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THE CHEMISTRY OF THE REACTION OF
URANIUM HEXAFLUORIDE WITH ACTIVATED CARBON

by

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ABSTRACT

THE EFFECTS OF TEMPERATURE, TIME AND OTHER VARIABLES ON THE RATE AND EXTENT OF REACTION BETWEEN UF_6 AND VARIOUS TYPES, GRADES AND PARTICLE SIZES OF COMMERCIAL ACTIVATED CARBON HAVE BEEN STUDIED EXPERIMENTALLY. IT IS SHOWN THAT BOTH HYDROLYSIS AND REDUCTION OF THE UF_6 OCCURS, THE LATTER MORE SLOWLY THAN THE FORMER. REDUCTION LEADS TO THE FORMATION OF A MIXTURE OF FLUOROCARBONS RANGING FROM CF_4 TO A WAX-LIKE MATERIAL VOLATILE ONLY ABOVE $250^\circ C$. THERE IS ALSO EVIDENCE FOR THE ADSORPTION OF UF_6 ON AN UNDETERMINED SUBSTRATE.

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Chief, Declassification Branch

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URANIUM HEXAFLUORIDE WITH ACTIVATED CARBON

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INTRODUCTION

In the course of an investigation of the adsorption of gaseous UF_6 by various materials, it was found that commercial activated carbon had a particularly high capacity, and that the residual UF_6 pressure was very low up almost to the saturation point.⁽¹⁾ Because of its outstanding properties in this respect, activated carbon was considered seriously as a charge for traps used to remove UF_6 from purge gases and other gas streams in the K-25 diffusion plant. In connection with a program of research designed to obtain engineering data on the UF_6 -activated carbon system for use in designing these traps, a study of the fundamental chemistry involved was undertaken in hopes of arriving at a more thorough understanding of the process. This was particularly necessary because of the desirability of recovering the uranium from the spent charge, and because of the possible hazards resulting from both the gaseous and the non-volatile reaction products.

The following discussion covers the results obtained in these experiments and the conclusions drawn from them with regard to the adsorption.

MATERIALS USEDActivated Carbon

The activated carbon used in these experiments was commercial material manufactured by the National Carbon Company. Except where noted, it was used in the following experiments after drying for 4 - 6 hours at 150°C, a treatment sufficient to remove most of the physical adsorbed moisture. Tests were made on the following types, grades and particle sizes:

(1) Type

Pelleted
Crushed

(2) Grade

High activity (70 - 75%)
Medium activity (50%)
Low activity (25%)
Zero Activity (0%)

(3) Size

2/4 mesh
4/6 mesh
6/8 mesh

The activity rating given by the National Carbon Company is the percent by weight of CCl_4 adsorbed by the carbon at 25°C from an inert gas stream saturated with CCl_4 at 0°C.

Analyses for carbon, hydrogen and ash content of samples of high and low activity carbon were performed by the S. A. M. Laboratories. The data obtained, which are given in Table 1, indicate that the dried material still contains hydrogen corresponding to about 4% by weight of water. The water may well be chemisorbed. The ash content was 5 - 8%. This is believed to be principally silica, with some alkali or alkaline earth oxides.

Uranium Hexafluoride

The material was used as received from the Harshaw Chemical Company. The principal impurity was HF, which was present to less than

TABLE 1

CARBON AND HYDROGEN ANALYSIS* ON ACTIVATED CARBON

<u>Dried Sample**</u>	<u>Low (25%) Activity</u>	<u>High (75%) Activity</u>
Weight % Carbon	92.5	86.2
" " Hydrogen	0.46	0.53
" " Ash	5.1	8.3
" " Water***	<u>4.2</u>	<u>4.8</u>
" " Total	101.8	99.3

* Analyses by Dr. W. F. Libby's group at SAM.

** Samples both lost about 1% by weight on drying six hours at 150°C.

Approximately the same weight loss was observed in a different sample after drying at 500°F in a current of dry G-74.

*** Assuming hydrogen to be present as chemisorbed water.

0.1% by weight.

Nitrogen

The commercial dry product was used as received. The dew point was reported to be below -30°C .

