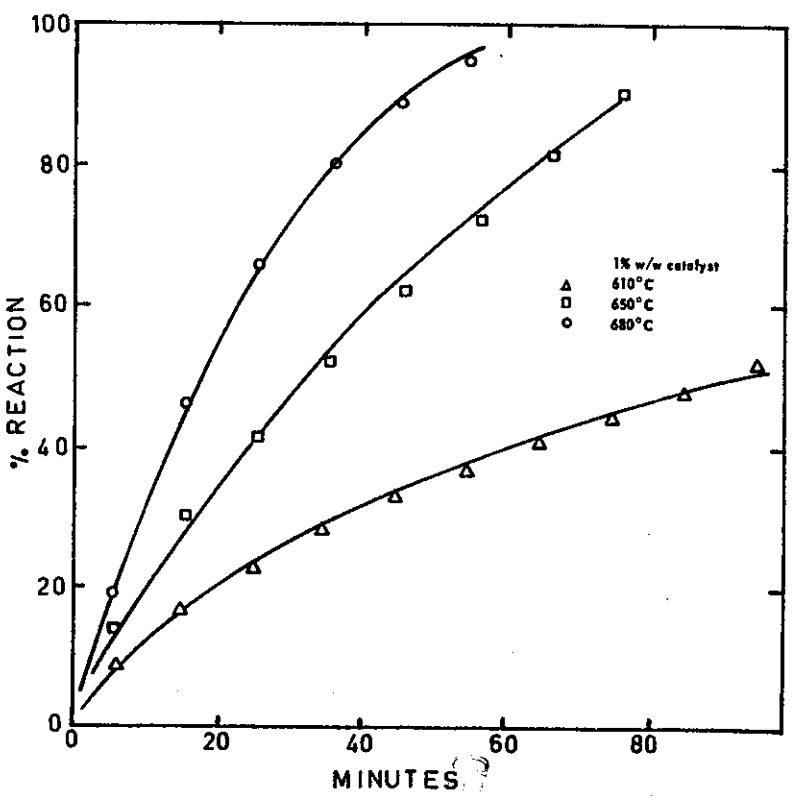


FIGURE A8. RATES OF REACTION OF UF_4 /CATALYST PELLETS AT VARIOUS TEMPERATURES

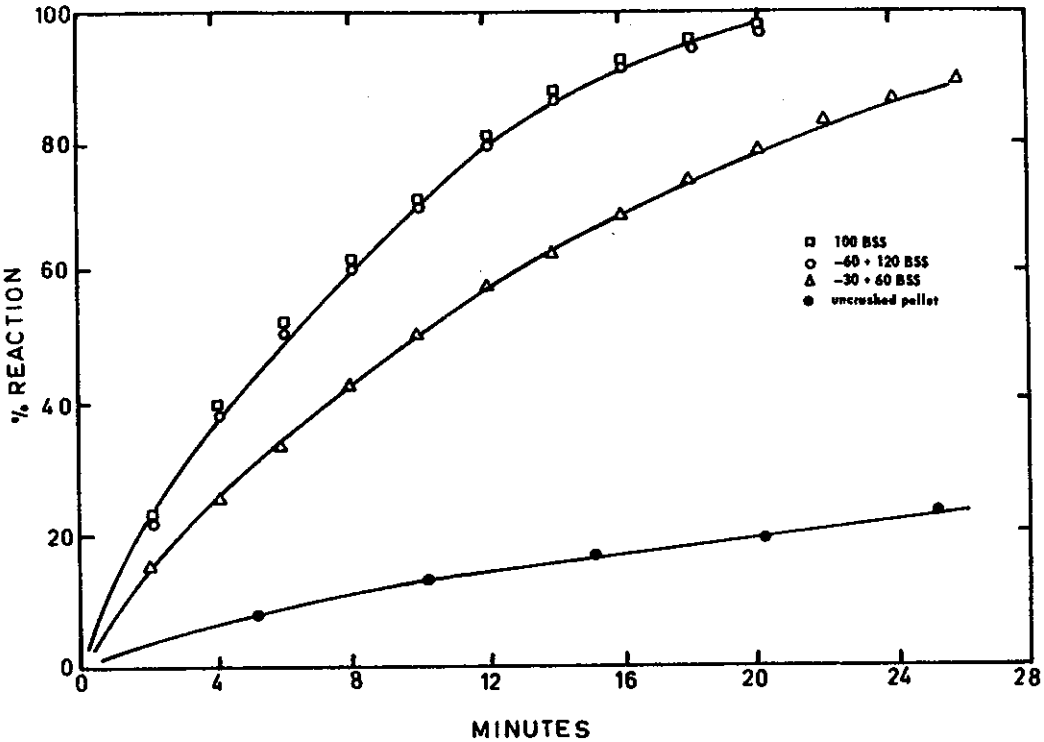


FIGURE A9. RATES OF REACTION OF CRUSHED UF_4/CATALYST PELLETS AT 610°C

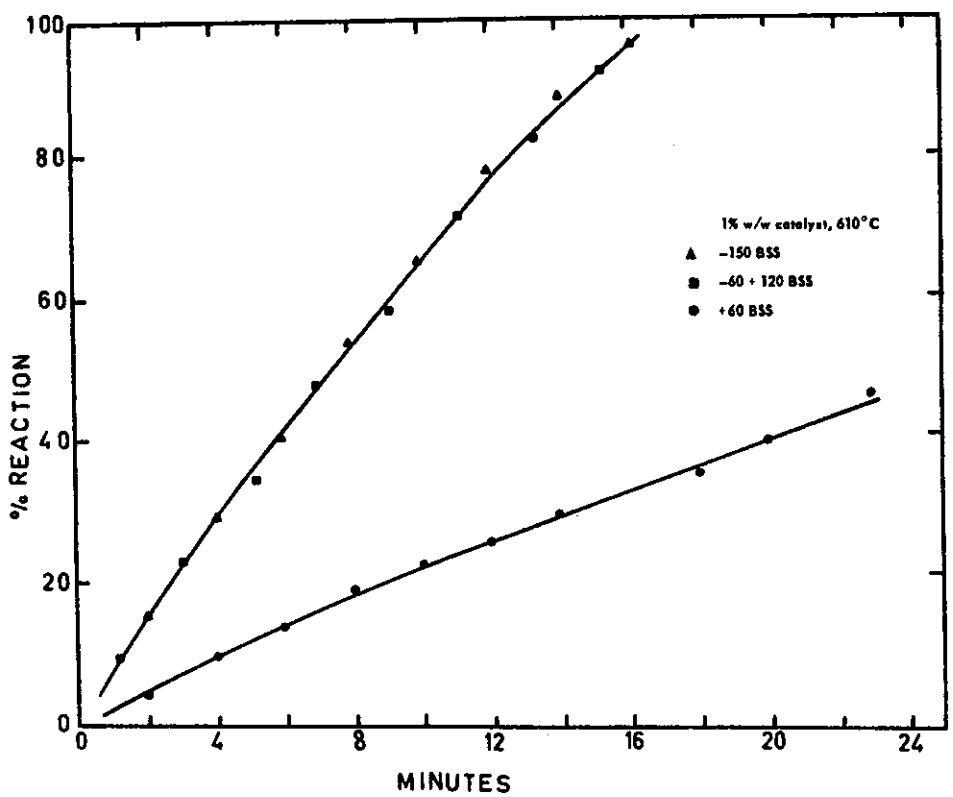


FIGURE A10. EFFECT OF UF_4 PARTICLE SIZE ON THE RATE OF REACTION OF UF_4 WITH OXYGEN

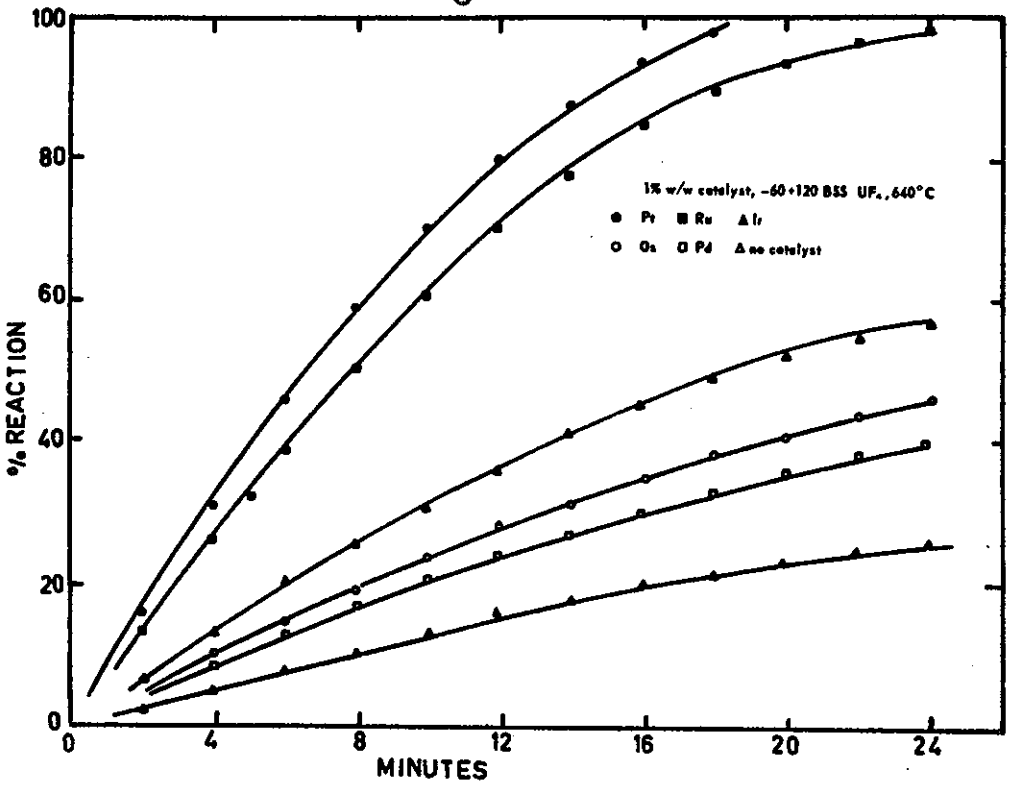


FIGURE A11. EFFECT OF VARIOUS CATALYSTS ON THE RATE OF REACTION OF UF_4 WITH OXYGEN

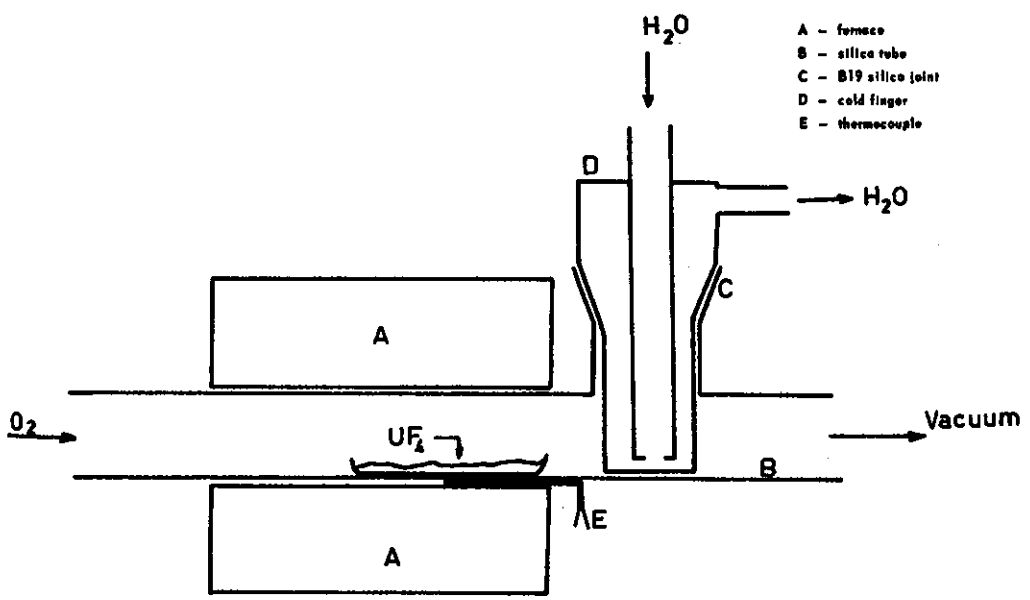


FIGURE A12. APPARATUS USED FOR ATTEMPTS TO DETECT U_2OF_8

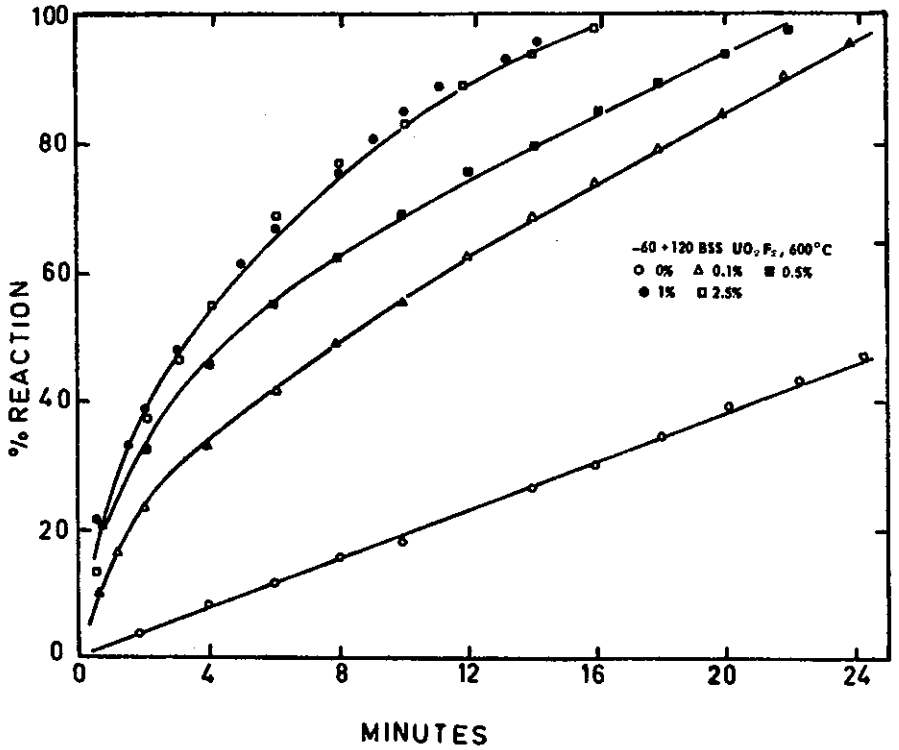


FIGURE A13. EFFECT OF CATALYST CONCENTRATION ON THE RATE OF REDUCTION OF UO_2F_2

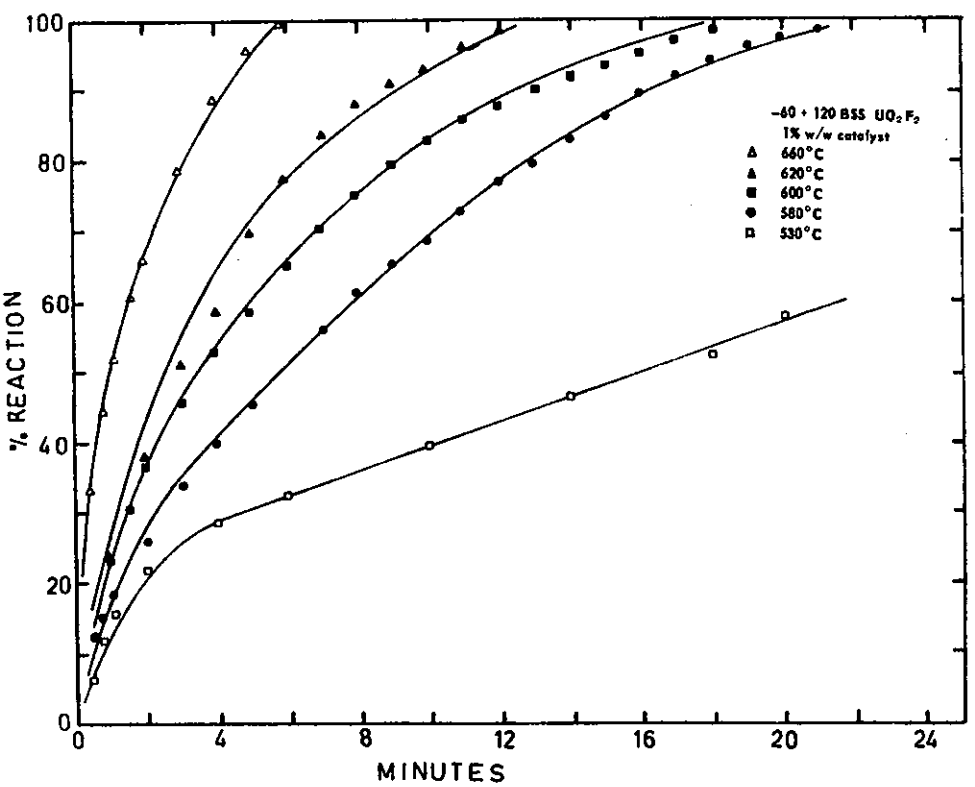


FIGURE A14. EFFECT OF TEMPERATURE ON THE REDUCTION OF UO_2F_2 BY HYDROGEN

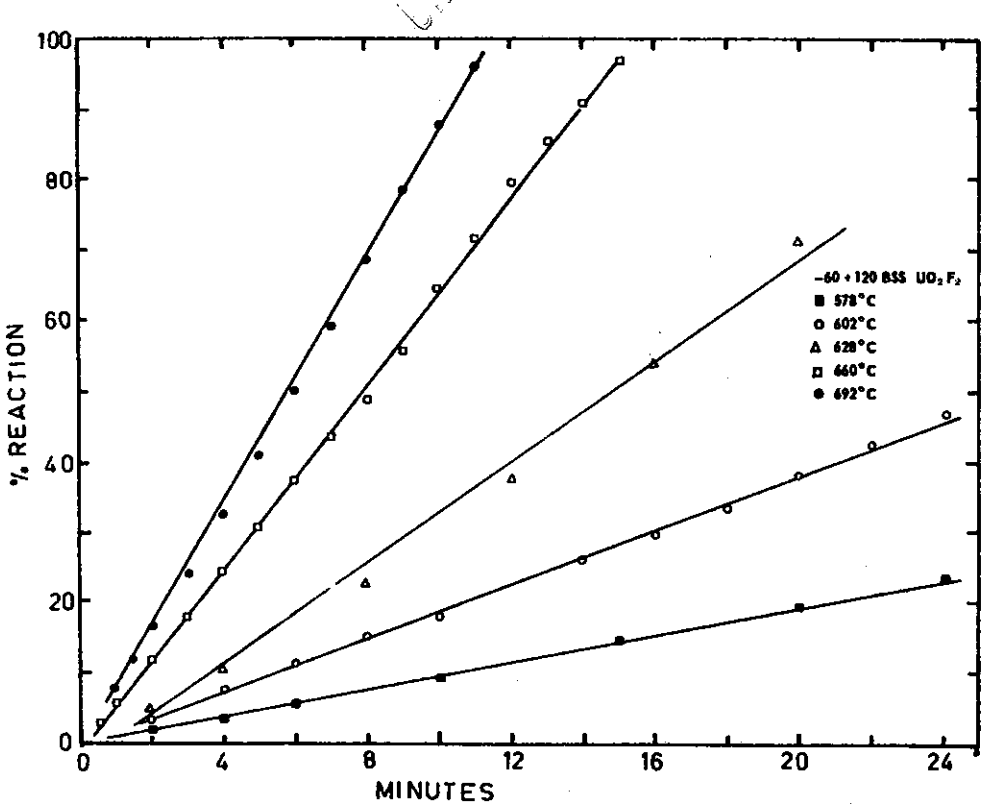


FIGURE A15. EFFECT OF TEMPERATURE ON THE REDUCTION OF UO_2F_2 IN THE ABSENCE OF CATALYST

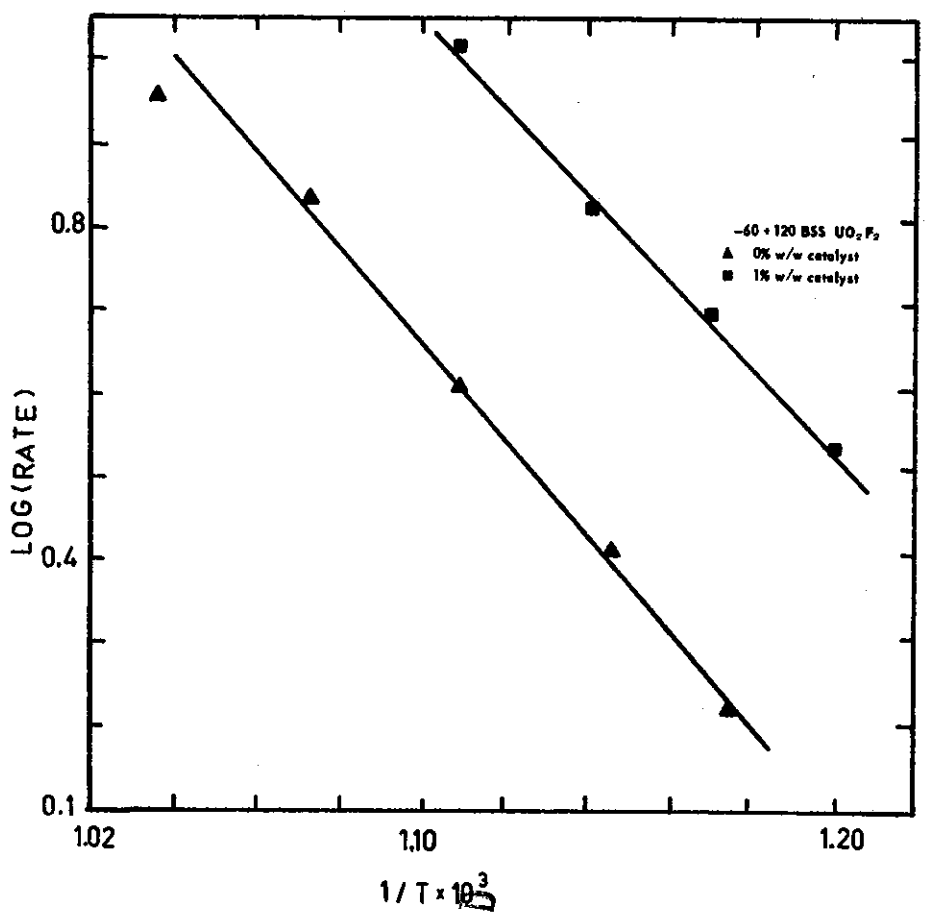


FIGURE A16. ARRHENIUS PLOTS OF THE REACTION OF UO_2F_2 WITH HYDROGEN

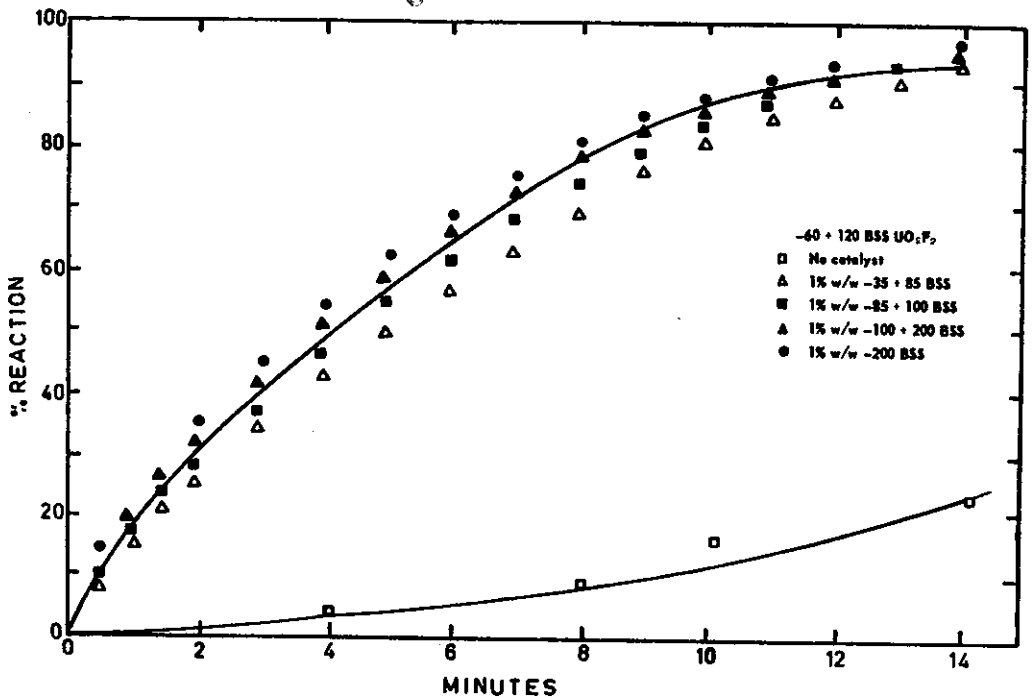


FIGURE A17. EFFECT OF CATALYST PARTICLE SIZE ON THE RATE OF REDUCTION OF UO_2F_2

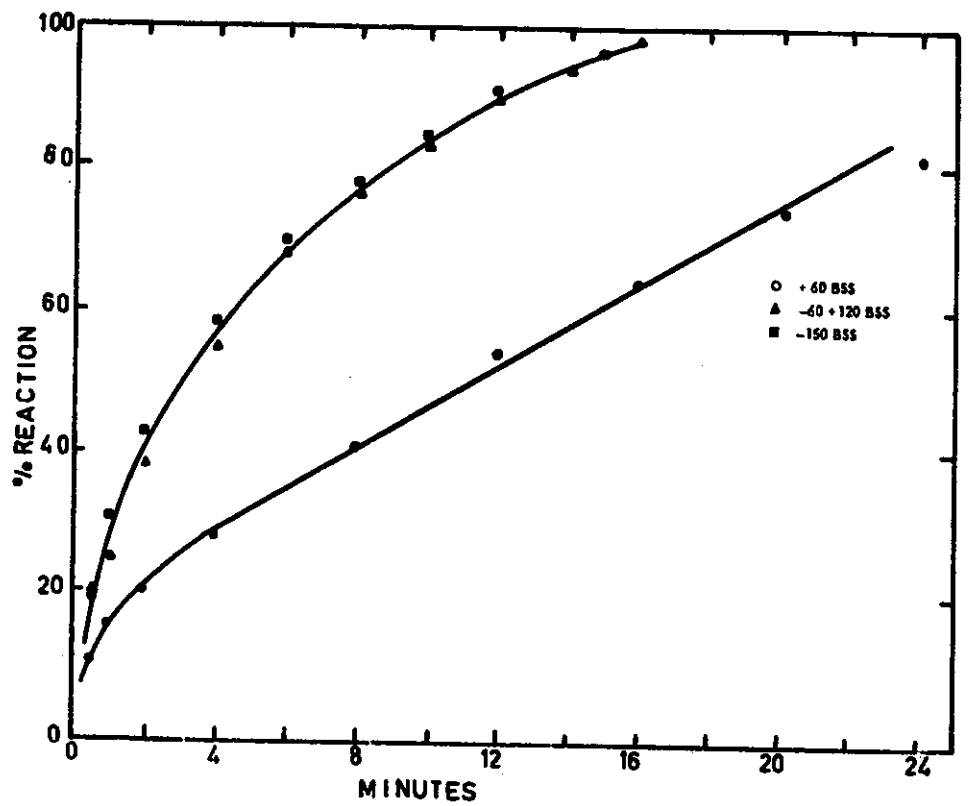