EXPERIMENTAL METHOD

Except where otherwise noted, the following technique was employed:

To make a gas mixture of UF_6 and N_2 containing 10% by volume of UF_6 , dry N_2 was saturated with UF_6 at 20°C by blowing it at atmospheric pressure through two 1 liter monel metal traps half filled with solid UF_6 and connected in series. The resultant gas mixture was then passed through a small weighed sample of carbon in a nickel tube immersed in a liquid thermostat. The weight gain of the carbon was followed as a function of time by periodically removing and weighing the reactor containing the carbon.

In order to obtain measurements under as nearly isothermal conditions as possible, the UF_6 flow rate was kept at about 5 gm./hr. A 2 gm. sample of carbon was generally used. The flow rate in these experiments was so low that measurements made in the first hour were of little significance. During that time most of the entering UF_6 was absorbed.

RESULTS OF EXPERIMENTS

Activity of Carbon

At a particular temperature, under the conditions outlined above, the efficiency of a given type of carbon, in terms of weight gain per unit weight of carbon is greater the higher the activity of the carbon. This may be seen by a comparison of results on various grades given in Figures 1, 2 and 3.

Size of Carbon Particles

At 200°F there is no detectable difference between 2/4 and 6/8 mesh pellets once saturation has been reached. At 500°F the larger par-

TABLE 2

COMPARISON OF UF_6 AND CCl_4 ADSORPTION ON ACTIVATED CARBON SHOWING
EFFECT OF TYPE OF CARBON ON THE ABSORPTION OF UF_6

Partial Pressure of UF_6 = 0.1 atm.

Exposure = 3 hrs.

<u>Carbon Used</u>	<u>Temperature</u>	<u>Efficiency* (UF_6)</u>		<u>Activity (CCl_4)</u>	
		<u>Pellets</u>	<u>Crushed</u>	<u>Pellets</u>	<u>Crushed</u>
6/8 High Activity	75°F	1.62	.99		
		1.64	1.14		
6/8 High Activity	200°F	2.50	1.55	0.526	0.490
		2.41	1.49	0.530	0.567
		2.55		0.523	0.496
		2.48			
6/8 Medium Activity	200°F	1.78	0.425	0.394	0.358
		1.76	0.581	0.399	0.341
			0.634		

* Both efficiency and activity are here expressed as: $\frac{\text{weight of adsorbate}}{\text{weight of adsorbent}}$

The activity is used here to refer to CCl_4 adsorption in general rather than the adsorption under the conditions specified by the National Carbon Company.

ticles have somewhat higher final efficiencies. The data are shown in Figure 2. As shown in Figure 3, the initial rate of adsorption of UF_6 is greater for the smaller particles.

Type of Carbon Pellets

Pelleted carbon shows a considerably higher UF_6 adsorptive capacity than crushed carbon of the same "activity" and particle size. Data are given in Table 2.

Moisture Content of the Carbon

One experiment was performed in which overall efficiencies were measured, and $\text{U}^{+4}/\text{U}^{+6}$ ratios determined, for two similar samples of carbon, one of which was dried in flowing N_2 at 250°C before exposure to UF_6 , while the other was used as received. The efficiency was 2.55 for the dried sample and 2.49 for the undried one. The $\text{U}^{+4}/\text{U}^{+6}$ ratios were, respectively, 0.69 and 0.86. The observed effect of drying in this one case was apparently to decrease the amount of quadrivalent uranium formed. The effect was, however, relatively small, and since it was not repeated, little significance has been attached to it.

TEMPERATURE OF CARBON

In Figure 1 is presented the data obtained on the effect of temperature on the adsorption efficiency of high, low and zero activity carbon pellets. From Figure 1 it will be seen that the adsorption efficiency depends both on the temperature and on the period of exposure. For exposures of one to six hours, the adsorption of C-616 increases with temperature up to 300°F or somewhat above, then decreases to a minimum around 400°F , then rises sharply. With longer periods of exposure the efficiency increases continuously with temperature. This behavior is less marked in low than in high activity carbon, and, within the accuracy of the measurements, no break is observed in the data on zero activity carbon.