FIGURE A18. EFFECT OF UO_2F_2 PARTICLE SIZE ON THE RATE OF REDUCTION IN THE PRESENCE OF 1% w/w CATALYST AT 600°C

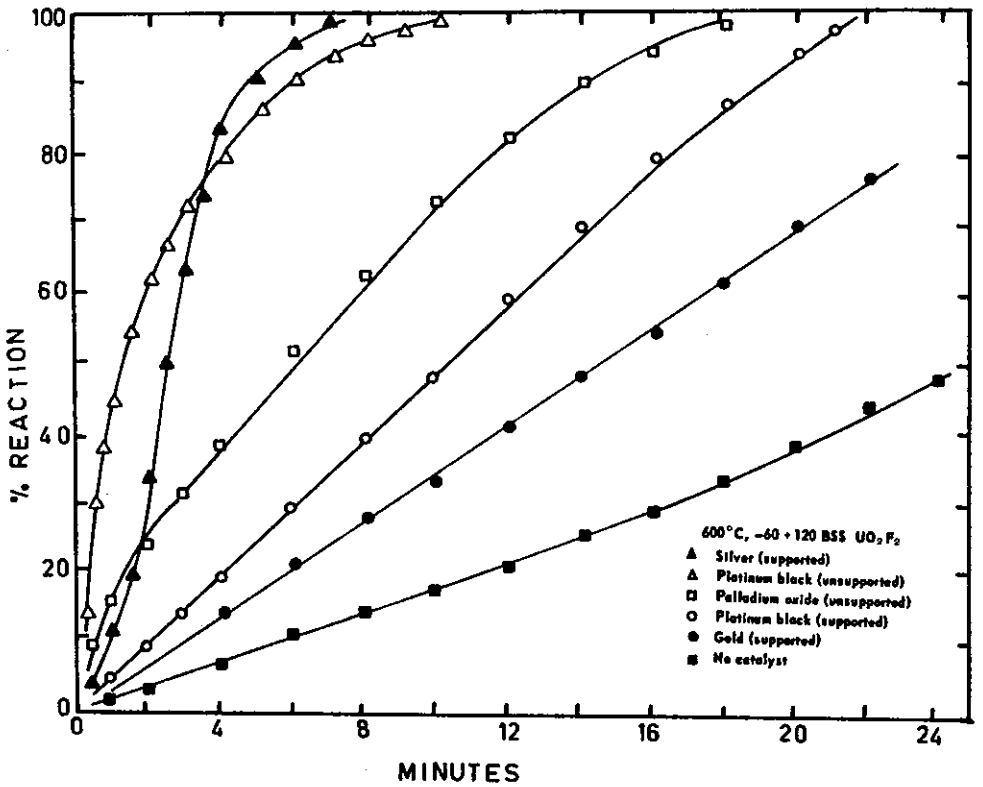


FIGURE A19. EFFECT OF VARIOUS CATALYSTS ON THE REDUCTION OF UO_2F_2

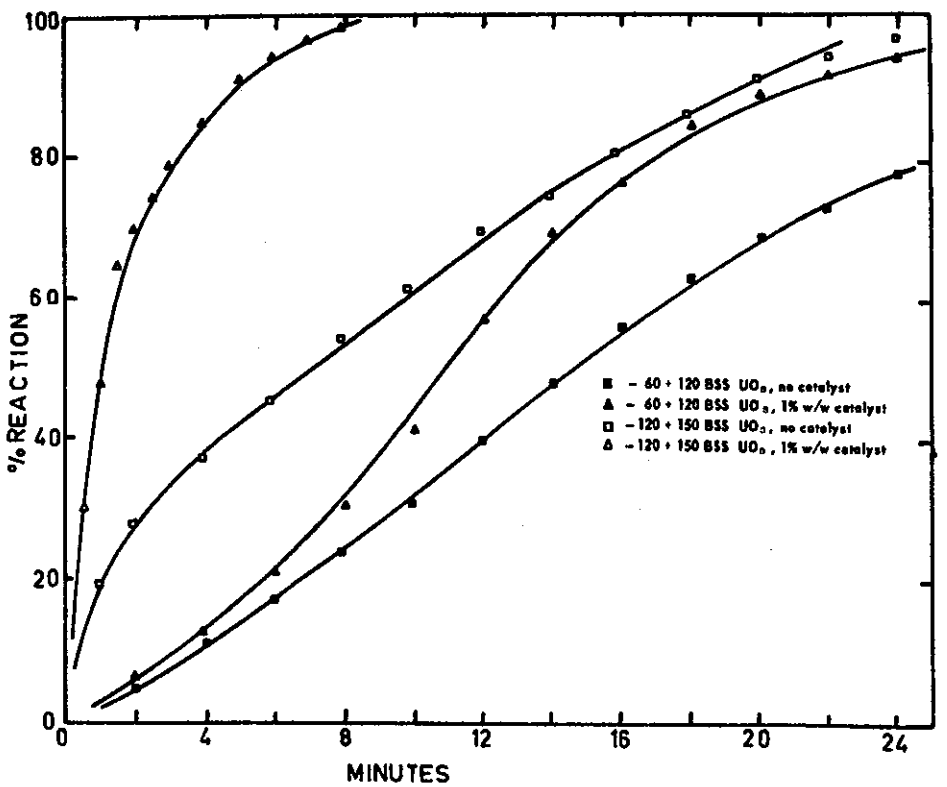


FIGURE A20. COMPARISON OF THE REACTION CURVES FOR THE REDUCTION OF DENITRATOR UO_3 AT 550°C

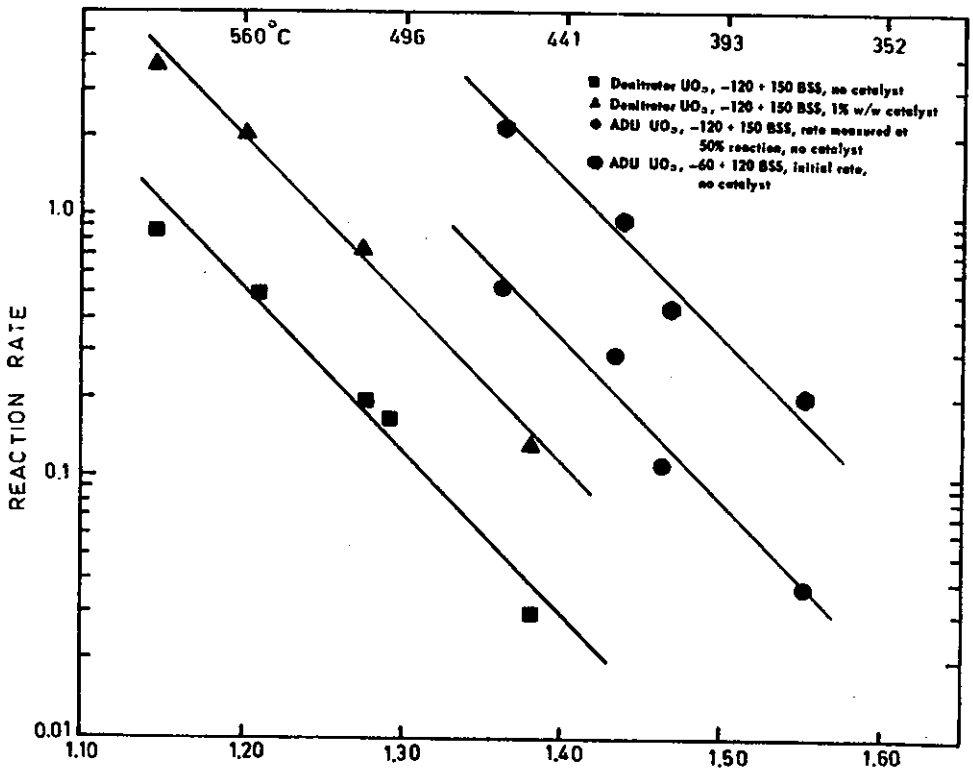


FIGURE A21. ARRHENIUS PLOTS FOR THE REDUCTION OF UO_3

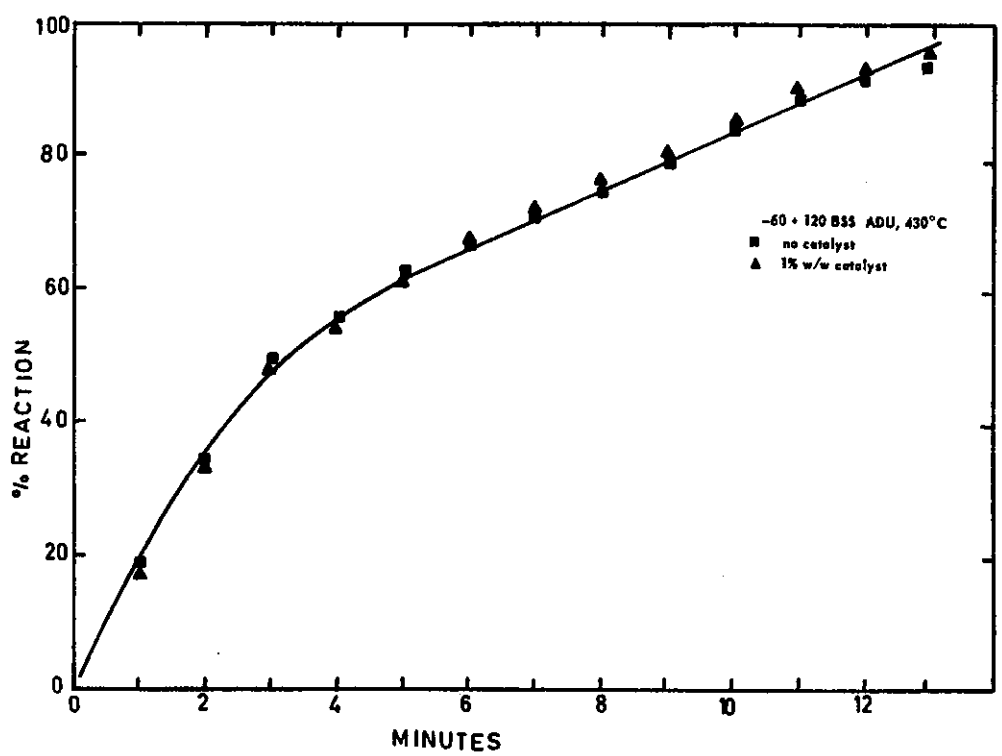
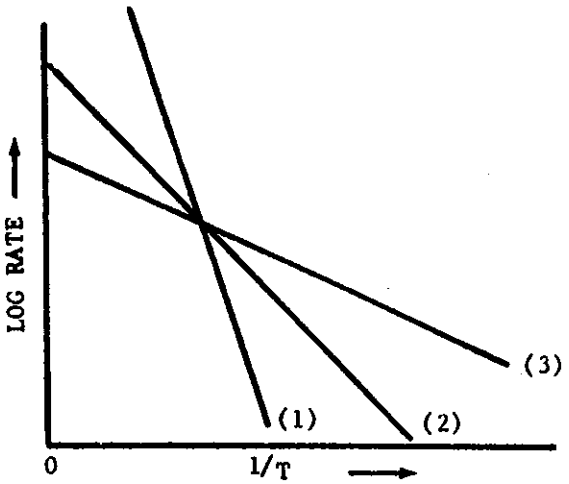
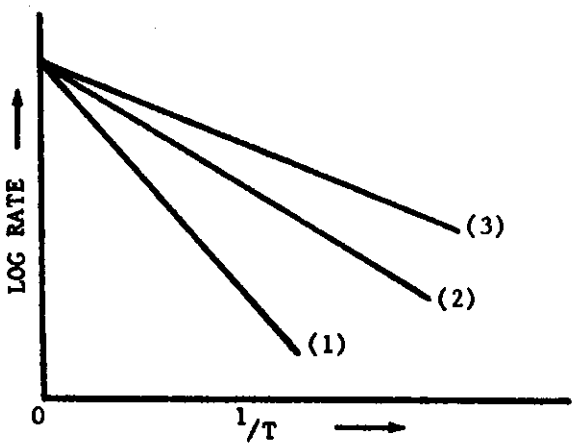


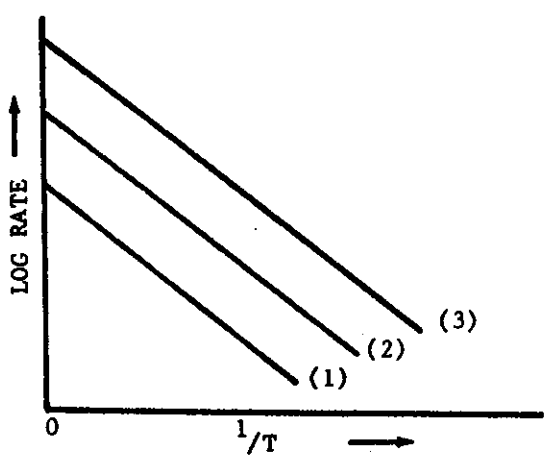
FIGURE A22. COMPARISON OF THE RATE OF REDUCTION OF ADU DERIVED UO_3 IN THE PRESENCE AND ABSENCE OF CATALYST



Case (a), Both A and E_A vary



Case (b) A is constant, but E_A varies



Case (c) E_A is constant, but A varies

FIGURE A23. POSSIBLE RELATIONSHIPS BETWEEN THE PRE-EXPONENTIAL FACTOR(A) AND THE ACTIVATION ENERGY (E_A) IN THE ARRHENIUS EQUATION FOR A SERIES OF CATALYSTS PROMOTING THE RATE OF A COMMON REACTION

shaded elements are active catalysts.

t = apparent time for 50% reaction at 640°C of a sample of UF_4 in the presence of 1 wt % of catalyst of 5 wt % metal or oxide on γ-Al_2O_3.

IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb
Sc ?	Ti >200*	V >200*	Cr >200*	Mn 100*	Fe >200*	Co 10	Ni >200*	Cu 100*	Zn >200*
Y ?	Zr >200*	Nb ?	Mo >200*	Tc ?	Ru 8	Rh 20	Pd 33	Ag 50	Cd >200*
La >200*	Hf >200*	Ta ?	W >200*	Re ?	Os 27	Ir 20	Pt 5	Au 25	Hg >200*

* absorbs UF_6

FIGURE A24. ELEMENTS EXAMINED AS CATALYSTS FOR UF_4O_2 REACTION IN PERIODIC TABLE ORDER

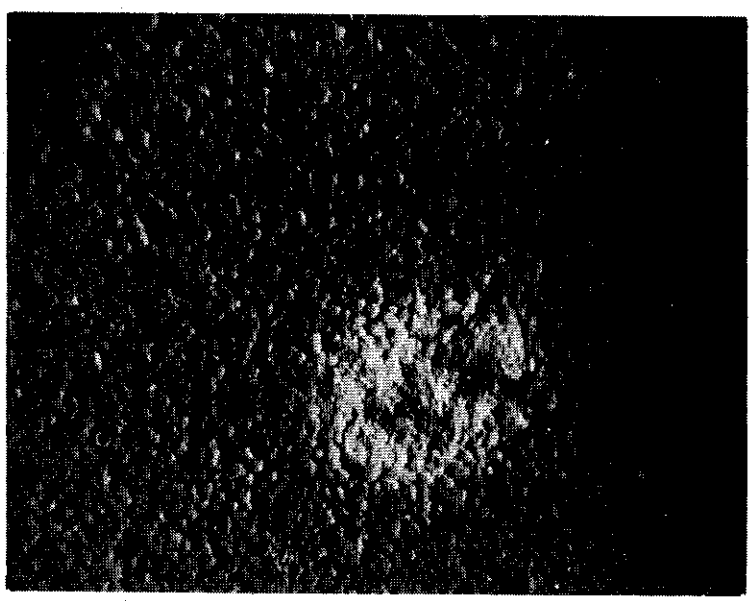


FIGURE A25. A CATALYST-UF_4 MIXTURE AFTER EXPOSURE TO OXYGEN AT 640°C FOR THREE MINUTES. THE PREFERENTIAL CONVERSION OF THE DARK UF_4 IN THE IMMEDIATE VICINITY OF THE CATALYST PARTICLE TO LIGHT UO_2F_2 CAN BE CLEARLY SEEN

SECTION B

THE PREPARATION, TESTING AND RECOVERY OF THE CATALYSTS

B1. INTRODUCTION

Following the observation that the reaction between UF_4 and oxygen could be catalysed by platinum, it was evident that a study designed to (a) determine the optimum conditions for the preparation of a platinum catalyst and (b) study the catalytic activity of other metals and metal oxides in this reaction, was necessary.

The literature abounds with reports of the preparation and application of platinum catalysts in a wide range of chemical processes. The majority of these are patented processes and as a result the details concerning the preparation of catalysts are scant and in most cases insufficient to permit duplication of the preparation. Non-metal catalysts, usually oxides, have found little application in inorganic processes. Of the metal catalysts, platinum is the most widely used. Metal catalysts are used as gauzes, evaporated films, powders or supported on inert supports. Supported catalysts are perhaps the most widely used.

In the preparation of supported catalysts the main factors to be considered are the nature of the support and the physical nature of the metal on this support. The information available on the effect of the type of support on the catalytic activity of metals appears confusing at first sight. It is possible to systematise the many results into classes of catalytic reactions. Boudart et al. (1966) considered catalytic reactions to be either "unhindered" or "hindered". Hindered reactions require a special configuration of surface atoms and therefore depend on the type of support and on the size of the metal crystallites on the support. Unhindered reactions are independent of both these factors. Slinkin and Fedorovskaya (1971) listed examples of reactions falling into both these classes. They concluded that with the present state of knowledge of catalytic reactions it is not possible to predict whether catalytic activity for a reaction will depend on either the nature of the support or the size of the dispersed metal.

A catalyst support makes it possible to regulate the particle size and orientation of the metal crystallites. With porous supports, it is generally possible to obtain stable dispersions of metal having a small particle size. The choice of support for our application was governed primarily by the nature of the reactions through which the catalyst was to be cycled; thus while silica, aluminosilicates and charcoal are common carrier materials in many industrial processes these were discarded in favour of materials which might be expected not to react with either hydrogen or oxygen at high temperatures.

Alumina is the most commonly used support material. It exists in at least nine known crystalline modifications most of which have been used at one time or another in catalytic processes. γ-alumina by virtue of its defect spinel structure is an active support, and as such has a large internal pore surface. α-alumina has a hexagonal close packed structure and would not be expected to be a suitable carrier.

In a supported catalyst it is desirable for maximum activity that the catalyst be highly dispersed, a factor which is quite sensitive to the method of preparation. The degree of dispersion of a metal on a support is defined as the ratio of surface metal atoms to the total number of metal atoms. Khassan et al. (1970) have shown that differences of only 100 degrees in the temperature at which platinum is deposited on γ-alumina can alter the size of the platinum crystallites from 20 to 100 Å. The use of a reduced pressure of hydrogen for the reduction of supported H_2PtCl_6 has also been shown to produce small platinum particles (Zhmud' et al. 1965). Considerable experimentation was therefore required to optimise the methods for the preparation of a catalyst for the Fluorox process.

As platinum is but one of a large number of commonly used catalyst materials, it was considered important from an economic standpoint to investigate the possibility of alternative catalyst materials. As platinum was an effective catalyst, it was highly probable that the other platinum metals would also catalyse the reaction although not necessarily to the same extent. A large number of metals and metal oxides which have found use as oxidation catalysts were also synthesised and examined. In addition, many examples have been reported where the use of mixed metal catalysts results in a catalyst whose activity is greater than catalysts prepared from the component metals alone. It is also possible to produce a physically stronger catalyst by using a combination of metals (Freifelder 1971).

In the process of optimising the activity of the catalyst, it was desirable that the end product be a catalyst material which (a) would have the physical strength and required density to permit its use in a fluidised bed without attrition, (b) could be recycled without loss of activity, (c) would have a low cost, and (d) would resist chemical attack under the process conditions.

B2. EXPERIMENTAL

B2.1 Preparation of Catalysts

Table B1 summarises the methods of preparation and sources of catalysts studied in this work. All platinum catalysts were prepared by the same general

TABLE B1

SUMMARY OF THE METHODS OF PREPARATION OF CATALYSTS

Catalyst Number	Type[a]	Method of Preparation or Source	Comments
1.	5% Pt on γ-Al_2O_3	Commercial - Johnson Matthey Chemicals Ltd	Very fine powder 50% less than 5 μm dia.
2.	5% Pt on boehmite[b]	ex H_2PtCl_6 [c]	Fine powder -300 BSS
3.	5% Pt on Merck γ-Al_2O_3	ex H_2PtCl_6 [c]	Fine powder -300 BSS agglomerated on deposition. Crushable to varying sizes
4.	5% Pt on Alcoa H151 alumina gel	ex H_2PtCl_6 [c]	H151 supplied as 1/4" balls is crushed to desired size before depositing H_2PtCl_6
5.	5% Pt on alumina Sol	ex H_2PtCl_6 [c]	
6.	Pt black (unsupported)	5% solution of H_2PtCl_6 neutralised with Na_2CO_3 and Pt precipitated by addition of HCHO	
7.	5% Pt black on boehmite [b]	H_2PtCl_6 stirred with support, Pt precipitated onto support by addition of formaldehyde	-300 BSS
8.	$PtO_2 \cdot xH_2O$ unsupported	Commercial - Johnson Matthey Chemicals Ltd	
9.	Platinum metal filings	Filed from 0.1 inch thickness platinum foil	Fine powder
10.	5% Pd on boehmite	ex $PdCl_2$ in dil.HCl [c]	-300 BSS
11.	PdO_2 (unsupported)	Commercial - Engelhard Industries Ltd	
12.	5% Ru on boehmite	ex $RuCl_3.3H_2O$ in dil. HCl (c)	-300 BSS
13.	5% Rh on boehmite	ex $(NH_4)_2$ $RhCl_6$ [c]	-300 BSS

TABLE B1 (Cont'd)

Catalyst Number	Type[a]	Method of Preparation or Source	Comments
14.	5% Ir on boehmite	ex $(NH_4)_2$ $IrCl_6$[c]	-300 BSS
15.	5% Os on boehmite	ex $(NH_4)_2$ $OsCl_6$[c]	-300 BSS
16.	5% Au on boehmite	ex $HAuCl_4$[c]	-300 BSS
17.	5% Ag on boehmite	ex $AgNO_3$[c]	-300 BSS
18.	Co_3O_4 (unsupported)	ex $Co(NO_3)_2.6H_2O$ heated in air at 700°C for 8 hrs	Fine powder
19.	5% Co_3O_4 on boehmite	as above but supported on boehmite	-300 BSS
20.	MnO_2 (unsupported)	Commercial	
21.	CuO (unsupported)	ex $CuSO_4.5H_2O$ heated in air at 800°C for 8 hours	Fine powder
22.	5% CuO on boehmite	ex $Cu(NO_3)_2$ deposited on support then heated in air at 700°C for 4 hrs	-300 BSS
23.	V_2O_5 on boehmite	ex NH_4VO_3 deposited on support then heated in air at 600°C for 4 hrs	-300 BSS
24.	MoO_3 (unsupported)	ex $(NH_4)_6$ $Mo_7O_{24}.4H_2O$ heated in air at 600°C for 4 hrs	Fine powder
25.	Fe_2O_3 (unsupported)	ex $Fe(NO_3)_3.9H_2O$ heated in air at 600°C for 4 hrs	Fine powder
26.	WO_3 (unsupported)	ex $(NH_4)_2$ WO_4 heated in air at 600°C for 4 hrs	Fine powder
27.	Ni_3O_4 (unsupported)	ex $Ni(NO_3)_2$ heated in air at 600°C for 4 hrs	Fine powder

TABLE B1 (Cont'd)

Catalyst Number	Type (a)	Method of Preparation Source	Comments
28.	5% Ni_3O_4 on boehmite	ex $Ni(NO_3)_2$ deposited on support then heated in air at 600°C for 4 hrs	-300 BSS
29.	ZrO_2 (unsupported)	Commercial sample	Fine powder
30.	La_2O_3 (unsupported)	ex $La(NO_3)_3.3H_2O$ heated in air at 600°C	Fine powder
31.	HfO_2 (unsupported)	Commercial sample	Fine powder
32.	Cr_2O_3 (unsupported)	Commercial sample	Fine powder
33.	ZnO (unsupported)	ex $Zn(NO_3)_2.6H_2O$ heated in air at 600°C	Fine powder
34.	CdO (unsupported)	ex $Cd(NO_3)_2.4H_2O$ heated in air at 600°C	Fine powder

(a) Those catalysts supported on boehmite were also prepared using Alcoa H151 alumina gel as the support. In these cases, unless otherwise stated, the catalyst number will refer to the boehmite supported catalyst.

(b) Boehmite is prepared by reaction of amalgamated aluminium with water (Brauer 1965). The powdered boehmite was dried at 600°C in air to convert it to a γ-alumina. It was used as a support in this form.

(c) Catalyst prepared by slurrying an aqueous solution of the metal salt or acid with the support, evaporating to dryness in a rotary evaporator, drying in air at 100°C for 2 hours then heating in hydrogen at 300°C for 3 hours.

TABLE B2

ALUMINA SUPPORTS USED IN CATALYST PREPARATION

Catalysts were 5 wt % Platinum on Alumina

Support	Crystalline Modification	BSS Range	$t_{\frac{1}{2}}$ (a) (mins)
BDH "Analar" Alumina	Mainly α-Al_2O_3	-100 + 200	> 50
BDH Chromatographic Alumina	mixture including α-Al_2O_3	-100 + 200	> 50
α-Alumina powder	α-Al_2O_3	-300	13
Crushed boiling stones	β-Al_2O_3	-100 + 200	> 50
¼" alumina balls	γ-Al_2O_3	- 60 + 100 -300	20 4
Alcoa F1 activated alumina	unknown	-300 - 60 + 100	11 25
Alcoa T61 Tabular alumina	unknown	-100 + 200	> 50
Merck γ-Alumina	γ-Al_2O_3	-300 - 60 + 100	4.5 42
Boehmite	γ-Al_2O_3	-300 - 60 + 100	4 9
Alcoa H151 gel	γ-Al_2O_3	-100 + 200	10

(a) $t_{\frac{1}{2}}$ = time taken for 50% of the UF_4 to react.

method unless otherwise indicated, with variations only in the nature of the support, and in the platinum concentration.

Mixed metal catalysts were prepared from mixtures of the respective salts or acids using the general method (a) in Table B1, with the exception of catalysts containing silver for which the silver had to be deposited on the support separately before the second metal was added.

B2.2 Preparation of Supports

Commercially available supports were used, with the exception of boehmite which was prepared by the method referred to in Table B1, Footnote (b).

The supports examined are shown in Table B2.

B2.3 Testing of Catalysts

Experimental details on the testing of catalysts are given in Section A2.

B3. RESULTS AND DISCUSSION

B3.1 Platinum on Alumina Catalysts

A large number of alumina samples were tested as suitable supports for platinum catalysts. In most cases the crystalline modification of the alumina was unknown and had to be characterised by X-ray crystallography. Table B2 lists the supports used, their crystalline form, and the activity of the platinum catalyst prepared in these supports. As expected, γ-alumina supports were the most suitable. α-alumina was suitable only in a very finely divided form, when the ratio of catalyst particles to UF_4 particles was high.

Even amongst the γ-alumina samples, considerable variation in activity was observed. Surface area differences were believed to account for the variations and this was borne out by data obtained from measurements of B.E.T. nitrogen absorption as shown in Table B3. For catalysts in the -60 +100 BSS size range there was a direct correlation between surface area and activity. The apparent inconsistency of the boehmite catalyst arose from the fact that it was formed by agglomeration of finer particles.

Crushing the catalyst particles produced very little increase in surface area. B.E.T. surface areas include both internal and external surface. For extremely porous materials such as γ-alumina samples, the majority of the surface is internal surface consisting of an extensive network of micropores (10-50 Å) and macropores ($\approx$100 Å) interconnected in a three dimensional array (Wall 1972). The higher the surface area of the support, the greater the surface available for reaction and hence the more active the catalyst. With large catalyst particles, the rate of reaction can be controlled by the rate of diffusion of oxygen into, or of activated oxygen from, the innermost pores of the catalyst.

TABLE B3

ACTIVITY OF γ-ALUMINA SUPPORTED Pt CATALYSTS AS A FUNCTION OF SURFACE AREA

Support	Surface Area (m^2/g)	$t_{\frac{1}{2}}$ for Pt Catalyst (min) [a]
Alcoa T61 tabular alumina -100 + 200 BSS	0.04 [b]	> 50
Merck γ-alumina - 60 + 100 BSS	90	42
Alcoa F1 activated alumina - 60 + 100 BSS	191	25
Boehmite (converted to γ-Al_2O_3) - 60 + 100 BSS	232	9
Alcoa H151 alumina gel - 60 + 100 BSS	298	12

(a) Catalysts prepared as 5 wt % platinum on support and tested as 1 wt % with UF_4.

(b) Data supplied by manufacturer.

Table B4 shows, however, that particle size did have a significant effect on activity. The reason for increased activity with very fine catalyst particles is related to the greater number of these particles that pack in the vicinity of each UF_4 particle. The proximity and number of catalyst particles around each UF_4 particle then becomes a more significant factor than the surface area of the catalyst in determining the rate of oxidation of the UF_4.

TABLE B4

EFFECT OF CATALYST PARTICLE SIZE ON ACTIVITY

Catalyst No. 4 (H151 alumina gel) tested as
1 wt % with -60 + 120 BSS UF_4

Particle Size	$t_{\frac{1}{2}}$ (mins)
-200 + 375 BSS	6.5
-100 + 200 BSS	10
- 60 + 100 BSS	12
- 36 + 72 BSS	13.5
uncatalysed	55

It was found that in the preparation of catalysts from finely divided Merck γ-alumina (-300 BSS), agglomeration of catalyst particles occurred during the evaporation of the chloroplatinic acid - alumina slurry. After sintering it was possible to sieve the resultant catalyst in sizes up to 18 BSS to give particles in any size range from 18 to 300 BSS. The activity of the agglomerated catalyst was found to be independent of particle size. This proved to be the most active of the catalysts that we were able to prepare in the size ranges -60 + 100 BSS and -100 + 200 BSS. Catalysts in these size ranges were desirable for use in a fluidised bed reactor.

The high activity can be explained if the catalyst is considered to have a bimodal pore-size distribution. Bidisperse structures are common in compacted catalysts where large channels surround the smaller particles in the agglomerated mixture (Clark 1970). These channels facilitate diffusion in the agglomerated catalyst in contrast to the diffusion limited reaction in 'solid' catalysts of the same size.

The boehmite catalyst (catalyst No. 2 -60 + 100 BSS) showed an activity approaching that of the agglomerated catalyst. These particles were readily crushed and were found to be composed of agglomerated smaller particles similar

to agglomerated Merck γ-alumina catalysts. The possibility of attrition of these catalysts made them undesirable for continuous operation in a fluidised bed reactor.

To improve the hardness while maintaining the high activity of these catalysts, samples were compressed into 12.7 mm diameter pellets using a hydrostatic press at different pressures up to 154.4 MNm^{-2}. The pellets were then crushed to the desired mesh size and tested. The resultant samples showed little gain in strength but no loss in activity. Pellets containing organic binders compressed in the same manner were similarly of poor strength.

The high activity of agglomerated catalysts was attributed to their channelled pore structure. We attempted to duplicate this structure by using an alumina sol mixed together with a low surface area alumina, or platinum-on-alumina. The samples were mixed, evaporated to dryness, then reduced in hydrogen at 350°C. Such dispersed alumina additions are known to improve porosity. A number of mixtures of aluminas were investigated. Representative results are given in Table B5. The samples produced in this manner were of good strength but of low activity compared with the samples of catalyst No. 3 (Table B1).

TABLE B5

CATALYSTS ON MIXED ALUMINA SUPPORTS

Catalyst	$t_{½}$ (mins)
50% of 5% Pt on Merck γ-Al_2O_3 agglomerated to -60 + 100 mesh + 50% alumina sol all coated with 1% Pt	18
25% of 5% Pt on γ-Al_2O_3 (T61 Alcoa tabular alumina) + 75% alumina sol all coated with 1% Pt	40

B3.2 Platinum Dispersion

Maximum dispersion of platinum was obtained when reduction of supported chloroplatinic acid was carried out at 350°C in flowing hydrogen. Using X-ray line broadening, measurements made of platinum crystallite size in these catalysts gave an average figure of 60Å. An improvement on this figure was obtained by performing the reduction at a reduced pressure of hydrogen. For platinum particles in the 60Å size range it is conceivable that considerable

blockage of the pore network would occur, since the size of micropores in activated γ-alumina samples has been found to be closer to 30Å (Bowen, Bowrey and Malin, 1967).

B3.3 Coverage of the Support

In studying the oxidation of UF_4 an added complication arises, since UF_6, the product of the catalytic reaction, is absorbed by alumina. In preparing the catalyst it was important that all of the alumina was effectively covered by platinum. The effect of uncovered alumina is shown in Figure B1. When increasing amounts of alumina are added to a fully covered platinum on alumina catalyst the observed rate of reaction was significantly decreased, an initial inhibition period appeared and the plateau indicating complete reaction occurred at apparent percentage reactions much below 100%.

To overcome absorption of UF_6 it was necessary to obtain more effective coverage of alumina either by increasing the platinum content or by treatment of the exposed support in some way to prevent absorption. For commercial application it is obviously desirable to have the platinum content of the catalyst as low as possible. Table B6 shows results of the variation of platinum concentration from 0.1% to 10%.

These figures indicate the difficulties in obtaining complete coverage of the carrier for low concentrations of platinum on alumina. For complete coverage both $t_{\frac{1}{2}}$ and $t_{\frac{1}{2}}$ corr. should be the same. This was only so for a 5% platinum on alumina catalyst. Increasing the catalyst concentration in the test reactions only increased the amount of uncovered support. Comparisons between catalysts containing different percentages of platinum can be misleading as pointed out earlier since to a great extent these figures depend on the duplication of the method of preparation. However, the results indicate that at least 2% platinum is required to provide adequate surface coverage.

Attempts were made to reduce the absorptive capacity of alumina to UF_6 by treating the support with gaseous HF. Figure B2 shows the increased activity of a hydrofluorinated alumina over a normal untreated alumina as catalyst supports. The addition of free hydrofluorinated alumina to this sample did not produce any significant decrease in rate whereas untreated alumina significantly decreased the apparent percentage reaction.

Treatment with gaseous HF of a platinum catalyst having incomplete coverage of the support by metal did not produce a significant change in catalyst activity.

TABLE B6

VARIATION OF PLATINUM ON ALUMINA CONCENTRATION

FOR CATALYSTS PREPARED ON H151 ALUMINA -100 + 200 BSS

Catalyst Concentration	% Pt on Alumina	$t_{\frac{1}{2}}$ (mins)	$t_{\frac{1}{2}}$ corr. (mins)
1%	0.1	25	12
10%	0.1	23	6
5%	0.5	11	5
10%	0.5	20	4
2%	1	6	5
5%	1	10	3
1%	2	8	8
2%	2	7	3
5%	2	15	1
1%	5	9	9
0	uncatalysed	50	50

$t_{\frac{1}{2}}$ corr. = time for the reaction to go to 50% of its limiting value.

It was noticed that one of the problems in obtaining uniform coverage of the alumina support was the uniformity of the H_2PtCl_6 deposited in a rotary evaporator. We found that a more satisfactory deposition was obtained if the alumina in the chloroplatinic acid solution was treated for 15 minutes in an ultrasonic bath before removal of the solvent in the rotary evaporator. This treatment assisted in the uniform distribution of chloroplatinic acid to the inner pores of the support.

The activity of the catalyst was considerably influenced by the presence of moisture. In many instances the support materials used were good desiccants, e.g. Alumina gel H151 is capable of absorbing up to 40% by weight of water. Effective dehydration of such materials required heating for several hours at a temperature as high as 600°C. Catalysts prepared on wet alumina supports were often unevenly coated and had a low activity. Best results were obtained by adding the aqueous chloroplatinic acid solution to freshly regenerated alumina, followed by ultrasonic treatment. The catalyst was then prepared in the manner referred to previously (Table B1).

Prolonged exposure of catalysts to air resulted in absorption of water. This had a detrimental effect on the rate of reaction of oxygen with UF_4 mainly due to the side reaction

$$3UF_4 + 6H_2O + O_2 \rightarrow U_3O_8 + 12HF \quad \ldots(13)$$

Moisture should therefore be removed by drying the catalyst at 300°C before use.

B3.4 Other Catalyst Supports

Alternative solid supports were examined with the aim of obtaining increased activity, increased strength and resistance to absorption of UF_6.

The supports examined are listed in Table B7. Most of these had surface areas and porosities much lower than those of the best γ-alumina samples. Although the activity of catalysts prepared on these supports was lower than alumina supported catalysts, it should be possible to achieve a higher activity by increasing the catalyst content of the reaction mixture from 1 wt % to 10 wt %. The added expense for such a high catalyst content could be diminished by reducing the platinum content of the catalyst from 5 wt % to 0.5 or 0.1 wt %. In the case of a low surface area support such as calcium fluoride such a reduction would be possible while maintaining a complete coverage of the support.

Calcium fluoride would be a desirable support material since it does not absorb or react with any of the components in the Fluorox reaction.

B3.5 Other Platinum Catalysts

In addition to the supported platinum catalysts several other platinum catalysts were prepared and examined. The results are given in Table B8. Both Adam's catalyst, $PtO_2.xH_2O$, and platinum black showed appreciable activity.

It is significant that platinum even in the low surface area form of metal filings should enhance the rate of the oxidation reaction. This indicates that the use of a fixed catalyst in the form of metal filings or a metal screen might be a suitable alternative form for a platinum catalyst in a fluidised bed reactor. The advantages in terms of ease of separation of this form of catalyst from the reaction mixture are obvious.

B3.6 Other Catalysts

A large number of potential catalysts other than platinum were prepared and examined. Details of the preparation are given in Table B1 while the study of catalytic activity is presented in Section A. No particular attention was paid to optimising the support, the dispersion of the metal and

TABLE B7

ACTIVITY OF PLATINUM CATALYSTS PREPARED AT DIFFERENT CATALYST SUPPORTS

(Tested at 640°C 1 wt.% with UF_4)

Catalyst	Support	Mesh Size BSS	$t_{\frac{1}{2}}$ (mins)
5% Pt	SiO_2	-300	11
5% Pt	MgO	-300	25
5% Pt	$BaSO_4$	-300	25
5% Pt	CaF_2	-300	40

TABLE B8

ACTIVITY OF PLATINUM CATALYSTS

(Tested at 640°C 1 wt % with UF_4)

Catalyst	$t_{\frac{1}{2}}$ (mins)
Platinum metal filings	28
Platinized platinum filings	28
Pt black	9
$PtO_2.xH_2O$	14
Blank in absence of catalyst	50

other factors as was done in the case of platinum. The method used for the preparation of the best platinum catalyst was applied for the preparation

B3.7 Recovery of Catalyst from the Reaction Mixture

In a continuous process for the preparation of UF_6 by the catalysed Fluorox reaction, the platinum catalyst will be recycled through the oxidation - reduction/hydrofluorination reactions a number of times. At some stage during the recycling it may be necessary to remove catalyst from its mixture with UF_4 and UO_2F_2.

Such a separation would require the following stages :

(a) dissolution of UO_2F_2,

(b) dissolution of UF_4, and

(c) filtration and if necessary dissolution of platinum.

The dissolution of UO_2F_2 in water will not present a problem, however, there are a number of possible methods for dissolving UF_4 and these were examined to find a technique which did not dissolve any of the catalyst. Katz and Rabinowitch (1951) list a number of possible methods :

(i) Fuming $HClO_4$

(ii) Nitric-boric acid mixtures

(iii) Ceric sulphate

(iv) NH_3 - H_2O_2

(v) $FeCl_3$

(vi) $Al(NO_3)_3$ boiling solution

(vii) Hot H_3PO_4

(viii) NaOH hot solution

(ix) H_2SO_4 - SiO_2 .

A report by Calkins (1949) examined some of these methods and in addition tested :

(x) H_2SO_4 - $(NH_4)_2\ S_2O_8$

(xi) molten $AlCl_3$ in a bomb.

Morris (1955) examined :

(xii) H_2O_2 - H_2SO_4 .

These methods rely on one of the following general reactions :

(a) Solution of UF_4 to give a soluble U^{4+} compound.

(b) Oxidation of UF_4 to a soluble uranyl compound.

(c) Dissociation of UF_4 (with or without oxidation) in the presence of ions forming stronger complex fluorides.

The above reports list methods (vi), (viii), (x), (xi) and (xii) as the most effective.

For the recovery of platinum, a scheme was sought in which platinum would be retrieved either as the metal or as some soluble salt which could then be used for the preparation of new catalyst or for resale to the suppliers as waste platinum.

The wide usage of platinum catalysts in chemical technology has meant that a plethora of data is available on recovery.

Some general methods among the patent literature on the recovery of platinum from alumina supported catalysts are :

(i) Solution of Al_2O_3 under pressure in HCl - H_2SO_4. Pt recovered by filtration.

(ii) Solution of Pt in aqua regia, filtration of solution with reprecipitation of Pt with hydrazine hydrate.

(iii) Solution of Al_2O_3 in 50% NaOH at 250°C under pressure. Pt recovered by filtration.

(iv) Volatization of Pt in a stream of $AlCl_3$ at 300°C.

(v) Volatization of Pt as a carbonyl halide using phosgene.

B3.7.1 Examination of separation methods

Uranyl fluoride was readily removed from the reaction mixture by washing it with water. The solution of UF_4 was examined by the methods given in Table B9 using mixtures of catalyst and UF_4. These methods were tested for completeness of solution of UF_4, dissolution of support and dissolution of platinum. Two different catalysts (numbers 3 and 4 of Table B1, were studied and Table B9 summarises the results. Experiments conducted on the Merck γ-alumina based catalyst showed that only a small percentage of the alumina was lost during the UF_4 dissolution stage whereas using the H151 alumina gel supported catalyst almost complete solution of the support occurred.

Results indicated that aluminium nitrate or H_2SO_4/H_2O_2 were the most effective reagents for dissolving UF_4. The latter method gave a very vigorous reaction in the presence of a platinum catalyst and was discarded in favour of the boiling aluminium nitrate method. Methods for platinum recovery were not tested in detail. For our purposes the conventional aqua regia solution technique proved adequate. The following method is recommended for the separation of UF_4 and uranyl fluoride and the recovery of platinum and was applied to the separation of these components from the mixture used in small scale fluidised bed reactor tests. The samples analysed had the approximate composition 160 g UO_2F_2, 12 g UF_4, 2 g catalyst. The recovery of platinum on duplicate runs was 100.4% and 100.9%.

TABLE B9

METHODS OF UF_4 DISSOLUTION

Catalyst	Catalyst Weight (g)	UF_4 Weight (g)	UF_4 Solution Method	Dissolution Time (Mins)	% Catalyst by weight recovered	Pt in filtrate	% Pt Recovery (as metal)
5% Pt on Merck γ-Al_2O_3 -100 + 200 BSS agglomerated	0.2	2.0	4 ml conc H_2SO_4, 20 ml H_2O, 0.2 ml H_2O_2	6	90.0	Nil	98.2
"	0.2	2.0	3 g $Al(NO_3)_3$. $6H_2O$ + 20 ml H_2O	8	95.8	Nil	97.5
"	0.2	2.0	25% H_3PO_4 in water	13	72.8	Nil	Not tested
"	0.2	2.0	4 ml HNO_3(conc) + 20 ml H_2O + 0.2 ml H_2O_2	9	90.2	Nil	Not tested
"	0.2	2.0	6 ml $HClO_4$ (conc) + 20 ml HNO_3 (conc)	5	88.5	Nil	Not tested
"	0.2	2.0	4 g NaOH in H_2O (20 ml) then acidify with conc HCl to dissolve ppt.	10	85.0	Nil	95.3
5% Pt on H151 Alumina gel -100 + 200 BSS	0.2	2.0	3 g $Al(NO_3)_3$ + 20 ml H_2O	8	4.48	Nil	Not tested
"	0.2	2.0	4 g NaOH in H_2O (20 ml) then acidify with conc HCl to dissolve ppt.	10	~20% (Pt too fine to recover)	Nil	Not tested

Method :

The sample from the reactor is added with stirring to water (200 ml). The solution is filtered, washed with water and the washings combined with the filtrate. This solution will then contain all the uranyl fluoride. The residue is added to a boiling solution of aluminium nitrate (20 g) in water (100 ml) and the mixture boiled for 15 minutes. The solution is filtered and washed with water. The washings will contain all the UF_4 as uranyl nitrate. The residue is dissolved in boiling aqua regia (20 ml). Additional concentrated HCl is added and the mixture fumed to remove all nitric acid.

The application of this method to the separation of larger quantities of components necessitates an appropriate scaling up of solution volumes. For satisfactory dissolution, the weight of aluminium nitrate used must be approximately twice the weight of UF_4 present.

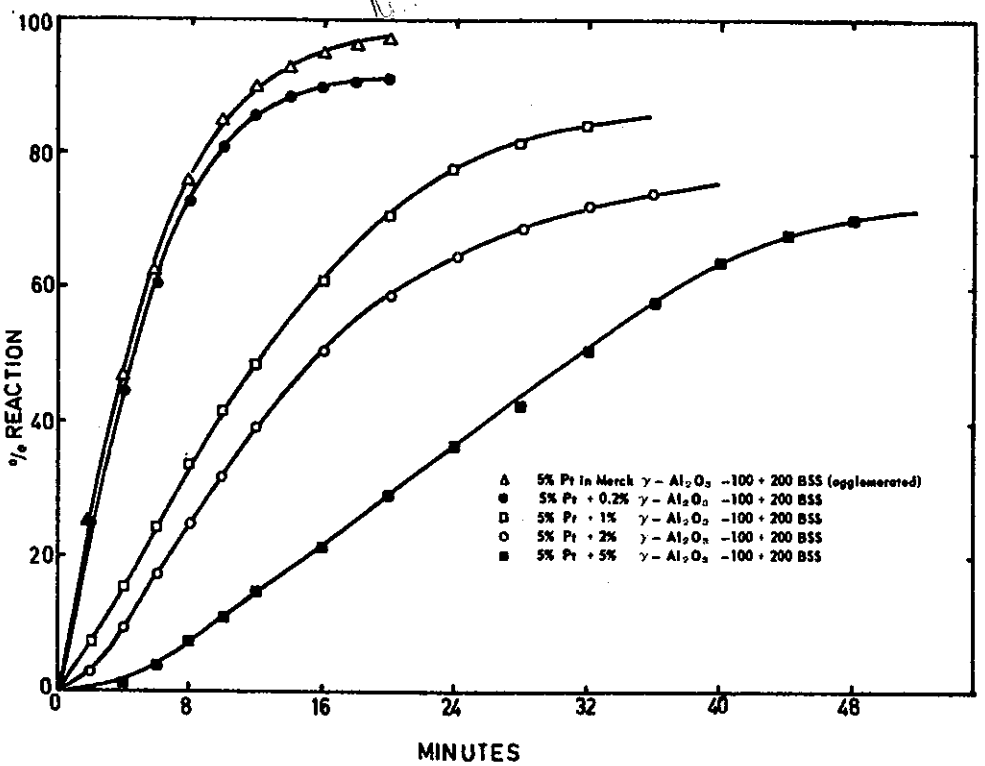


FIGURE B1. EFFECT OF UNCOVERED ALUMINA ON CATALYTIC REACTION OF UF_4 WITH O_2

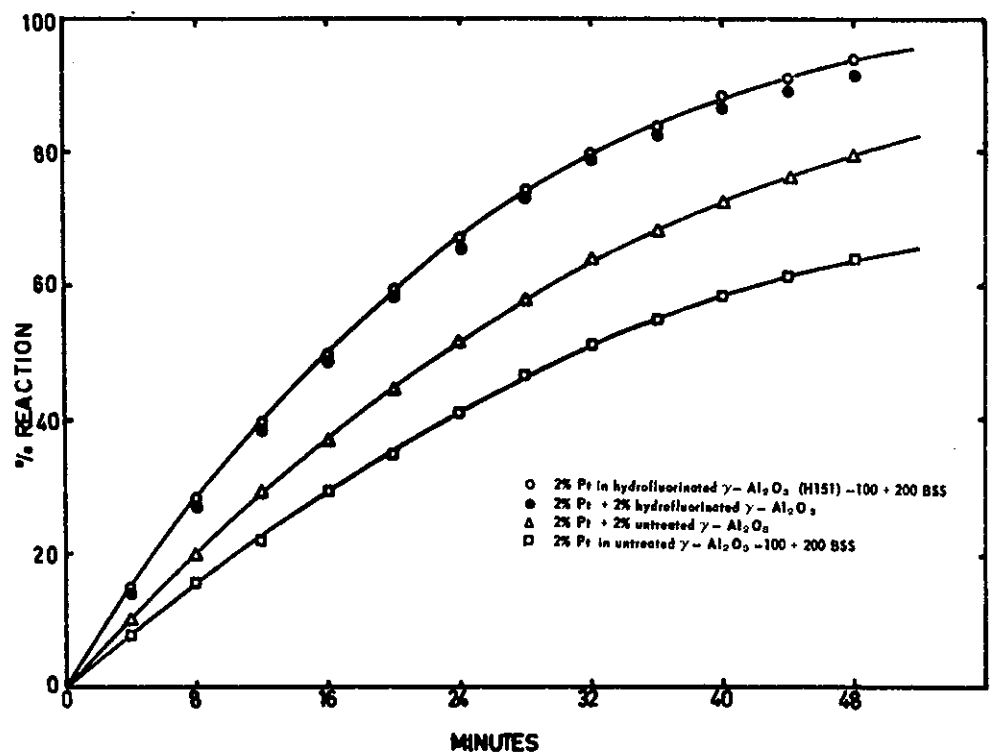


FIGURE B2. EFFECT OF ALUMINA HYDROFLUORINATION

SECTION C

LABORATORY-SCALE STUDIES IN A FLUIDISED BED REACTOR

C1. INTRODUCTION

The conventional Fluorox reaction was investigated in 0.1 m diameter fluidised bed reactors at Oak Ridge National Laboratory (Scott et al. 1960) and by the South African Atomic Energy Commission (Geertsma et al. 1965). Both groups achieved satisfactory rates of reaction at 800 to 850°C, and Scott et al. (1960) demonstrated that the reaction proceeded at a rate comparable to that measured in a thermobalance (Ferris 1959). However, the high temperatures used resulted in serious corrosion of the Inconel fluidised bed reactors, and this was a significant factor in discouraging commercial exploitation of the process.

The results from experiments in a thermobalance (Section A of this report) show that the rate of the catalysed reaction at about 600°C was comparable to that of the uncatalysed reaction at about 800°C, and this suggests that an improved Fluorox process may be developed which is free from serious corrosion problems.

An important initial step in the development programme was the selection and demonstration of a gas-solid reactor which was suited to the special requirements of the catalysed reaction. The fluidised bed reactor was chosen for the following reasons :

(a) the good temperature control available should minimise local temperature excursions which could negate the advantage of low temperature for the catalysed reaction;

(b) the considerable mobility of particles normally found in fluidised beds should give each catalyst particle a much greater sphere of influence than in a fixed bed;

and (c) the techniques of fluidisation are well-known and amenable to scale-up.

However, there are inevitable uncertainties and these relate principally to (b) above. Firstly, it is known that fairly minor differences in particle density result in segregation in fluidised beds (Rowe et al. 1972), and in the worst case this behaviour could effectively isolate the UF_4 from the catalyst. On the other hand it may be possible to exploit the segregation to advantage; this point is discussed more fully in Section D. Secondly, the use of a mobile rather than a fixed bed may interfere in some unexpected way with the mechanism of the reaction, which is thought to rely on the formation of active oxygen species (Section A).

The work covered in this section was a preliminary experimental study carried out in a small (42 mm diameter) fluidised bed reactor to investigate

the viability of the catalysed Fluorox process in fluidised bed reactors. In particular, we wanted to compare the rate of the catalysed reaction in this type of equipment with that observed in a thermobalance (Section A).

C2. EXPERIMENTAL

C2.1 Feed Materials

The UF_4 and UO_2F_2 powders used in the fluidised bed studies were derived from UO_3 produced by the calcination of ammonium diuranate, and their method of preparation is described in Section A. Several 150 g batches of powder were blended to form homogeneous batches of each material sufficiently large for several fluidised bed experiments, and then stored in a desiccator until required.

The size of the UF_4 and UO_2F_2 powders was -60 + 120 B.S.S. in all experiments and the typical pour and tap densities were 2.0 g cm^{-3} and 2.2 g cm^{-3} respectively for the UF_4, and 1.1 g cm^{-3} and 1.3 g cm^{-3} respectively for the UO_2F_2. The uranium content of both the UF_4 and UO_2F_2 varied from stoichiometric by ± 3%, possibly because of incomplete conversion or impurities, such as moisture, in the powder.

Number 4 catalyst (Table B1) which was used in all experiments contained 5 wt.% platinum support on -60 + 100 BSS alumina powder. The alumina support had a pour density of 0.9 g cm^{-3} and a tap density of 1.1 g cm^{-3}. In one experiment 6 mm alumina spheres (Alcoa H151) coated with 0.5 wt. % platinum were used as the catalyst.

C2.2 Apparatus

The equipment used for carrying out most of the experiments is shown schematically in Figure C1. The fluidising gases, either oxygen (medical dry breathing) or nitrogen (oxygen-free high purity), were metered by flowmeters and then passed through two copper driers (40 mm diameter, 0.30 m long) containing silica gel and activated molecular sieves (Type 5A). The dried gases had typical moisture contents of about 5 ppm and 20 ppm for the oxygen and nitrogen respectively. The copper preheater (36 mm diameter, 0.3 m long) was packed with fused silica powder (~ 10 BSS) to aid heat transfer, and was mounted in a manually controlled furnace of 2 kW capacity. A similar furnace controlled to ± 2°C by a three term controller was used to heat the reactor. The reactor was made of 42 mm diameter nickel pipe, 0.5 m long with the bed support plate (gas distributor) and off-gas filter made of nickel Rigimesh. An inclined side-arm located near the top of the reactor allowed powders to be loaded into the reactor while it was hot.

The cold trap used for collecting the UF_6 consisted of a copper vessel (70 mm diameter, 0.25 m long), immersed in a Dewar flask containing a slurry of dry ice and trichloroethylene, which produced a cold bath temperature of about -80°C. Bellows-sealed valves with 25 mm diameter ports were fitted to the inlet and outlet branches (25 mm inside diameter); the inlet branch extended to the bottom of the vessel.

A chemical trap (36 mm diameter, 0.3 m long) packed with 0.25 kg sodium fluoride pellets (3 mm diameter) was placed after the cold trap to remove any residual UF_6 from the off-gases. The chemical trap was wrapped with heating tapes, and manually controlled to about 100°C.

Copper piping was used after the preheater, and was connected with stainless steel compression fittings which enabled the vessels to be readily disconnected and removed for weighing at the end of an experimental run. The piping between the reactor and the cold trap was trace heated by heating tapes to about 100°C. Reinforced rubber tubing was used in preference to polyvinylchloride before the preheater to eliminate ingress of moisture into the process gases.

An electrolytic moisture meter using a cell coated with phosphorus pentoxide was incorporated into the rig to monitor the inlet gases continuously.

C2.3 Procedure

All runs were carried out batch-wise and, with one exception, the feed UF_4 was diluted with UO_2F_2 to minimise the tendency of sintering and the formation of intermediate fluorides, as suggested by the experinece of the Oak Ridge National Laboratory workers (Scott et al. 1960).

Prior to the commencement of a run the oxygen and nitrogen were purged through the driers and the preheater for up to 48 hours, until the moisture content of the gases fell to less than 20 ppm. To minimise reaction of UF_6 with the walls of the reactor, cold trap or chemical trap (thus lowering the yield of UF_6) these vessels were fluorinated with elemental fluorine before each run. This was achieved by heating the vessels to approximately 150°C and then pressurising with fluorine at 100 kPa. As well as passivating the inner surfaces of the vessels the prefluorination served to remove any water from the vessels by converting it to hydrofluoric acid.

Preliminary tests showed that UO_2F_2 absorbed moisture rapidly (about 3.5 wt. % per hour at room temperature), but this was readily released at 120°C; therefore the uranium compounds were dried overnight in a vacuum oven at 160°C immediately before use. A weighed quantity (typically 160 g) of UO_2F_2 was loaded into the reactor at room temperature while a small flow of dry nitrogen

was maintained. The dryness of the UO_2F_2 was further ensured by heating it to 400°C in the reactor and then applying a vacuum for about half an hour. The UF_4 (typically 40 g) and catalyst were then introduced into the reactor through the inclined side-arm and the powder mixture was heated rapidly to the reaction temperature while being fluidised by 27 cm^3s^{-1} of dry nitrogen. At the desired reaction temperature the nitrogen was replaced by oxygen (27 cm^3s^{-1}). A typical temperature programme is shown in Figure C2. During the reaction the top of the reactor was periodically tapped to encourage powder adhering to the underside of the off-gas filter to fall back into the bed. At the conclusion of the reaction time oxygen was replaced by nitrogen as the fluidising gas and the reactor and preheater were allowed to cool.