PARTIAL PRESSURE OF UF_6

The effect of UF_6 partial pressure was determined only at 200°F using exposure times of about half an hour, and UF_6 flow rates more than sufficient to saturate the carbon in the time allowed. The UF_6 partial pressure was controlled by controlling the temperature of the solid UF_6 in the saturation through which the N_2 passed. The total pressure was one atmosphere. Under these conditions the efficiency of 6/8 mesh high activity carbon pellets is given approximately by:

$$(1) \quad E = 2.95 \, p^{0.1}$$

where $E = \text{gms. } UF_6 / \text{gm. carbon}$
 $p = UF_6 \text{ partial pressure, atm.}$

Efficiencies calculated from the equation agree to within 15% with the rather scattered data obtained experimentally for partial pressures of UF_6 from 0.001 to 1 atm. The uncertainties are large and the pressure effect rather small.

RATE OF UF_6 ADSORPTION

Where a gas and a powdered solid react rapidly with the evolution or absorption of heat, the heat transfer processes occurring are too slow to take care of the heat immediately. However, if the reaction is slow, the temperature rise may be negligible, the reaction occurring at substantially isothermal conditions.

Both fast and slow reactions appear to occur when carbon is exposed to UF_6 . The initial adsorption is extremely rapid and highly exothermic. After this initial period a slower reaction occurs, slow enough so that under some conditions it may be treated as isothermal. The rates of both of these processes have been studied.

An attempt was made to keep the faster reaction as nearly isothermal as possible while still maintaining a sufficient supply of UF_6 in the gas phase at all times. To this end, reactors were made of copper tubing, $1/2''$ O.D. x $3/8''$ I.D. x $6''$ and were mounted in an air thermostat. The carbon charge was diluted in all cases with an equal volume of fused alumina, an inert material having a relatively high heat capacity. UF_6 , at atmospheric pressure, was passed through the reactors during the experiments at 10 - 50 gm. per gm. of carbon per minute, a rate sufficient to saturate the 1 - 3 gm. of carbon used in less than a minute. In spite of the high heat capacity and rate of heat loss from the reactors, an initial temperature rise occurred as measured on the outside of the copper reactor. The first stages of the reaction cannot, then, be considered isothermal.

In Figure 3 are given the results of experiments performed with this apparatus to determine the effect of temperature, carbon activity and particle size on this initial reaction rate. The smaller particles adsorb the UF_6 too fast for the measurements to have any significance. The difference in initial rates for 2/4 and 6/8 mesh high activity carbon probably means that the rate, at least for the larger particles, is controlled by a diffusion process. The temperature coefficient of the rate in the case of the 2/4 mesh particle is apparently somewhat high for such a process, the rate changing by ~~about~~ a factor of about three in going from a nominal temperature of 200° to 400°F . The increased rise in actual temperature and in extent of reaction due to the more rapid evolution of heat in the latter case, may account for this in part.

The data obtained on carbon efficiency as a function of time and temperature at lower UF_6 flow rates may be used in treating the subsequent slow reaction. The data in Figure 1 on 6/8 mesh high and 2/4 mesh low

REACTION RATE
WEIGHT GAIN / UNIT WEIGHT OF CARBON / HOUR

869 013

activity carbon pellets, when replotted as efficiency vs. time of exposure, make a simple and fairly accurate estimate of the starting rate of the secondary reactions. Rather surprisingly, these rates for the two types of carbon, expressed as efficiency units per hour, are identical so far as can be determined. The logarithms of the rates obtained in this way have been plotted against $1/T$ in Figure 4. The best straight line through the points may be represented by:

$$(2) \quad \ln (dE/dt) = \frac{9700}{RT} + 9.2$$

Here E is the efficiency as defined previously, t is time in hours, T is temperature in $^{\circ}K$ and R is the gas constant in calories. The measured rate at $500^{\circ}F$ was multiplied by 1.5 before plotting, because at that temperature it is believed that U_2F_9 rather than UF_5 is formed. This correction will be discussed later. The points deviate from the linear relation by an average 20%. This is no greater than the probable uncertainty in the rate determinations.

The fact that the data apparently follow a relation of the type given indicates that some activated process is the rate determining factor. The activation energy is typical of many chemical processes.

HEAT OF ADSORPTION OF UF_6 BY ACTIVATED CARBON

A rough determination of the heat of adsorption of UF_6 by high activity carbon at $25^{\circ}C$ was made. It was concluded that during the period of rapid adsorption, (the only region investigated) the heat of adsorption was 45 ± 5 Kcal. per mole of UF_6 . This is quite close to the 44 Kcal per mole which is the heat of formation of a 1 molar aqueous solution from gaseous UF_6 and water. Since in the latter case the heat of solution of the HF formed is considerable, the higher value should be reduced before comparing the two.