The reactor cold trap and chemical trap were weighed separately before and after the run. Any UF_6 collected in the cold trap was transferred to a Kel F tube by sublimation under vacuum, for weighing and inspection. The contents of the reactor were analysed by the method described in Section B3.7.1 to determine the quantities of UF_4 and UO_2F_2 present at the end of the run. This analysis was not able to distinguish the quantity of UF_5 present as it reverted to UF_4 and UO_2F_2 when contacted with water.

C3. RESULTS AND DISCUSSION

C3.1 Mixing of Components in the Fluidised Bed

An important consideration in this work was the homogeneity of the fluidised bed. Thus preliminary experiments were carried out at room temperature in a 42 mm diameter silica fluidised bed reactor to determine how well the different particle types to be used in the Fluorox process would mix when fluidised.

The fluidisation of 50/50 mixtures of UF_4 and UO_2F_2, and 90/10 mixtures of UF_4 and the catalyst support, alumina, were investigated visually using the strong contrast in the colours of the components to assess the degree of segregation. However the beds appeared to be completely homogeneous even after prolonged fluidisation at two to three times the minimum fluidisation velocity.

The mixing of alumina and UO_2F_2 could not be observed because they were both a light colour. Instead, a 90/10 mixture of UO_2F_2 and alumina was fluidised for half an hour and then sectioned horizontally by a vacuum suction probe into ten portions which were analysed by dissolving the UO_2F_2 in water and weighing the dry alumina residue. The concentration of alumina in each section was found to be approximately the same.

Although fluidisation of a three component mixture was not investigated it was assumed that since a combination of any two components mixed well then a mixture of all three would be homogeneous when fluidised together.

TABLE C1

SUMMARY OF EXPERIMENTS TO DETERMINE RATE OF REACTION AT 600°C AND 650°C

REACTION CONDITIONS			FEED MATERIALS					RESULTS						
Temp: (°C)	Oxygen Flow Rate ($cm^3\ s^{-1}$)	Duration of Reaction (h)	UF_4 (g)	Surface area of UF_4 ($m^2\ g^{-1}$)	UO_2F_2 (g)	Catalyst (g)	Total U in feed (g)	Loss in Weight of reactor + contents (g)	UF_6 trapped in cold trap (g)	U in residue soluble in H_2O (g)	U as UF_4 in residue (g)	U balance (a) %	UF_6 (b) yield %	UF_4 (c) conversion %
600	27	0.25	39.2	1.9	160	4.0	156.7	4.2	5.0	137.0	8.9	95.8	22.1	70.9
600	27	0.5	40	1.9	160	4.0	157.4	6.5	6.0	146.0	2.1	96.6	26.0	96.6
600	27	1.0	40	1.9	160	4.0	157.4	9.0	7.0	127.6	1.5	86.5	30.3	95.4
650	27	0.25	40	1.25	160	4.0	158.0	1.0	1.0	132.6	13.1	93.1	4.5	58.2
650	27	0.5	43	1.25	157	4.0	158.0	9.0	7.0	147.4	5.8	99.2	29.1	84.4
650	27	0.75	40	1.25	160	4.0	158.0	8.0	9.0	138.1	1.8	93.8	40.2	94.25
650	27	1.0	40	1.25	160	4.0	158.0	10.0	11.0	143.1	3.1	96.8	49.1	89.8

(a) U balance = $\frac{\text{Total uranium analysed at end of experiment}}{\text{Total uranium in feed}} \times 100$

(b) UF_6 yield = $\frac{\text{Weight of } UF_6 \text{ collected}}{\text{theoretical maximum } UF_6 \text{ based on 100\% conversion of } UF_4} \times 100$

(c) UF_4 conversion = $\frac{UF_4 \text{ consumed}}{UF_4 \text{ in feed}}$

C3.2 Rates of Reaction in the Fluidised Bed Reactor

A series of experiments of varying duration were carried out at 600°C and 650°C with a starting mixture containing 20 parts UF_4, 80 parts UO_2F_2 and 2 parts catalyst, as detailed in Table C1. The data for UF_4 conversion for these experiments were combined to give the rate curves shown in Figure C3. The results correspond reasonably closely to a first order dependency with respect to unconverted solid, i.e.

$$\frac{dW}{dt} = -kW \qquad \ldots(14)$$

where W is the amount of unconverted solid, and k is the first order rate constant. This is demonstrated in Figure C4, where the smoothed rate data are plotted as log (UF_4 remaining/UF_4 initial) versus time and give a straight line plot over much of the range. The initial non-linear portion was possibly related to the period required for the oxygen concentration to build up to 100 vol % after changing from nitrogen. It is unlikely that in these studies the nonlinearity was caused by the loss of UF_4 to form UF_5, as was suggested for experiments carried out in the thermobalance (Section A3.1.2). This is because any UF_4 consumed according to the reaction,

$$UF_4 + UF_6 \longrightarrow 2UF_5 \qquad \ldots(15)$$

would have remained in the reactor, and have been analysed as UF_4 when the residue was contacted with water, i.e.

$$2UF_5 + 2H_2O \longrightarrow UF_4 + UO_2F_2 + 4HF \quad . \qquad \ldots(16)$$

The first order rate constants, estimated from Figure C4, were 5.2 h^{-1} and 3.9 h^{-1} for reactions carried out at 600°C and 650°C respectively.

The rate of reaction at 600°C was higher than at 650°C probably because the surface area of the UF_4 used in the runs at 600°C was 1.9 $m^2\ g^{-1}$ while the surface area of the UF_4 used at 650°C was 1.25 $m^2\ g^{-1}$. Ferris (1959) showed previously that the rate of the conventional Fluorox reaction was first order with respect to the surface area of the UF_4 and this trend was also evident for the rates of the catalysed reaction in a thermobalance (Table A5). When normalised for surface area, the rate constants for the catalysed reactions at 600°C and 650°C were 8.7 x 10^{-3} and 9.9 x 10^{-3} mol m^{-2} h^{-1} respectively. Based on these results the activation energy of the catalysed reaction in the fluidised bed reaction was 17.6 kJ mol^{-1}. It should be noted that an estimate of the activation energy using the initial reaction rates gave a similar value.

The measured activation energy in the fluidised bed was considerably lower than the 96.3 kJ mol^{-1} obtained in the thermobalance. This could have been due to either a different rate controlling step pertaining to the fluidised bed

reactions or to inaccuracies in the measurements. The latter is thought to be a more likely explanation. Thus although the activation energies differ by a factor of 5.5 this corresponds to a factor of less than 2 in the ratios of the reaction rates for the two systems. Errors in the activation energy derived from the fluidised bed results could have been due to comparing rate data built up from a series of separate experiments carried out at two temperatures only. Alternatively, the discrepancy could be explained by errors of about ± 30% in the surface area correction, resulting from either inaccurate measurement of surface area, or from differing degrees of sintering due to the different temperature histories followed for experiments in the fluidised bed and the thermobalance. This second point was invalidated when it was shown that at 650°C, in the thermobalance, there was no difference between reaction rates for a standard experiment, and one incorporating a temperature history similar to that followed in the fluidised bed experiments.

C3.2.1 Effect of catalyst concentration

There was a significant effect of catalyst concentration on the rate of reaction (Figure C5), although the incremental improvement in rate for additional amounts of catalyst was found to decrease. This is demonstrated more clearly in Figure C6 where the time for 50% conversion, $t_{½}$, is plotted against catalyst concentration, showing little improvement beyond a catalyst to UF_4 ratio of 10% i.e. the standard starting mixture of UF_4, UO_2F_2 and catalyst in the ratio 20 : 80 : 2. A similar effect was observed in the thermobalance studies (Figure A1), where little improvement was found beyond a catalyst to UF_4 ratio of 1%. It is of interest to note that the standard starting mixture used in the fluidised bed was approximately equivalent to taking an initial batch of pure UF_4 with 1 wt. % catalyst and reacting it to 90% conversion (this point is discussed more fully in C3.2.3). The fact that enhancement of rate levels in both systems at an effective initial catalyst concentration of 1 wt. % is probably fortuitous. However it does suggest that, by using the standard mixture in the fluidised bed experiments, the rate of reaction was not limited by the availability of catalyst particles in close proximity to incompletely converted UF_4 particles.

C3.2.2 Effect of UF_4 concentration

Results from experiments carried out with starting mixtures having different concentrations of UF_4 in the UO_2F_2 showed an apparent decrease in conversion for an increase in initial UF_4 content (Table C2). This effect is thought to be due to either the increased formation of UF_5 or increased sintering and loss of reactivity for a higher concentration of UF_4. The formation of UF_5 is

believed to be more likely, even though the analytical technique used could not determine its presence in the residue. Material frequently observed on the filter at the end of an experiment was a light grey colour, and therefore visually resembling UF_5.

TABLE C2

EFFECT OF INITIAL CONCENTRATION OF UF_4 ON CONVERSION FOR A REACTION PERIOD OF ONE HOUR

	Initial Concentration of UF_4 (%)		
	10	20	100
Temperature (°C)	Conversion (%)	Conversion (%)	Conversion (%)
600	95.4 (a)	-	60.0 (b)
650	93.2 (b)	84.0 (b)	-

NOTE

Catalyst to UF_4 ratio

(a) 10%

(b) 5%

During the batch fluidised bed studies at Oak Ridge National Laboratory (Scott et al. 1960), the formation of intermediate fluorides was a considerable problem, and particularly when the UF_4 concentration in the bed was high. This problem was eliminated in continuous operation by using lower concentrations of UF_4 and by judicious use of a filter blow-back system.

C3.2.3 Comparison with rates of reaction in the thermobalance

Comparison of the rates of reaction in the fluidised bed and the thermobalance has certain limitations which need to be stated at the outset. Firstly, the conversion of UF_4 measured in the thermobalance included material consumed in the formation of UF_5, whereas this was not the case for the fluidised bed experiments, as discussed above. On this basis, lower rates of conversion would be observed in the fluidised bed reactor. Secondly, the standard starting mixture used in the fluidised bed of UF_4, UO_2F_2 and catalyst in the ratio 20 : 80 : 2 parts by weight was approximately equivalent to taking a batch of 180 parts UF_4 with 2 parts catalyst (i.e. approx. 1 wt. %) and reacting it to 90% conversion. The difference between the fluidised bed starting mixture, and that produced by a 90% conversion of pure UF_4, is that in the former the UF_4 component is present as discrete particles whereas in

the latter it forms part of incompletely reacted particles.

TABLE C3

COMPARISON OF RATES IN THE FLUIDISED BED AND THE THERMOBALANCE

	UF_4 surface area ($m^2\ g^{-1}$)	Temperature (^oC)	$t_{\frac{1}{2}}$ (a) (h)
Fluidised Bed	1.25	650	0.20
	1.9	600	0.15
Thermobalance	1.9	640	0.20

(a) $t_{\frac{1}{2}}$ = time taken for 50% of the UF_4 present at the start of the experiment to react.

NOTE

UF_4 : size range - 60 + 120 BSS.

Catalyst : type No. 4 (Table B1) size range -60 + 100 BSS.

Table C3 compares the thermobalance data and the fluidised bed data in terms of the time to 50% conversion, $t_{\frac{1}{2}}$. These data suggest that for the coarse catalyst required for satisfactory fluidisation, i.e. -60 + 100 BSS, the rate in the fluidised bed was faster than that in the thermobalance. However it should be noted that the rate in the thermobalance was almost doubled when using a finer catalyst, -200 + 350 BSS (Table B4).

A further comparison was obtained by reacting a mixture in the thermobalance with the same size range of particles and the same ratio (20 : 80 : 2) of components as used in the fluidised bed experiments. The reaction proceeded very slowly. Only when a fine catalyst (-100 +200 BSS) was used did the rate in the thermobalance approximate that achieved in the fluidised bed with a catalyst of size -60 +100 BSS. By using the same weight of a finer catalyst the number of catalyst particles was increased approximately eightfold thereby improving the probability of close proximity or contact of UF_4 and catalyst particles.

The improved rates of reaction obtained in the fluidised bed confirm the view that mobility of the particles increases the sphere of influence of the catalyst, and that the fluidised bed reactor is well suited to the special requirements of the catalysed Fluorox reaction.

C3.2.2 Comparison with rates of the uncatalysed reaction in fluidised beds

In a single uncatalysed experiment, a conversion of 35% was achieved in one hour at 650°C (Figure C5). The same conversion was obtained in 0.14 hours for the standard catalysed mixture (20 : 80 : 2), which was an increase of about sevenfold in the reaction rate. Assuming the activation energy of 96.3 kJ mol^{-1} determined in the thermobalance to apply, a temperature of about 820°C would be required for the rate of the uncatalysed reaction to equal that of the catalyst reaction at 650°C.

It was shown earlier that the rate data for the fluidised bed experiments were reasonably correlated by a first order plot (Figure C4). As a result, it was possible to estimate the rate constant from a knowledge of $t_{\frac{1}{2}}$, thus,

$$k = 0.693/(t_{\frac{1}{2}}) \quad . \qquad \ldots(17)$$

However it was found that the rate constant calculated in this way was about 10% lower than that estimated from the first order plot (Figure C4). If it is assumed that the rate was proportional to the surface area, a rate constant which is independent of surface area can be calculated from,

$$k' = k/(\text{surface area of } UF_4 \text{ in } m^2\ mol^{-1}) \qquad \ldots(18)$$

TABLE C4

COMPARISON OF CATALYSED AND UNCATALYSED REACTION RATES FOR BATCH EXPERIMENTS IN FLUIDISED BED REACTORS

	$k^{(a)}$ (h^{-1})			$k' \times 10^3$ (b) (mol m^{-2} h^{-1})		
Temp:	This work		ORNL (Scott et al. 1960)	This work		ORNL (Scott et al. 1960)
(°C)	Catalysed	Uncatalysed	Uncatalysed	Catalysed	Uncatalysed	Uncatalysed
600	4.6	-	0.01	7.7	-	0.4
650	3.5	0.49	0.03	8.9	1.25	1.2

(a) $k = 0.693/(t_{\frac{1}{2}}$ in hours)

(b) $k' = k/(\text{surface area in } m^2\ mol^{-1})$

Both k and k′ are presented in Table C4 for temperatures of 600 and 650°C, with and without catalyst. These data substantiate the sevenfold increase in reaction rate obtained in this work. When compared with earlier data obtained from batch experiments in a fluidised bed (Scott et al. 1960) the

values of k´ at 650°C for the uncatalysed reaction were in good agreement. Moreover at 600°C the rate constant (k´) for the catalysed reaction obtained in this work was almost a factor of twenty greater than that achieved in the earlier studies. These results demonstrate the dramatic improvements obtainable in the rate of the Fluorox reaction by the addition of a small quantity of catalyst, and confirm the suitability of the fluidised bed reactor for this process.

C3.3 Yield of UF_6 from the Fluidised Bed Reactor

In all experiments the yield of UF_6 (defined as the ratio of the weight of UF_6 collected to the theoretical maximum weight for 100% conversion) was lower than the conversion of UF_4; typical results are given in Table C1 and Figure C7.

Overall mass balances were close to 100% and it is believed that all the UF_6 which left the reactor was collected in the cold trap; no UF_6 was detected in the chemical trap. Thus it appears that the unaccounted UF_6 did not leave the reactor, and this can be attributed to a number of different factors.

Firstly, it is possible that some UF_6 was consumed in the formation of intermediate fluorides, such as UF_5. On the basis of equations (15) and (16) the maximum amount of UF_6 which could have been consumed in the UF_5 side reaction was equivalent to the amount of unreacted UF_4 in the residue. However even if all the UF_4 detected during the analysis was derived from UF_5 it was insufficient, in most cases, to explain the discrepancy between yield and conversion.

Secondly, there are other side reactions which could have consumed UF_6, including reactions with the walls of the reactor, with moisture, or with impurity uranium oxides in the UF_4 and UO_2F_2. However the possibility of reaction with the walls of the reactor was largely eliminated by prefluorination and stringent measures were taken at all stages to minimise the moisture in the system. These procedures included drying all the components of a reaction mixture before an experiment. The amount of impurity oxides was believed to be small and would not have consumed a significant quantity of UF_6.

A third possibility relates to the observation that the amount of catalyst used had a significant effect on the UF_6 yield (Table C5). With a catalyst to UF_4 ratio of 5% (i.e. a 20 : 80 : 1 mixture), yields up to 67% were obtained, which represented UF_6 recoveries of 60 to 80%. For the standard mixtures, with a catalyst to UF_4 ratio of 10%, yields up to 49% were obtained, which represented UF_6 recoveries of 26 to 55%. With a catalyst to UF_4 ratio of 25% no UF_6

was collected. It is therefore possible that the UF_6 was absorbed by the alumina support of the catalyst, and this hypothesis is corroborated by the results shown in Figure B1. In practice, it is probable that all three factors discussed above contributed to the consumption of UF_6 in the reactor, although it is believed that the absorption onto alumina was the most significant.

TABLE C5

EFFECT OF CATALYST CONCENTRATION ON

RECOVERY OF UF_6

(REACTION AT 650°C)

Catalyst to UF_4 ratio (%)	Duration of reaction (h)	UF_4 conversion (a) (%)	UF_6 yield (b) (%)	UF_6 recovery (c) (%)
5	0.5	57.7	40.0	69
5	0.5	52.6	31.8	60
5	1.0	93.2	63.5	68
5	1.0	84.0	67.0	80
10	0.5	84.4	29.1	34
10	0.5	94.7	25.3	26
10	1.0	89.8	49.1	55
25	0.25	71.4	0	0

(a) UF_4 conversion $= \dfrac{UF_4 \text{ consumed}}{UF_4 \text{ in feed}}$

(b) UF_6 yield $= \dfrac{\text{Weight of } UF_6 \text{ collected}}{\text{Theoretical maximum } UF_6 \text{ based on 100\% conversion of } UF_4} \times 100$

(c) UF_6 recovery $= \dfrac{UF_6 \text{ collected}}{UF_6 \text{ expected based on } UF_4 \text{ consumed}} = \dfrac{UF_6 \text{ yield}}{UF_4 \text{ conversion}}$

These batch experiments do not indicate whether the catalyst would lose activity if the alumina support became saturated with UF_6, as would probably occur with continuous operation, particularly if a fixed catalyst were used (C3.4). However in the catalyst recycle experiments carried out in thermo-balance (A3.1.3) saturation would have occurred, particularly as the initial catalyst to UF_4 ratio was 1%. These tests showed no significant loss of catalyst activity. However, if UF_6 absorption is a problem it should be noted that it can be reduced by pre-hydrofluorination of the catalyst (B3.3) and furtherfore alternative supports are available which do not absorb UF_6 (B3.4).

Finally, the results do not exclude the possibility that some of the UF_4 was consumed in the formation of an undetected fluoride or oxyfluoride of uranium, the production of which was enhanced by the presence of the catalyst. However, tests carried out in separate experiments (A3.1.9) failed to detect the formation of any unusual oxyfluoride.

C3.4 Use of Non-fluidised Catalyst Spheres

There are obvious advantages for a continuous process in which the catalyst is immobile, i.e. each reactor has a fixed inventory of catalyst which is not required to pass on to the next stage. To examine the efficacy of a segregated bed an experiment was carried out with a non-fluidised catalyst in the form of 6 mm diameter alumina spheres (Alcoa H151) coated with 0.5 wt. % platinum. A sufficient number of spheres were used to cover the bed support plate with a single layer, giving a UF_4 : UO_2F_2 : catalyst ratio of 20 : 80 : 6.

A conversion of 64.5% was obtained in one hour at 650°C, corresponding to a two-fold increase in reaction rate compared with the uncatalysed reaction. This enhancement of the reaction rate was probably due to the recirculation of UF_4 particles, bringing them to the bottom of the bed and in close proximity to the static catalyst, rather than the active species travelling any appreciable distance in the bed.

Whilst the enhancement achieved in this experiment was not great it did demonstrate the possibility of using a segregated catalyst. It is most probable that the optimum conditions were not used and that further improvement could be obtained with a different form and/or arrangement of catalyst.

C4. CONCLUSIONS

These preliminary studies have indicated that,

(a) the catalysed Fluorox reaction proceeds at a rapid rate in a fluidised bed at temperatures of 600 to 650°C,

(b) for similar conditions the rate in the fluidised bed is faster than in the thermobalance,

(c) satisfactory rates may be obtainable in a fluidised bed using a segregated catalyst.

Further investigations are required at a larger scale and with continuous operation, to demonstrate the viability of the catalysed Fluorox process in fluidised bed equipment.