FLUOROCARBON PRODUCTION DURING UF_6 ADSORPTION.

Several types of experiments were performed to determine the nature of the fluorocarbons produced in the reaction. In the first, a stream of 100% UF_6 at 1 atm. pressure was sent into a bed (12" x 1 1/2") of 6/8 mesh high activity carbon. The exit gases were passed through a washing tower containing standard sodium hydroxide designed to absorb any HF, then through a tube containing Ascarite and Drierite to remove H_2O , and finally through a dry ice trap followed by a liquid nitrogen trap, after which any residual gases were vented to the atmosphere. After collecting the samples they were pumped for a short time to remove O_2 and N_2 and then stored in glass bulbs with break off seals until mass spectrographic analyses could be made.

In the first experiment, in which the carbon temperature was 400-500°F, nothing was collected in the dry ice trap, and back titration of the standard sodium hydroxide solution indicated no HF, within the experimental accuracy. This may be because the reaction proceeded only about three quarters of the way through the reactor. Practically nothing was found in the dry ice trap, but 3 cc. of colorless liquid was collected in the liquid nitrogen trap.

Dr. Nier's analysis of the resultant gas samples may be summarized as follows:

(1) The bulk of the sample consisted of saturated fluorocarbons of molecular weight 188 or less, with C_5F_8 accounting for a good part of the mixture. (The evacuation of the samples before sealing would lead to some loss of CF_4).

(2) Traces of higher fluorocarbons up to C_8F_{16} were found.

(C_8F_{16} was used as a manometric fluid in the apparatus)

(3) Traces of hydrocarbons appeared to be present.

(4) About 5% of the gas was nitrogen and oxygen.

Another experiment was performed in which the reactor was kept below 150°F , but the samples obtained were too small for satisfactory analysis, even by mass spectrograph. Again very little was collected in the dry ice trap. The material in the liquid nitrogen traps appeared to contain unsaturated fluorocarbons, in contrast to the high temperature run in which the fluorocarbons were predominately saturated.

After performing these experiments, another apparatus was built to produce larger quantities of fluorocarbons so that a more reliable identification of products might be made. The apparatus consisted of a high pressure UF_6 supply, an oven jacketed reactor, and a fluorocarbon collection train. UF_6 was bled in shots into the reactor, where the pressure first fell, then rose slowly. As the pressure rose, products were slowly bled into the cleaning and collecting train.

By this method, operating at temperatures of $500^{\circ} - 900^{\circ}\text{F}$, about 100 cc. of liquid fluorocarbons at liquid nitrogen temperatures were obtained. Operation at lower temperatures failed to produce significant quantities of fluorocarbons and was therefore abandoned.

The liquid produced in the experiments, after a short pumping to remove G-74 and O_2 , was sent to the M. W. Kellogg Co.'s analytical laboratory where a distillation curve on the material was obtained using a Podbielniak low temperature fractionating column. Although mechanical difficulties in the distillation introduced some error, the results of the analysis given in Table 3 are believed to be correct to within a few percent. For CF_4 a good flat was observed at -182°F (cf. -198°F , Handbook of Chemistry and Physics). The next fraction boiled in the range -120° to -98°F . with possibly a small amount coming over at -75°F .

TABLE 3

DISTILLATION OF 100 CC. OF FLUOROCARBONS FROM
THE UF₆ CARBON REACTION

<u>Boiling Range</u> <u>°F</u>	<u>Probable</u> <u>Compounds</u>	<u>Volume of</u> <u>Gas, Liters</u>	<u>Mol % of</u> <u>Gas Collected</u>
-200° to -150°	CF ₄ CF ₄	32	82
-150° to -75°	C ₂ F _x	5.5	14
-30° to +30°	C ₃ F _x	1.5	4
Residue (liq.)	C ₄ -C _n	2.5 ml (liq.)	-

Both C_2F_6 and C_2F_4 are reported to boil at $-108^\circ F$. Data on the higher members of the series were not readily available, but interpolation between the data on C_7F_{16} and those reported should lead to fairly accurate estimates. On this basis, the boiling point of C_3F_8 should be $-40^\circ F$. The flat in this region is at $-25^\circ F$. The residue undoubtedly consisted of compounds containing four or more carbon atoms per molecule.

In addition to the highly volatile compounds mentioned above, a certain amount of viscous oil and some hard wax was found in the trap just outside the reactor after runs at $900^\circ F$. It is quite probable that these materials were formed in the other experiments also, but the temperature was not high enough to drive them out of the reactor. This material, which could cement carbon particles together, may be the explanation for the plugging and caking of carbon in UF_6 atmospheres at high temperatures. A vacuum distillation was carried out on the viscous material and two fractions taken at 4 mm. pressure, one boiling at about $200^\circ C$, the other between $230^\circ C$ and $250^\circ C$. Molecular weights of each fraction were determined by measuring the boiling point elevation of C_7F_{16} solutions of the fluorocarbons, and values of about 500 and 800 respectively obtained.

To determine the extent of heavy fluorocarbon production as a function of the carbon temperature, a series of flow runs was made at temperatures from 200° to $700^\circ F$. Runs were made with 1 atm. of 100% UF_6 flowing at 2.15×10^{-2} lbs./ft² - sec. for 1000 seconds into a 12" x 1 1/2" reactor filled with 2/4 mesh high activity carbon. At the end of this time the bottom six inches of the bed were removed, ground to a powder, and extracted with C_8F_{16} for 7 hours. The C_8F_{16} was then distilled off from the extract and the residue weighed.

The results are given in Table 4 as milligrams of heavy fluorocarbon extracted per gram of sample. This is correlated with the average carbon

TABLE 4

PRODUCTION OF HEAVY FLUOROCARBONS IN THE

UF₆ CARBON REACTION

<u>Run No.</u>	<u>Average Temp., °C.</u>	<u>Heavy Fluorocarbon Extracted, mg/gm. of sample</u>	<u>U⁺⁴ mg/gm. of sample</u>
32	300	0.25	54
35	320	0.48	130
37	480	3.0	136
34	705	5.8	179
36	850	10.8	210

bed temperatures during the runs. In addition the table shows the U per gm. of sample for each of the runs. It will be noted that this does not rise nearly as rapidly with temperature as does the heavy fluorocarbon production.

Besides the heavy fluorocarbon oils and waxes mentioned above it was observed in at least one case when carbon was exposed to 10% UF_6 at $400^\circ F$ for 24 hours that a considerable quantity of clear needle-like crystals of a material answering the visual description of $(CF)_x$ were formed.

EFFECT OF IMPURITIES IN CARBON

In an attempt to determine experimentally the relative importance of the hydrolytic, reductive and adsorptive reactions, two similar charges of 6/8 mesh high activity carbon pellets were exposed to UF_6 at $200^\circ F$ for 2 hours. One was then closed off and heated to $650^\circ F$ for four hours to possibly convert any UF_6 present to UF_4 . Analyses for U^{+4} and U^{+6} were then performed on the charges from the blank and the heated reactor. The data obtained are given in Table 5. Some reduction of U^{+6} apparently occurred at the high temperature. In view of the uncertainties in the interpretation of the analytical data there is some question as to the absolute accuracy of the results. They could be explained, if it was assumed that the reduced uranium was present as UF_5 at first, but was converted to U_4F_{17} or UF_4 at $650^\circ F$. This would mean a hydrolytic reaction of UF_6 with impurities in the carbon had occurred to the extent of about 1.5 efficiency units. This last is not unreasonable on the basis of the analytical data on the carbon (Table 1).

ANALYSIS FOR URANIUM ON CARBON AFTER EXPOSURE TO UF_6 .