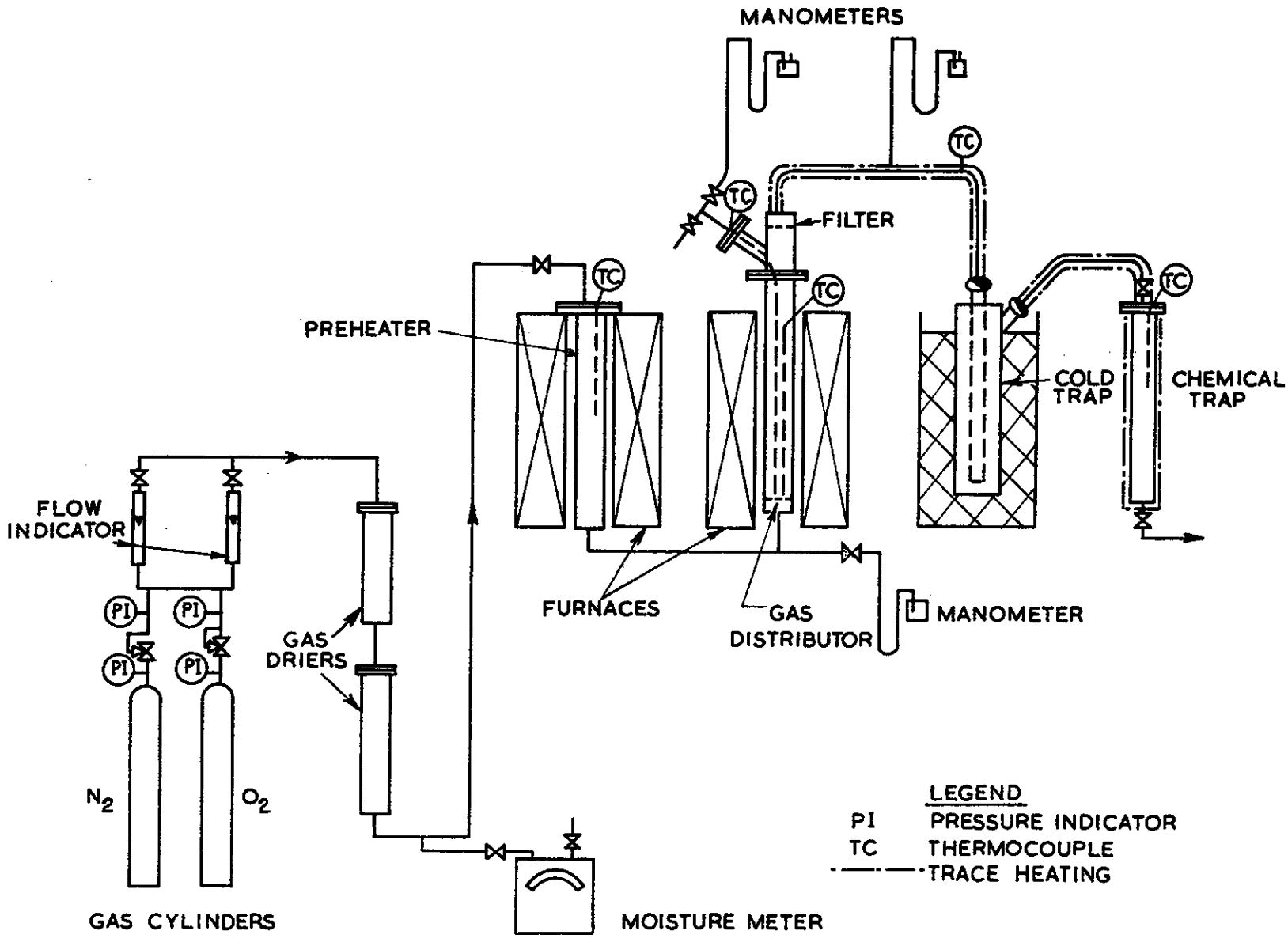


FIGURE C1. LABORATORY-SCALE FLUIDISED BED EQUIPMENT

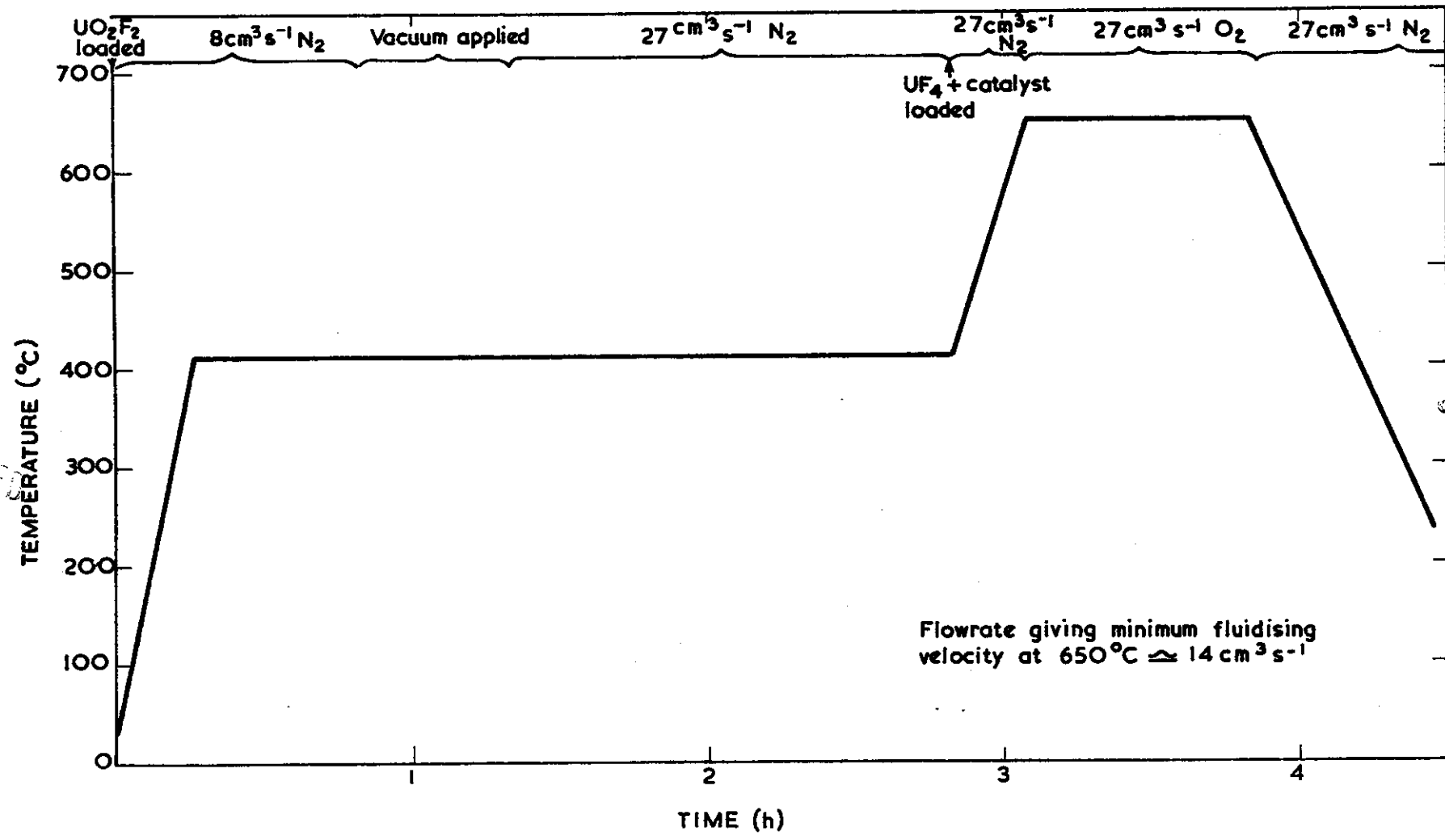


FIGURE C2. A TYPICAL TEMPERATURE PROGRAMME AND OPERATING PROCEDURE

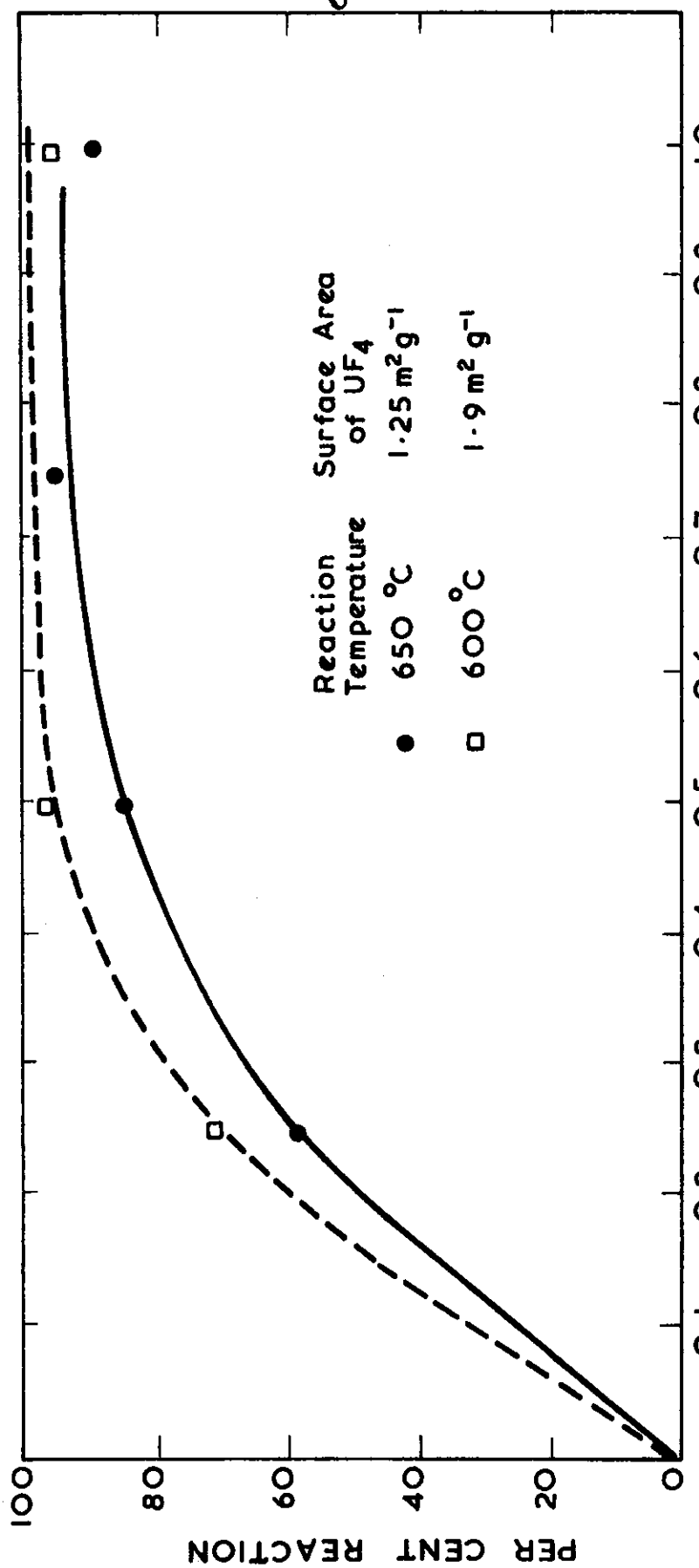


FIGURE C3. RATES OF REACTION IN THE FLUIDISED BED REACTOR

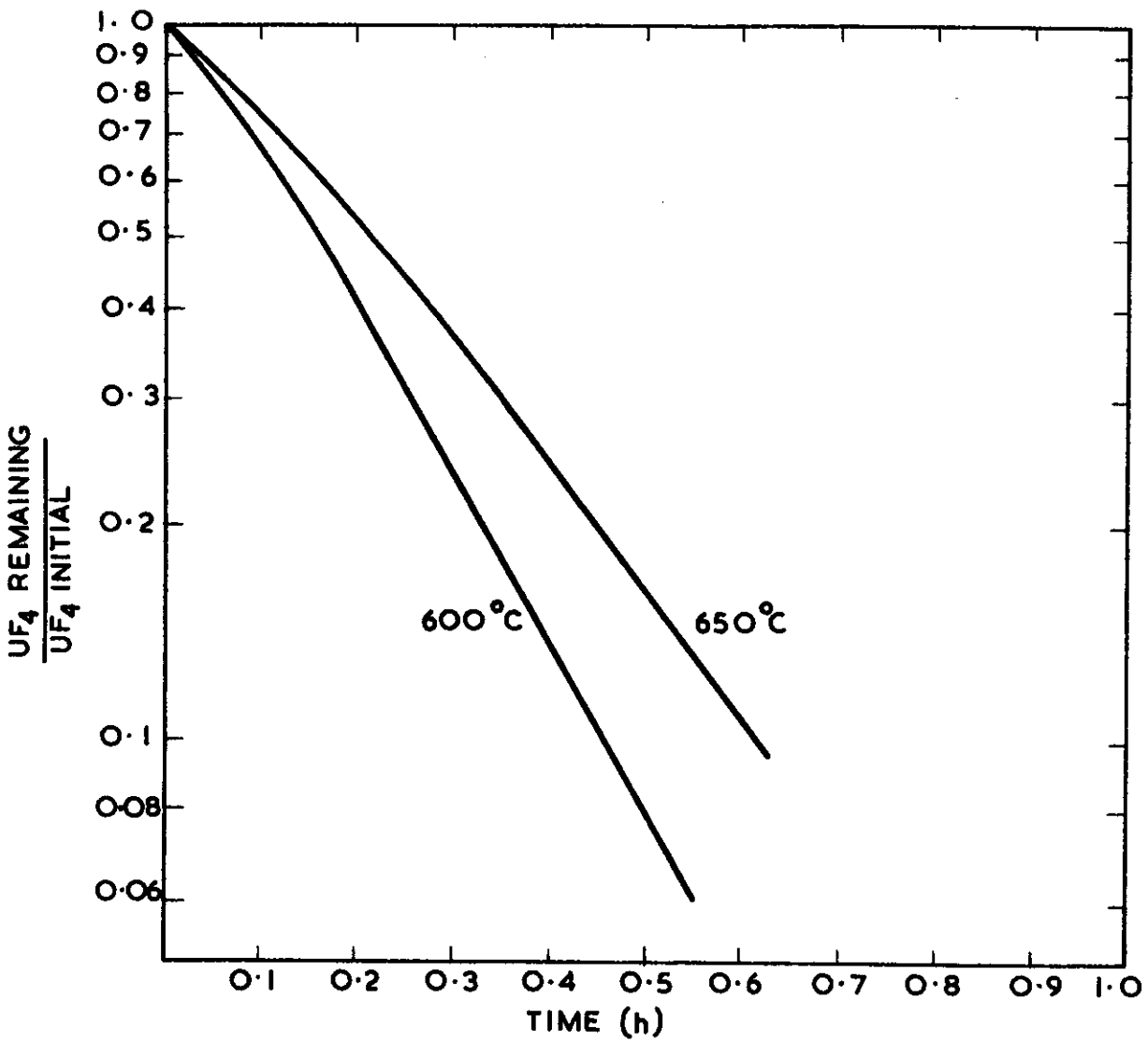


FIGURE C4. SMOOTHED RATE DATA PLOTTED ACCORDING TO FIRST ORDER KINETICS

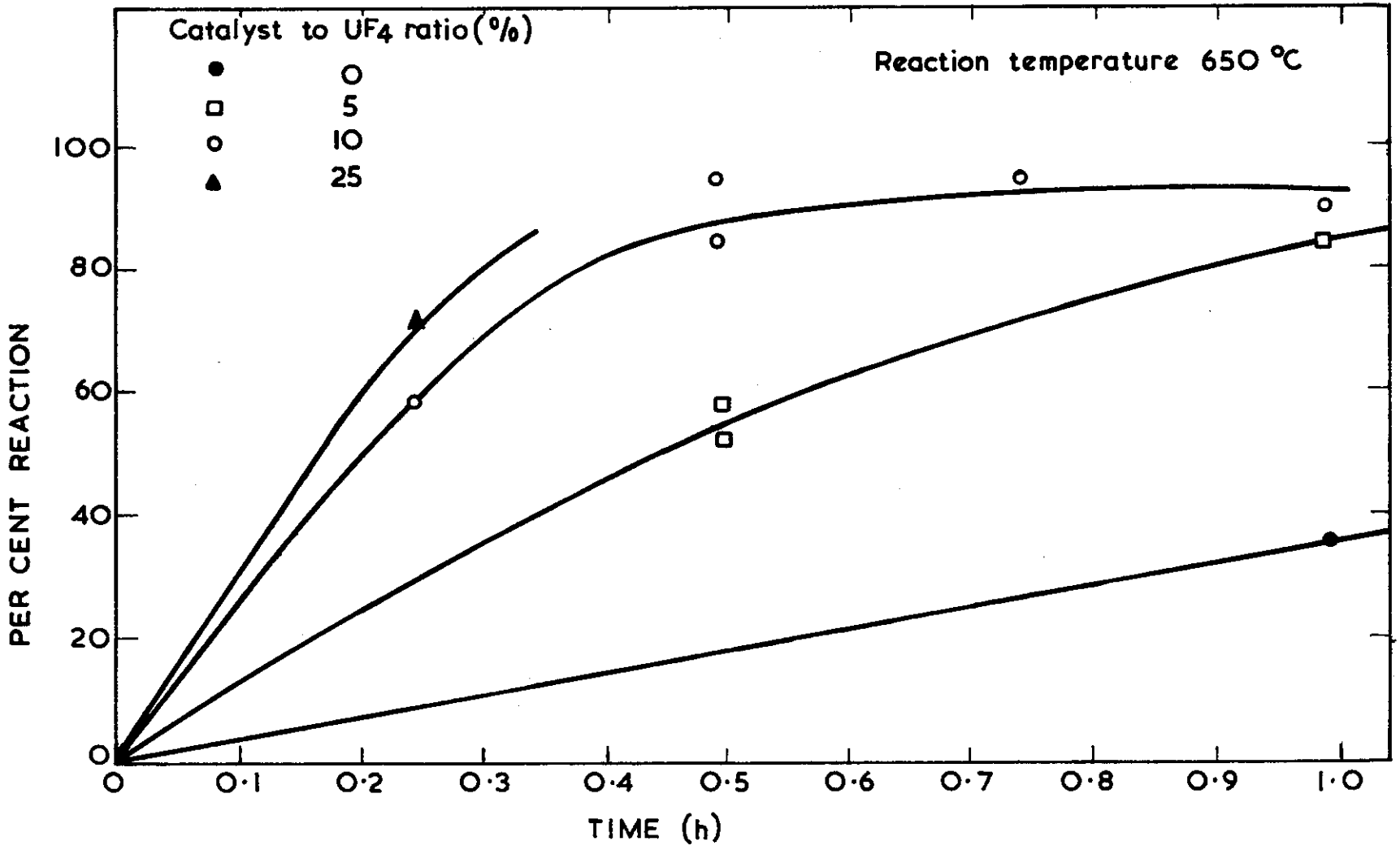


FIGURE C5. EFFECT OF CATALYST CONCENTRATION ON UF_4 CONVERSION

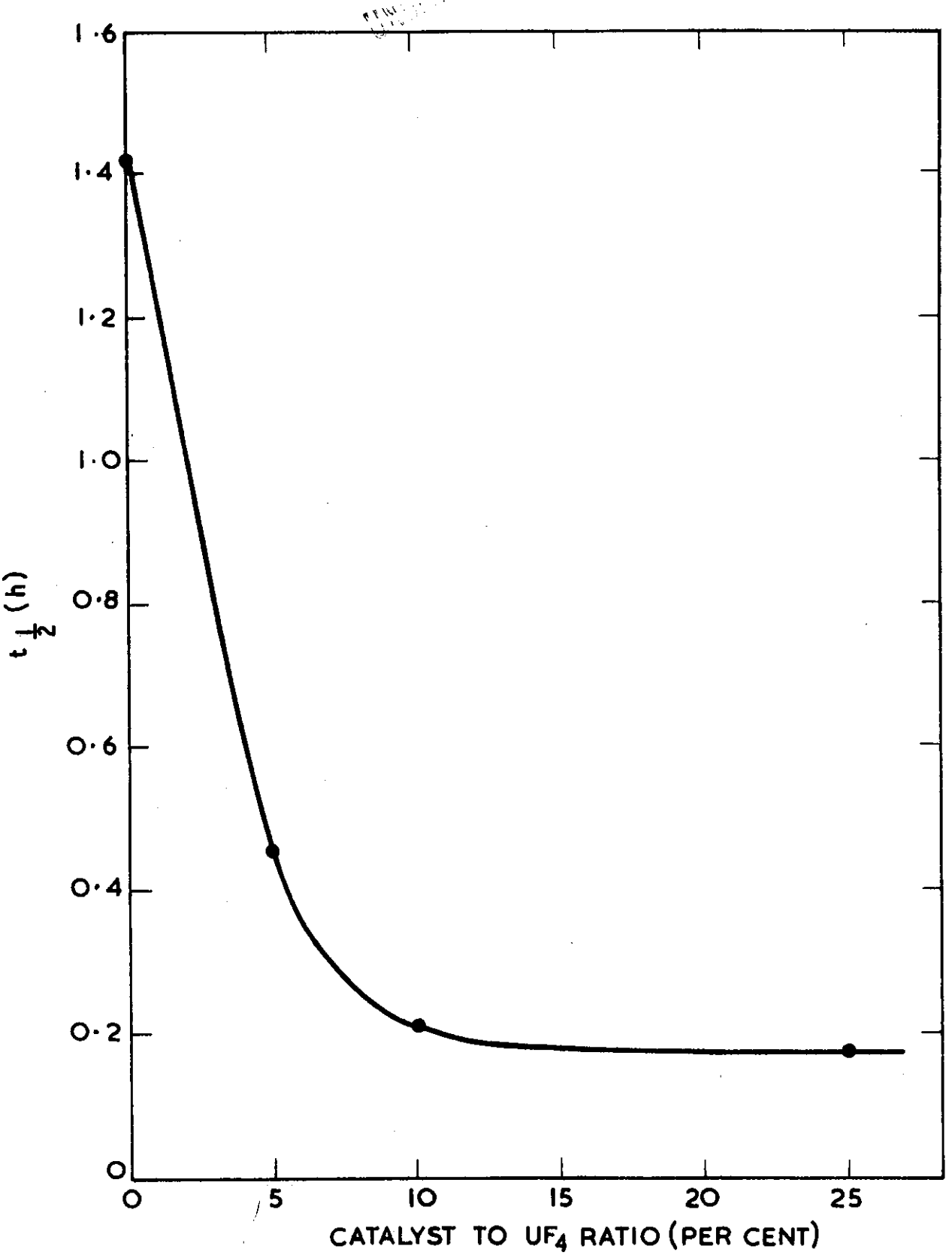


FIGURE C6. EFFECT OF CATALYST CONCENTRATION ON $t_{1/2}$ FOR REACTION AT 650°C

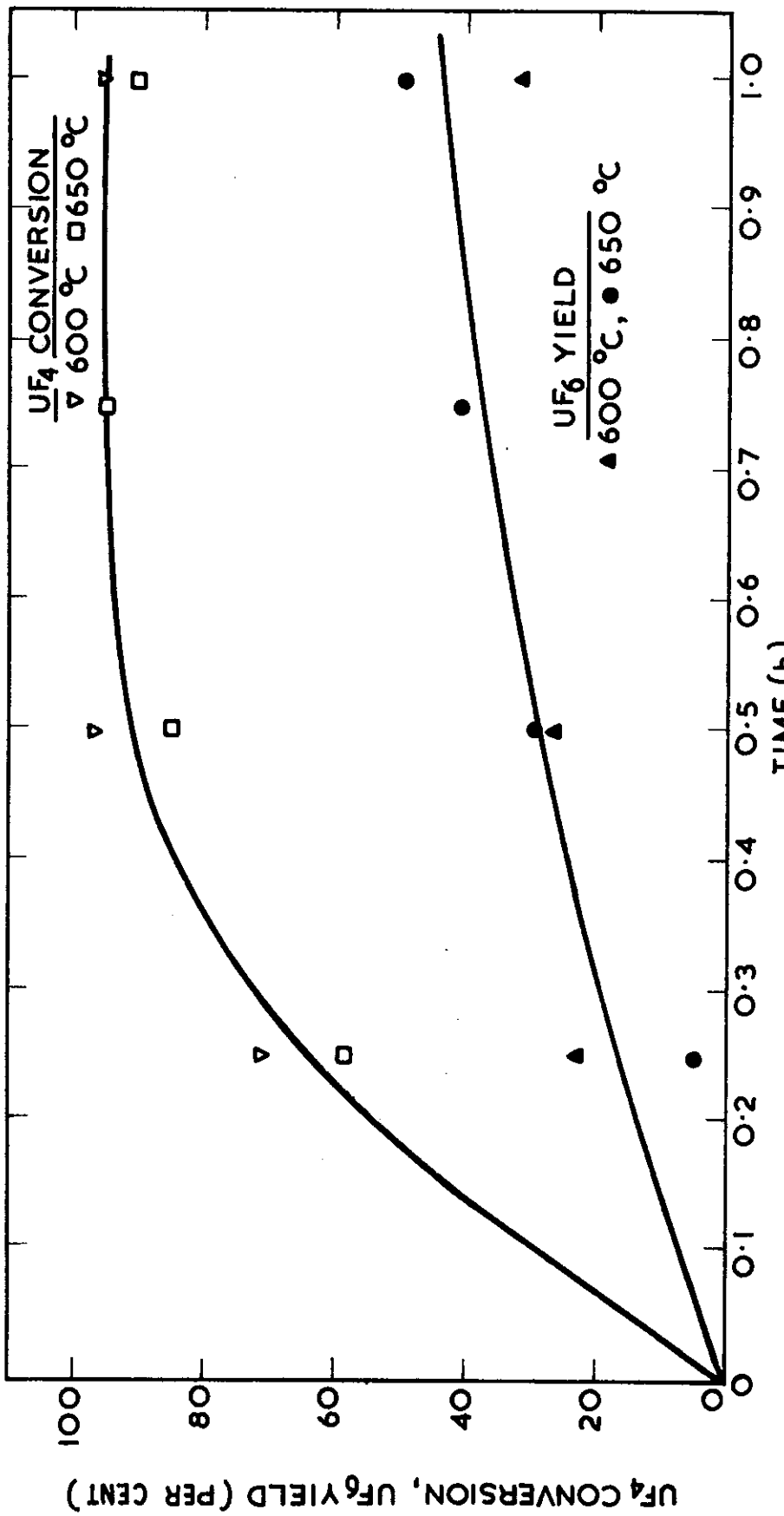


FIGURE C7. TYPICAL RESULTS FOR UF_4 CONVERSION AND UF_6 YIELD
(UF_4:UO_2F_2:CATALYST RATIO 20:80:2)

SECTION D

DISCUSSION OF THE CATALYSED FLUOROX PROCESS FOR THE PRODUCTION OF UF_6

The incentive for the development of a process for the production of UF_6 based on the Fluorox reactions lies to a large extent in the elimination of the fluorine plant, which has an estimated capital cost of $3M for a 5,000 tonnes per annum UF_6 plant. In place of the fluorine plant, the Fluorox process requires an additional two (or, as will be discussed below, possibly only one) fluidised bed reactors as well as a somewhat more complex conversion plant in which at least one-half of the feed has to be recycled. Nevertheless, economic assessments of the process in South Africa and in the U.S. have shown that the uncatalysed process does have an economic advantage over the conventional fluorination process, with respect to both capital and operating costs. This conclusion has been confirmed by a preliminary cost analysis of the catalysed Fluorox process carried out by the Chemical Engineering Section at the A.A.E.C. (Fane, A.G., 1972, private communication). Although these savings are not large, they are likely to be of some significance in the competitive marketing situation likely to persist for some years (Silver and Richmond, 1972). While it is unlikely that the Fluorox process will replace existing conventional plants, it is possible that the catalysed Fluorox process, once proven on a pilot plant scale, could be considered for new UF_6 production facilities, particularly for those to be situated in countries which do not have an established fluorine generating capacity.

The two pilot plant studies of the conventional Fluorox process have indicated two major problems, the first being a direct result of the very high temperatures required for the oxidation reaction which lead to the excessive corrosion of the Inconel reactor and to the sintering of the UF_6 feed. The second problem, which was particularly severe in the South African experience, is the formation of the intermediate uranium fluorides UF_5, U_2F_9 and U_4F_{17} according to the reaction sequence

$$UF_4 + UF_6 \rightarrow 2UF_5 \qquad \ldots(19)$$

$$UF_5 + UF_4 \rightarrow U_2F_9 \qquad \ldots(20)$$

$$U_2F_9 + 2UF_4 \rightarrow U_4F_{17}. \qquad \ldots(21)$$

These compounds are predicted on thermodynamic grounds to decompose to UF_4 and UF_6 in the temperature range of 500 to 800°C (Ferris, 1950), but the South African study showed that these intermediates persisted in the fluidised bed, eventually forming a liquid phase which prevented the fluidising of the bed, and further development of the process appears to have been abandoned largely because of the inability to overcome this problem. It should be noted, however, that this problem did not arise in the Oak Ridge study and, although UF_5 was observed to be formed in the bed and to collect on the exit filters of

the oxidation reactor, a programme of frequent 'blow-backs' successfully returned the accumulated UF_5 to the bed where it decomposed to UF_4 and UF_6. The latter study showed that conversion yields in excess of 90 per cent could be obtained over extended periods and at temperatures in the vicinity of 800°C.

The catalysis of the Fluorox reaction and the associated reduction in the operating temperature from 800 to approximately 600°C is expected to greatly reduce the corrosion and sintering problems in the oxidation reactor. However, the effect of the reduction of the operating temperature on the formation and decomposition of the intermediate fluorides is more difficult to evaluate. The present laboratory experiments and the bench-scale fluidised bed studies have clearly shown that UF_5 is formed during the catalysed reaction at temperatures of 600 to 640°C, but these experiments have not yielded any information on the subsequent fate of the UF_5.

A typical flowsheet for the production of UF_6 by the catalysed Fluorox process is illustrated in Figure D1. UF_4, mixed with the appropriate amount of make-up catalyst, is fed directly into the oxidation reactor. The UF_6 formed is condensed, while the unreacted UF_4, the UO_2F_2 and the catalyst are fed into the reduction reactor to be converted to UO_2. The excess hydrogen and the HF formed during the reduction are passed to a HF recovery section, while the UO_2 is converted to UF_4 in the hydrofluorination reactor. The UF_4/catalyst mixture is then passed back to the oxidation reactor. It should be noted that in a conventional UF_6 production plant the hydrofluorination of UO_2 to UF_4 is usually carried out in two fluidised bed reactors, connected in series. This is because the reversibility of the reaction,

$$UO_2 + 4HF \rightleftharpoons UF_4 + 2H_2O \quad , \qquad \ldots(22)$$

requires a considerable partial pressure of HF to give high conversion to UF_4, which is most effectively achieved in a multi-stage, counter current reactor system. Whilst a high conversion to UF_4 is necessary in a conventional UF_6 production plant, it is less crucial in the Fluorox recycle scheme. The optimum conversion to UF_4 will be obtained by balancing the excess HF usage with the loss of throughput in the oxidation reactor.

Two aspects of this flowsheet warrant further consideration, the first and most important being the ability of the catalyst to remain active during the recycling reactions. The small scale laboratory experiments (Section A) have shown that the catalyst does indeed maintain its activity through at least five complete cycles, but the conditions in a full scale production facility are likely to be quite different from those found in the laboratory, particularly with respect to catalyst attrition in the fluidised bed. It is