A large number of determinations of U^{+6} and U^{+4} contents of spent carbon from the low flow rate experiments described above were carried out in hopes of arriving at a clearer picture of the chemistry of the adsorption

TABLE 5

ANALYSIS FOR URANIUM ON CARBON AFTER UF₆ EXPOSURE

SPECIAL TEST

UF ₆ Exposure	<u>A</u>	<u>B*</u>	
UF ₆ Partial Pressure, atm.	0.10	0.10	0
Temperature, °F.	200	200	650
Time, hrs.	2	2	4
Wt. U ⁺⁴ /Wt. U	0.22	0.39	
Wt. U ⁺⁶ /Wt. C	1.33	1.18	

* B was first exposed to UF₆ under conditions identical with those used in Sample "A". It was then sealed under N₂ at atmospheric pressure and heated to 650°F. as indicated.

process. The analytical method developed for this analysis by Dr. R. H. Lafferty and co-workers in the analytical group is described elsewhere (2)

. The method involves the extraction of the soluble U^{+6} , followed by a complete combustion to determine the residual uranium. The latter is assumed to have been quadrivalent. The data were in general reproducible when the reaction with UF_6 and the analysis were repeated under comparable conditions. Blanks prepared by mixing UF_4 , UO_2F_2 and HF (solution) with activated carbon could be analyzed accurately. There is some reason for believing, nevertheless, that the U^{+4} contents reported, particularly when only a slight amount of reaction had occurred, may be somewhat high. This will be discussed later.

The data obtained are summarized in Table 6. They are expressed in terms of $\frac{e}{A}$ weight of U^{+4} present per unit weight of total uranium, and weight of U^{+6} present per unit weight of activated carbon originally present. The latter function in particular is liable to show a larger percentage error than the actual analytical data, both because of the large effect small analytical discrepancies will have, and because of the assumptions made in calculating it. It was found in calculating U^{+6}/C that the best agreement between the analytical results and the measured efficiencies was obtained, if it were assumed that none of the reaction products were volatile. The alternative assumptions tried were that UF_4 , UO_2F_2 and volatile compounds, or UF_4 , UF_6 and volatile compounds were formed. Undoubtedly some intermediate assumption might improve the agreement.

Although the accuracy of the functions reported may not be high, there are no grounds for not relying on them qualitatively, and, at least in the major features, relatively. On this basis, it is concluded that the U^{+4}/U ratio increases, or at least does not decrease, with time, over periods of UF_6 exposure greater than one hour. The fact that this ratio is less than

TABLE 6

ANALYSIS OF CARBON FOR URANIUM CONTENT AFTER UF₆ EXPOSURE

Temp., °P.	Time of UF ₆ Exposure, hrs.	Analysis,*		Analysis,*	
		Wt. U ⁺⁴ /Wt. U		Wt. U ⁺⁶ /Wt. C	
		<u>6/8 Mesh</u>	<u>2/4 Mesh</u>	<u>6/8 Mesh</u>	<u>2/4 Mesh</u>
<u>High Activity Carbon Pellets</u>					
200	1	0.26±0.15	0.11±0.07	0.82±0.11	0.80±0.02
200	24	0.40±0.02	0.39±0.04	1.22±0.09	1.15±0.05
300	1	0.30±0.03	0.18±0.03	1.10±0.13	0.64±0.14
300	22	0.31±0.10	0.26±0.03	1.89±0.12	1.52±0.40
400	24	0.47±0.03	0.48	2.46±0.40	1.87
500	24	0.77±0.01	0.74	1.40±0.35	1.83
<u>Low Activity Carbon Pellets</u>					
200	1	0.24±0.12	0.24±0.02	0.21	0.21±0.01
200	17	0.42	0.41	0.33	0.35
300	1	0.51	0.45±0.03	0.26	0.21±0.01
300	21	0.52±0.01	0.54	0.42±0.06	0.68
400	24	0.48±0.06	0.52±0.03	1.33±0.23	1.00±0.13
500	24	0.69±0.06	0.71±0.03	1.44±0.30	1.33±0.30

* The mean deviation is given when two experiments were performed.

0.5 at temperatures below 400°F and rises rapidly between 400°F and 500°F appears also to have been established. The U^{+6}/C ratio increases with temperature, for 24 hours exposure time, up to 400°F, and falls again at 500°F. It also increases with time of exposure at 200° and 300°F.