quite possible that a portion of the recycle stream will have to be bled off to a catalyst recovery stage so that catalyst properties can be maintained at a steady state. This question can only be investigated in the pilot plant facility currently being constructed. An alternative approach would be to circumvent the problems of catalyst recycle by use of an immobile catalyst, which does not pass out of the reactors with the solid overflow. This may be achieved either by the use of large or heavy catalyst particles which segregate to the lower regions of the bed, or by some form of fixed catalyst (e.g. in an array of rods suspended in the bed or incorporated in the gas inlet system, etc.). The first approach was demonstrated in the bench-scale fluidised bed using large, pelletised, catalyst particles.

The second aspect is concerned with the reduction and hydrofluorination reactions. It is obvious that the capital cost of a full scale plant could be considerably reduced if the reduction and hydrofluorination steps could be carried out simultaneously in the same reactor. Previous attempts to achieve this in other laboratories have not been entirely successful mainly, it would seem, because the rate of reduction of UO_2F_2 is slow compared to the rate of hydrofluorination of UO_2. The UO_2F_2 particles are thus rapidly coated with UF_4 and this leads to incomplete conversion. However, the present work has shown that the reduction of UO_2F_2 can be catalysed and it is possible that a simultaneous reduction and hydrofluorination of UO_2F_2 in the presence of the catalyst can be achieved. An aspect of this scheme which needs to be considered is how the reversibility of the hydrofluorination reaction is affected by the simultaneous reactions. Again, the answers to these questions can only be obtained from pilot plant studies.

One of the attractive features of the Fluorox process is that, in theory, it allows considerable flexibility in the nature of the feed material. For example, Figure D2 shows a flowsheet for the Fluorox reaction using UO_3 as feed although UO_2F_2, and more importantly ADU, could be used as well. Another possibility is to apply the principles used in the Allied Chemical Process (Rush et al. 1960, Sutton et al. 1963, Turner 1964) in which crude UF_4, UO_3 or ADU can be used as the feed and the UF_6 produced is purified to nuclear standards by distillation, a simplified flowsheet for this approach being shown in Figure D3. However, it may be necessary to limit the nitrate and/or sulphate contents of these alternative feed materials, firstly to avoid poisoning the catalyst and secondly, to minimise corrosion of the nickel-alloy reactor required for service with hydrogen fluoride.

The results of preliminary experiments described in Section A have shown

that large amounts of heavy metal impurities do not have a deleterious effect on the performance of the catalyst, although the level of sodium in the feed must be carefully controlled as this impurity adversely affects the sinterability of the UF_4. It is expected that the effects of sodium in the Fluorox reaction will be more serious than in the Allied Chemical Process since the Fluorox reaction requires higher operating temperatures and may require higher concentrations of UF_4 in the bed. Depending on the success of the operation of the catalysed Fluorox reaction pilot plant, laboratory studies designed to determine the precise levels of sodium which can be tolerated, and to develop efficient and economic methods for the removal of sodium from crude ADU or UO_3 may be warranted. It has been reported (Turner 1964) that the washing of ADU with ammonium sulphate solution does remove sufficient sodium to make the material suitable for conversion to UF_4 which may then be used as feed for the Allied Chemical Process, but it is not certain that this procedure reduces the sodium impurity sufficiently for the Fluorox process.

In the Australian context, it would appear to be desirable to process uranium to the ADU precipitation stage at the mine site, and then to remove excessive sodium impurity, and to carry out the conversion stage at a central plant. If this approach is shown to be technically and economically feasible, it would remove the incentive to develop a process for the production of nuclear purity grade UF_4 by a 'wet-way' route at the mine site, e.g. the PNC process (Takada, Amanuna and Fukuda 1971). This process is claimed by the Japanese to be particularly suitable for the production of high purity UF_4 at the mine site, but there would be little incentive to use UF_4 as feed for an integrated catalysed Fluorox process in which a 'dry-way' UF_4 production stage will be an essential part.

The extensive laboratory studies on various aspects of the catalysed Fluorox process over the past year have not provided any results which raise serious questions about the feasibility of the process from a purely chemical point of view. Taking these results in conjunction with the bench-scale demonstration of the feasibility of fluidised bed processing and the favourable results reported from the Oak Ridge pilot plant study, there appears to be a good chance of successful operation of the catalysed Fluorox process pilot plant and then a full scale production facility.

Ultimately, the economic viability of a UF_6 conversion plant will depend to a substantial extent on the ability of the plant to use feed materials from widely differing sources (a) successfully and (b) to achieve a high conversion consistently. In the case of a catalysed Fluorox process, the

ability of the catalyst to remain active through a considerable number of recycle reactions if the catalyst is mobile or over an extended period if the catalyst is fixed, and/or the ability to recover the catalyst efficiently and cheaply from the reaction mixture, must also be of considerable importance. Whether or not the above conditions can be achieved in the catalysed Fluorox process can be answered in a definitive way only from the experience gained from the extensive operation of a pilot plant.

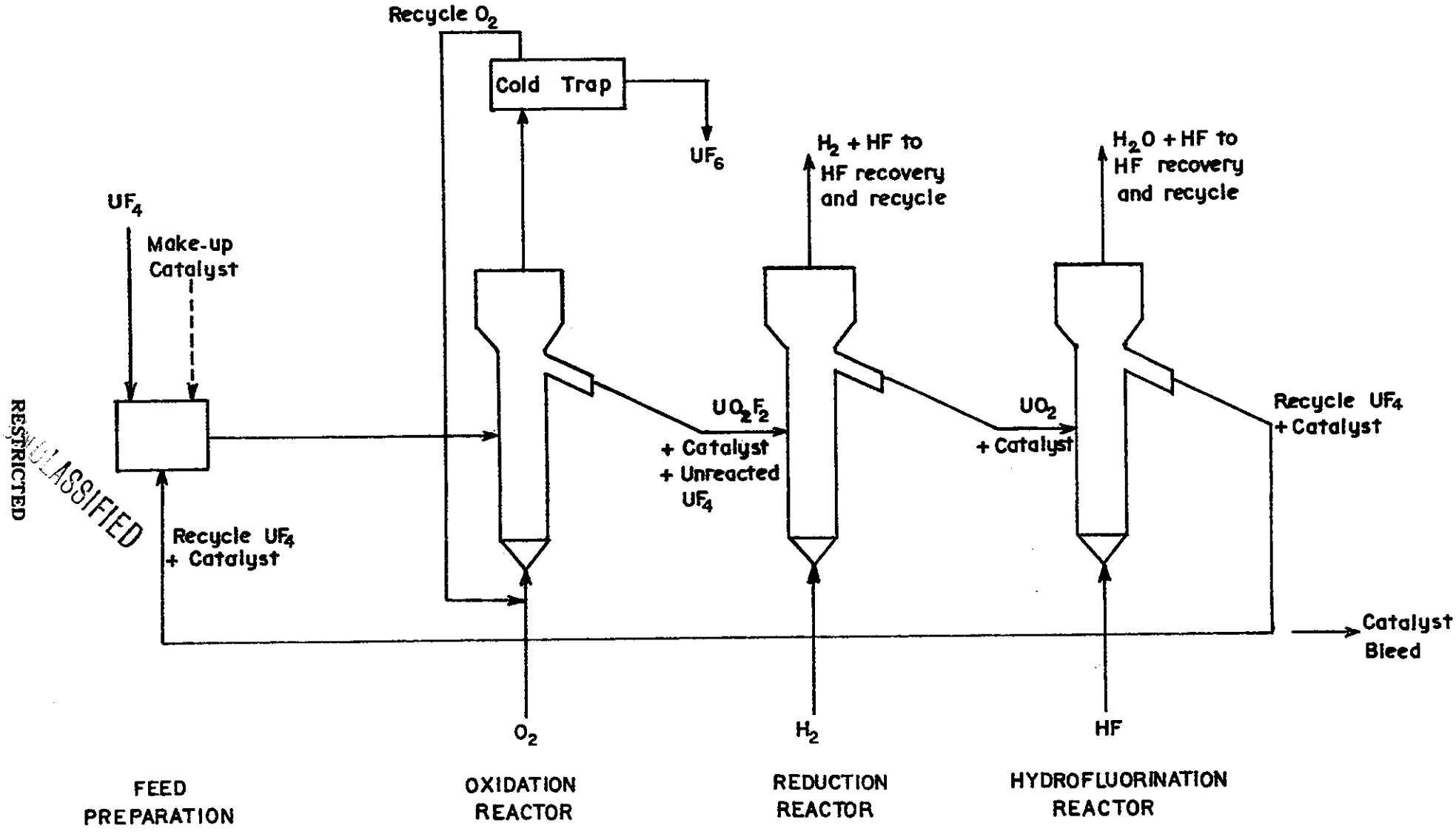


FIGURE D1. PROCESS CHEMICAL FLOWSHEET FOR PRODUCTION OF UF_6 FROM UF_4 WITH RECYCLE IN FLUIDISED BEDS

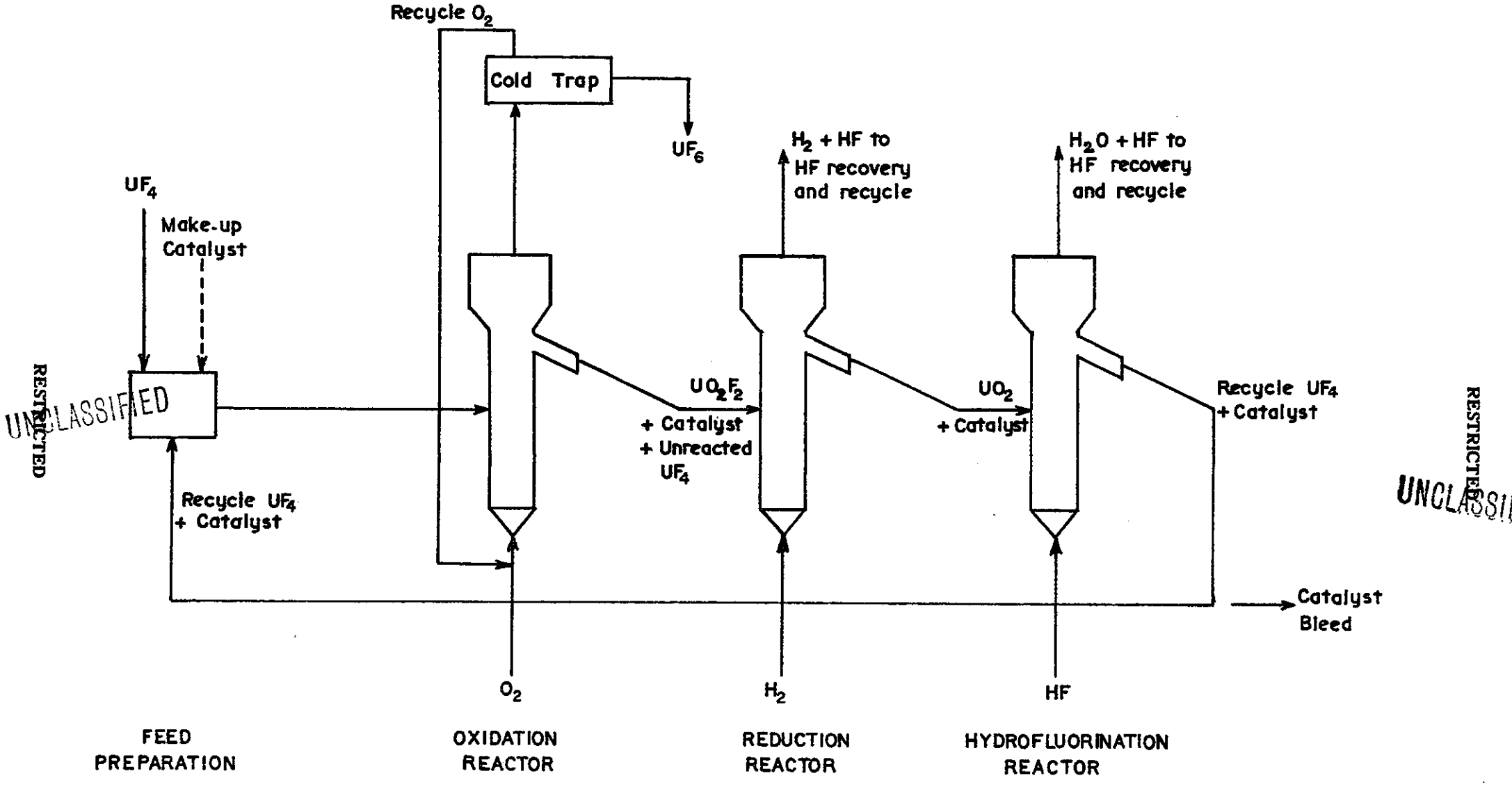


FIGURE D2. PROCESS CHEMICAL FLOWSHEET FOR PRODUCTION OF UF_6 FROM UO_3 BY SIMPLIFIED PROCESS WITH RECYCLE IN FLUIDISED BEDS

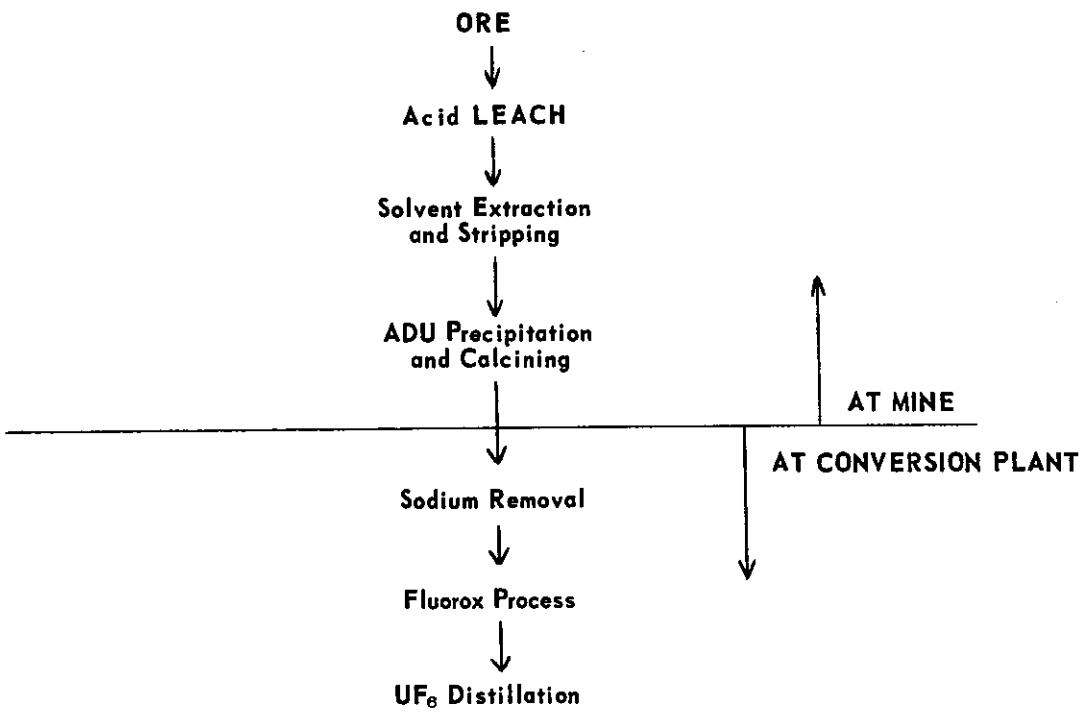


FIGURE D3. SIMPLIFIED FLOWSHEET FOR THE PRODUCTION OF UF_6 BY THE FLUOROX PROCESS USING IMPURE FEED MATERIALS

SECTION E

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SECTION F

BIBLIOGRAPHY OF PATENTS, PAPERS AND REPORTS RELATING TO THE FLUOROX PROCESS

PATENTS

PREPARATION OF UF_6

R.M. Hainer

US Patent 2,535,572 (1950)

Describes the preparation of UF_6 by reaction of UF_4 with oxygen gas.

METHOD OF PREPARING UF_6

Davidson, R., Fried, S.

US Patent 2,910,344. Oct. 27 (1959).

A method is described of preparing uranium hexafluoride without the use of fluorine gas by reacting uranium tetrafluoride with oxygen gas under rigorously anhydrous conditions at 600 to 1300 K within a prefluorinated nickel vessel.

CONTINUOUS PROCESS FOR PREPARING URANIUM HEXAFLUORIDE FROM URANIUM TETRAFLUORIDE AND OXYGEN

Adams, J.B., Bresee, J.C. et al.

US Patent 3,009,768. Nov. 21 (1961).

A process for preparing UF_6 by reacting UF_4 and oxygen is described. The UF_4 and oxygen are continuously introduced into a fluidised bed of UO_2F_2 at a temperature of 600 to 900°C. The concentration of UF_4 in the bed is maintained below 25 weight per cent in order to avoid sintering and intermediate compound formation. By-product UO_2F_2 is continuously removed from the top of the bed and recycled. In an alternative embodiment, heat is supplied to the reaction bed by burning carbon monoxide in the bed. The product UF_6 is filtered to remove entrained particles and is recovered in cold traps and chemical traps.

CONTINUOUS PROCESS FOR PREPARING URANIUM HEXAFLUORIDE FROM URANIUM TETRAFLUORIDE AND OXYGEN

British Patent 897,793. May 30 (1962) (To US Atomic Energy Commission).

A large-scale process is given for preparing UF_6 from impure UF_4 without the use of F_2. The process gives high yields and avoids problems from UF_4 sintering and formation of intermediate fluorides. The process comprises continuously introducing finely divided dry UF_4 and dry O_2 into a bed of dry UO_2F_2 under fluidisation conditions, maintaining the bed at 600 to 900°C and at a UF_4 concentration less than 25 wt.% continuously removing the solids from the top of the bed, and recovering the UF_6 gas. Apparatuses for conducting the process, some of which recycle UO_2F_2 or off-gases, are described.

VERFAHREN ZUR HERSTELLUNG VON URAN HEXAFLUORID

J.B. Adams, J.C. Bresee, L.M. Ferris and C.D. Scott

German Patent 1,148,533 (1964)

A process for the production of UF_6 by reaction of UF_4 with O_2 is described. Identical to US Patent 3,009,768.

PAPERS AND REPORTS

THE PREPARATION OF UF_6 FROM UF_4 AND O_2

Fried, S. et al.

N-1722 1944. Decl.1956. 4p.

The observation that UF_6 can be prepared by the reaction of dry O_2 gas with UF_4 is reported.

THE REACTION OF URANIUM TETRAFLUORIDE WITH DRY OXYGEN

Kirlis, S.S. et al.

K-567 1950. Decl. 1955. 36p.

The reaction of dry oxygen with dry UF_4 has been studied over a range of elevated temperatures under various conditions of oxygen flow. The reaction had been reported to proceed at 800°C according to the equation; $2\ UF_4 + O_2 \rightarrow UO_2F_2 + UF_6$. It was found that a minimum temperature of 740°C was required to produce detectable amounts of UF_6. Using a steady O_2 flow passing over fused lumps of UF_4 at 830°C at a linear velocity of approximately 80 cm/min., the exposed portions of the lumps reacted rapidly to form UO_2F_2 and UF_6, but the centres of the lumps remained unreacted after several hours of oxidation. In addition, approximately 20% of the U was found distributed on cooler downstream portions of the reactor wall in the form of UO_2F_2, UF_4 and intermediate uranium fluorides. The yield of UF_6 was roughly 60% of the quantity predicted by the equation written above. When the oxidation reaction was carried out with alternating O_2 pressure and vacuum, less UF_6 was formed and a white solid $UO_{0.5}F_4$, was blown out of the reactor. Under these conditions, ten grams of UF_4 lumps were converted completely to products in 30 to 45 minutes at 830°C. Chemical analysis, X-ray diffraction patterns and thermal decomposition studies showed that the white solid oxidation product was a uranium oxyfluoride not previously observed, with the formula $UO_{0.5}F_4$. This compound was probably an intermediate in the oxidation of UF_4 to give UO_2F_2 and UF_6.

INTERIM EVALUATION OF THE FLUOROX PROCESS FOR UF_4 AND UF_6 MANUFACTURE

Moore, J.E.

ORNL-1985 1955. Decl. 1957. 10p.

The Fluorox Process for the conversion of UNH to UF_4 and UF_6, utilising moving-bed techniques, is outlined. The process involves the following steps: denitration of UNH to UO_3; pelleting of UO_3 with recycled UO_2F_2; reduction-hydrofluorination to UF_4; and oxidation of UF_4 to UF_6 product and UO_2F_2 intermediate. Advantages of the Fluorox Process include substitution of HF

for F_2, reduction in HF requirements, and reduction in plant-size and mechanical complexity.

HYDROFLUORINATION OF FLUOROX PELLETS

Rampy, G.A.

GAT-L-434 1957. 6p.

In order to obtain data needed to express mathematically the hydrofluorination-reduction step of the Fluorox Process, the changes in surface area and physical dimensions of the pellets as a result of reaction were determined. Data were also obtained on the chemical changes taking place during hydrofluorination.

A STUDY OF THE REACTION: $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$

I. Side reactions and thermodynamics

Ferris, L.M. (Oak Ridge National Lab., Tenn.)

J. Am. Chem. Soc. 79, 5419-21, Oct. 20 (1957)

The reactions of UF_4 with dry O_2 has been investigated in the temperature range of 600 to 900°C. In addition to the expected products, UF_6 and UO_2F_2, UF_5 was isolated from the system, and is postulated to be the product of a side reaction between UF_6 and UF_4. Only slight decomposition of UO_2F_2 was observed in this temperature range in accordance with thermodynamic predictions.

CHEMICAL TECHNOLOGY DIVISION, UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT (for) JANUARY 1958

Bresee, J.C., Haas, P.A. et al.

CF-58-1-137 1958. 41p.

In two Fluorox fluidised bed reactor runs UF_6 recoveries of 47 and 70% theoretical were attained.

PROGRESS REPORT ON THE FLUOROX PROGRESS FOR APRIL 30, 1957 - JANUARY 14, 1958

Adams, J.B., Ferris, L.M. et al.

CF-58-9-66 1958. 32p.

Progress in the Fluorox program is reported. The chemical reaction of primary interest in the Fluorox program is the oxidation of UF_4 with O_2, $2UF_4 + O_2 \rightarrow UO_2F_2 + UF_6$; however, to study this process at higher temperatures the thermal decomposition of UO_2F_2, $3UO_2F_2 \rightarrow \frac{2}{3} U_3O_8 + UF_6 + \frac{1}{3} O_2$, is being investigated by thermogravimetric methods in the temperature range 750 to 900°C. A fluidised bed reactor and a flame reactor have been used successfully to perform the continuous oxidation of UF_4 with O_2. The 3 in. fluidised bed reactor was operated up to 825°C on both a continuous and batch basis while the flame reactor was used to continuously react finely divided UF_4 with O_2 in a CO-O_2 flame at temperatures greater than 1200°C.

KINETICS OF THE THERMAL DECOMPOSITION OF URANYL FLUORIDE

I. Preliminary results

Ferris, L.M. and Gabbard, E.F.

ORNL-2401 (1958)

The thermal decomposition of UO_2F_2 in the range 750 to 880°C was studied by a thermogravimetric technique. Thermodynamic considerations, X-ray analyses of the residues, weight losses and chemical analyses showed conclusively that UO_2F_2 decomposition below 900°C and, in the absence of moisture, according to the reaction $3UO_2F_2 \rightarrow \frac{2}{3} U_3O_8 + UF_6 + \frac{1}{3} O_2$. Below 850°C the rate is extremely slow. In dry He the rate of reaction was first order with respect to the mass of UO_2F_2 with indications that it was also dependent on the gas flow rate. The rate constant, determined a constant flow of dry He, may be expressed as $\log k\ (min^{-1}) = 11.57 - (15{,}700/T)$ from which an activation energy of 72 kcal $mole^{-1}$ was calculated. In preliminary experiments with dry air and O_2 the rate decreased with increasing partial pressure of O_2. However, data were insufficient for a quantitative relation to be derived. UO_2F_2 sublimed, as a parallel first order process, above 825°C.

OXIDATION OF URANIUM TETRAFLUORIDE IN A MOVING-BED REACTOR

Franz, H.W. and Toye, R.H.

ORNL-2409 1958. 32p.

A short study was made of the oxidation of UF_4 to UF_6 with three runs in a 4 in. diameter moving-bed reactor. Combustion of controlled additions of powdered C or CO was used to obtain reaction temperatures. Qualitative data indicate that UF_6 was produced during all runs. Additional experimental work will be necessary before a large-scale pilot plant can be designed and operated.

REACTION OF URANIUM TETRAFLUORIDE WITH DRY OXYGEN: A NEW SYNTHESIS OF URANIUM HEXAFLUORIDE

Fried, S. and Davidson, N.R.

TID-5290, Book 2, 688-95 (1958)

The reaction of UF_4 with dry O_2 at 800°C is $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$. At 350°C there is no rapid reaction. This reaction is a new method of synthesis for UF_6. It does not require the use of elemental fluorine. When the reaction was carried out in a Ni tube, the yield of UF_6 varied between 10 and 40% of theoretical. The UO_2F_2 appeared to be somewhat volatile at 800°C and to sublime out of the Pt boat used to contain the UF_4. It appears that the success of the common analytical procedure of igniting UF_4 to U_3O_8 without loss at 800°C is due to hydrolytic conversion of UF_4 to oxide by moisture.

Calculation of the free energy changes for the reactions $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$; $3UO_2F_2 \rightarrow UF_6 + \frac{2}{3} U_3O_8 + \frac{1}{3} O_2$; $UF_4 + O_2 \rightarrow UO_2F_2 + F_2$; $UF_4 + \frac{4}{3} O_2 \rightarrow \frac{1}{3} U_3O_8 + 2F_2$; $UF_4 + H_2O + \frac{1}{2} O_2 \rightarrow UO_2F_2 + 2HF$; and $UO_2F_2 + H_2O \rightarrow \frac{1}{3} U_3O_8 + 2HF + \frac{1}{6} O_2$ are presented as a function of temperature.

CHEMICAL TECHNOLOGY DIVISION UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT (for) JANUARY 1959

Bresee, J.C., Haas, P.A. et al.

CF-59-1-74 1959. 72p.

Two Fluorox fluidised bed runs were made, of 9 and 58 hour duration, in which dry air and oxygen were used as oxidising and fluidising gases.

CHEMICAL TECHNOLOGY DIVISION, UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT (for) FEBRUARY 1959

Bresee, J.C., Haas, P.A. et al.

CF-59-2-45 1959. 87p.

During Fluorox run FBR-22, 80.4% of the theoretical amount of UF_6 formed was collected in cold traps and chemical traps.

CHEMICAL TECHNOLOGY DIVISION, UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT (for) MARCH 1959

Bresee, J.C., Haas, P.A. et al.

CF-59-3-61 1959. 69p.

A short Fluorox run made with crude UF_4 in the 4 in. fluidised bed showed that UF_6 could be produced from the impure feed.

CHEMICAL TECHNOLOGY DIVISION, UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT (for) APRIL 1959

Bresee, J.C., Haas, P.A. et al.

CF-59-4-47 1959. 94p.

The results from the first Fluorox run made with crude UF_4 showed that 85.3% of the theoretical amount of UF_6 was accounted for, with 17.9% being collected in cold traps and the remainder being consumed in various side reactions.

CHEMICAL TECHNOLOGY DIVISION, UNIT OPERATIONS SECTION MONTHLY PROGRESS REPORT (for) MAY 1959

Bresee, J.C., Haas, P.A. et al.

CF-59-5-47 1959. 103p.

In the second Fluorox run with crude UF_4 which lasted for 28 hours, a total material balance of 94.8% was obtained and 17.9% of the theoretical amount of UF_6 was collected in cold traps and chemical traps.

THE DEVELOPMENT OF A FLUIDISED BED REACTOR FOR THE FLUOROX PROCESS: UNIT OPERATIONS MONTHLY STATUS REPORTS FOR THE PERIOD NOVEMBER 1958 THROUGH MAY 1959

Bresee, J.C., Scott, C.D. et al.

CF-59-5-93 1959. 42p.

Results of four experimental runs in the Fluorox fluidised bed reactor system are reported. The engineering feasibility of UF_6 production from UF_4 by use of dry air or O_2, $2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2$, in an Inconel fluidised bed reactor at 800 to 850°C was demonstrated in two experimental tests in which greater than 90% of the theoretical amount of UF_6 was collected or measured. Two runs made with crude UF_4 (produced from unpurified mill concentrate) as the feed material, showed that UF_6 could be produced at 700 to 725°C but corrosion on Inconel was prohibitive.

PRELIMINARY ECONOMIC EVALUATION OF THE FLUOROX PROCESS FOR MANUFACTURING UF_4 AND UF_6

Moore, J.E.

CF-55-9-51 1955 Decl. 1960. 16p.

Process flow diagrams, process-equipment description, and a preliminary economic evaluation of the Fluorox process are presented. (See also CF-55-5-176.)

FLUOROX MOVING-BED PROCESS FOR PRODUCING UO_3, UF_4, AND UF_6: BIBLIOGRAPHY

Moore, J.E.

ORNL-2117 Aug. 21, 1956. Decl. Mar. 28 1960. 22p.

A bibliography of 105 reports on the Fluorox moving-bed process is given. The reports are arranged in sections on ORNL summary reports, ORNL periodic reports, other reports on moving-bed reactors, production of UO_3, production of UF_4, production of UF_6, and corrosion. These are mostly highly detailed progress reports, and only a small fraction deal directly with the Fluorox Process.

FLUOROX PROCESS: PRODUCTION OF UF_6 IN A FLUIDISED BED REACTOR

Scott, C.D., Adams, J.B. et al.

ORNL-2797 Oct. 27, 1960. 59p.

The engineering feasibility of producing UF_6 from UF_4 by oxidation with dry air or oxygen in a continuous 4 in. diameter fluidised-bed reactor was demonstrated in eight runs at bed temperatures of 700 to 850°C. With refined UF_4 feed and either dry oxygen or air as the oxidising and fluidising gas, up to 90% of the theoretical amount of UF_6 formed was collected in cold traps, and the remainder was accounted for by side reactions. With crude UF_4

feed, corrosion of the Inconel reactor was excessive. A method of preparing feed for the reactor by compacting fine UF_4 to +20 BSS and grinding the compact to -20 +150 BSS was developed. A cost estimate was made for an integrated Fluorox plant, including feed preparation, oxidation, and provision for recycle of the by-product UO_2F_2, with a capacity equivalent to 5000 tons of U_3O_8 per year.

A DISCUSSION ON THE PROGRAMME OF THE SOUTH AFRICAN EXTRACTION METALLURGY DIVISION 1ST TO 3RD DECEMBER, 1965

Geertsma, J.C., MacMillan, I., Paynter, J.C., Van Rensburg, I.

PEL - 121, Vol. II, 1965.

A highly detailed account of the South African Atomic Energy Boards experience in the operation of the Fluorox Pilot Plant, including their economic assessment of the process. The report critically examines the problems encountered and is in general unfavourable. As a result of this experience further development work on this process appears to have been discontinued in South Africa.

DECOMPOSITION OF URANYL FLUORIDE BETWEEN 700 AND 950°C

Ferris, L.M. and Baird, F.G.

J. Electrochem. Soc., 107, 305 (1960)

The thermal decomposition of uranyl fluoride was studied by a thermogravimetric technique between 700 and 950°C. At temperatures below 900°C, the main decomposition reaction is $3UO_2F_2 \rightarrow \frac{2}{3} U_3O_8 + UF_6 + \frac{1}{3} O_2$. In an atmosphere of dry helium, the rate of decomposition was first order with respect to uranyl fluoride. The rate constants, determined with a constant helium flow rate of 270 cm^3min^{-1}, were $k = 3.72 \times 10^{11} \exp(-71{,}800/RT)$. Sublimination of uranyl fluoride, as a parallel, first order process, occurred at temperature above 825°C.