DISCUSSION OF RESULTS

Before discussing the data obtained in this work, an analysis of the physical adsorption of UF_6 by activated carbon on purely hypothetical grounds is instructive. According to the Brunauer-Emmett-Teller theory⁽³⁾ the adsorption isotherm may be represented in general by the equation

$$\theta = \frac{cx}{(1-x) [1 + (c-1)x]} \quad (3)$$

where θ is the monolayers adsorbed, c is a constant and x is the relative pressure, the actual gas phase pressure of the adsorbate divided by the vapor pressure of the liquid adsorbate at that temperature. c has the form

$$c = e^{-(E_L - E_1)/RT} \quad (4)$$

where E_1 is the heat of adsorption of the first layer of molecules adsorbed, and E_L is the heat of condensation of the bulk liquid.

The CCl_4 adsorption data obtained at 25° and 95°C (Table 2) are sufficient to make possible an estimate of c in equation (3) for the CCl_4 , activated carbon system. The calculations, which will not be reproduced here, lead to the conclusion that c must be very high, approaching infinity. If so, the adsorption measured at 200°F, where the CCl_4 relative pressure was only about 0.03, represents the adsorption of approximately one monolayer of CCl_4 .

Calculations using the relative molecular volumes of CCl_4 and UF_6 on this basis leads to the conclusion that one monolayer of UF_6 on high activity

carbon would correspond to an efficiency of about 1.3 gm. UF_6 per gram of carbon.

The relative pressure of UF_6 at 1/10 atmosphere partial pressure and 200°F is about 0.03. If the c constant for the UF_6 activated carbon system is not very large, practically no adsorption of UF_6 should occur at this, or higher, temperatures. Unless "chemisorption" occurs there is no reason to expect such a high c constant for this system. It seems necessary, then, to account for the relatively high UF_6 adsorption efficiency at all temperatures on the basis either of chemisorption or of chemical reaction.

In studies of the corrosion products obtained when metals are exposed to UF_6 at 140°F it has been shown that, in the absence of hydrolytic reactions, $\text{U}^{+4}/\text{U}^{+6}$ is usually very close to unity. This has been interpreted as due to the formation of UF_5 from UF_4 in the presence of excess UF_6 at these temperatures. It has also been shown⁽⁴⁾ that UF_5 is stable in the presence of 1/10 atmosphere partial pressure of UF_6 up to temperatures around 400°F . Above 400°F , U_2F_9 is formed, which at still higher temperatures may dissociate forming U_4F_{17} . In the absence of reasons for believing the contrary, it must be assumed that the compound formed by reduction of UF_6 on carbon will be the U_xF_y compound stable in bulk at the temperature in question.

The experimental observations may be reconciled at least qualitatively with the above discussion on the following basis:

1. "Hydrolytic" reaction of UF_6 with impurities on the carbon.
2. Reduction of UF_6 by carbon to UF_5 or U_2F_9 , with the accompanying formation of a mixture of saturated, and perhaps unsaturated, fluorocarbons.
3. Chemisorption of UF_6 , perhaps only on the hydrolysis products.

From the rate experiments it may be concluded that two reactions, one

rapid, the other slow, occur when activated carbon is exposed to UF_6 . The analyses of the spent carbon show a low U^{+4}/U ratio when only a short time is allowed for reaction, and an increase in this ratio with time of exposure.

One experiment indicates that the major fraction of the U^{+6} present in the first stages of the reaction of UF_6 with high activity carbon pellets cannot be reduced to U^{+4} by prolonged heating at 650°F , although in cases where the carbon is kept in an atmosphere of UF_6 at 500°F , only about 25% of the uranium left on the carbon is hexavalent.

Carbon and hydrogen analyses of the activated carbon pellets show the presence of relatively large quantities of impurities probably including chemisorbed water. They would be quite sufficient to react with UF_6 equivalent to the 1.0 - 1.5 efficiency units required to account for the unconverted uranium in the experiment mentioned.

From the above it is concluded that the initial rapid reaction of UF_6 with activated carbon is a result of UF_6 hydrolysis on the surface. This may explain the apparent agreement found between the heat of adsorption of UF_6 on activated carbon and the heat of solution of UF_6 in water. From the fact that the particle size has a considerable effect on the rate of this reaction while the temperature apparently has little effect it seems probable that the rate controlling process in this reaction at least when 2/4 mesh pellets are used is the rate of diffusion of UF_6 to the internal surface of the carbon.

From the increase in U^{+4}/U with time it may be concluded that the slow secondary reaction is the reduction of UF_6 . Although at least in the case of low activity carbon, relatively large amounts of impurities may still remain in the carbon while this reaction is proceeding, the small effect of extent of reaction over a relatively wide range and the product-

ion of fluorocarbons would lead to the conclusion that reaction is occurring principally with the carbon.

The analyses for the U^{+4}/U ratio, in experiments performed at 400° F or below show that here the ratio is 0.5 or below. This would be expected if UF_5 and hydrolysis products were being formed. At 500° F, U^{+4}/U is 0.7 - 0.75. This agrees well with the theoretical ratio 0.75 for U_2F_9 , which should be the stable U_xF_y compound at this temperature. The reaction at temperatures above 300° - 400° F leads to the formation of a mixture of fluorocarbons, principally saturated ones. An appreciable fraction of these fluorocarbons does not appear to be volatile below 800° - 900° F. From the color of the higher molecular weight oils and waxes found at high temperatures, as well as from the mass spectrographic data in the low temperature runs some unsaturation is indicated.

As mentioned previously, the fact that the reduction rates of UF_6 by high and low activity carbon are the same, so far as these experiments show, is rather unexpected. More experiments would have to be performed to establish this point with certainty. In the meantime it will merely be assumed with the qualitative support of the analytical data that the slow reaction in both cases is a result of UF_6 reduction by carbon. The activation energy appearing in the expression for the rate of this reaction cannot be definitely assigned to any particular step in the reaction process.

One of the most striking features of the experimental data is the effect of temperature on efficiency when the time is low. Between 100° and 300° F the short time efficiency increases with temperature, while between 300° and 500° F it decreases. Behavior of this sort is rarely encountered in ordinary chemical reactions, but is characteristic of adsorption data in the temperature region where activated adsorp-

tion begins to occur at a detectable rate. On this basis the efficiency data would be explained if the UF_6 adsorption rate were low below 300°F and relatively high above it.

The data obtained are not sufficient to permit the drawing of any definite conclusions as to the material on which the UF_6 is adsorbed. It might be the carbon itself, the hydrolysis products or the reduction products. Measurements of the adsorption isotherm of UF_6 on UO_2F_2 at 100°C (5) show what might be interpreted as a slow activated adsorption of UF_6 , but while this may be necessary it can hardly be regarded as sufficient grounds for concluding that UO_2F_2 is the adsorbent in this case. Whatever the substrate, the mechanism offers an attractive explanation for some of the observations.

Presumably the principal difference between high and low activity carbon is the extent of the available surface. On this assumption, high (75%) activity carbon has about three times the surface area of low (25%) activity carbon. If so, the data on efficiencies of the two grades of carbon as a function of temperature for short exposure times may be explained if, both the amount of hydrolysis products formed, and the amount of UF_6 adsorbed are proportional to the surface area. The estimated peak efficiency at 300°F and zero time, obtained by a linear extrapolation of the efficiency vs. time curves, is almost 3.0 for high activity carbon and very nearly 1.0 for low activity carbon pellets. At 400°F the values are 1.8 and 0.6 respectively. It is interesting to note that the value at 500°F for high activity carbon pellets, about 1.0, is close to the value of 1.3 predicted for a monolayer of UF_6 on the basis of the CCl_4 measurements.

Quantitatively, the agreement between the analytical results obtained and predictions based on the proposed mechanism together with the measured

efficiencies is not particularly good. Predictions based on the assumptions that UF_5 is formed from UF_6 reduction at temperatures of $400^\circ F$ or below and U_2F_9 at $500^\circ F$, that the slow weight gain is due to UF_6 reduction, and that the remaining uranium present is hexavalent are presented in Table 7, together with the comparable analytical results. In all cases the calculated values of U^{+4}/U are below the predicted ones. This is particularly true at $200^\circ F$. It would be expected, if the extraction method used for U^{+6} determination did not remove all the U^{+6} , because of adsorption by the carbon. Experimental work in which carbon was saturated with UO_2F_2 solution and the UO_2F_2 then extracted by the standard procedure failed to show any irreversible adsorption large enough to account for the observed discrepancy. Nevertheless the success of the proposed mechanism in explaining the qualitative features of the adsorption, and the difficulties of the analysis, particularly since the impurities in the carbon may react with UF_6 , make it appear possible that the difficulty lies in the analytical results.

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