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EXCHANGE BETWEEN URANIUM HEXAFLUORIDE AND SOME OF ITS COMPLEXES

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SUMMARY

Rapid exchange between free and complexed uranium hexafluoride was observed by ^{19}F nmr in several systems. The distribution of the uranium containing species was measured in each of the phases for these systems. No significant enrichment was found when the reactants were distributed between the phases in the two phase liquid system sulfur dioxide-dichlorodifluoromethane.

INTRODUCTION

The enrichment of isotopes by chemical exchange was first used for the separation of nitrogen-15 [1]. The principal use of this method to date has been in the separation of isotopes of boron [2]. The underlying theory has been presented but its application to complex systems is fraught with difficulties [2-5]. Separation of uranium isotopes by exchange between U(V) - U(VI) [6] and U(IV) - U(VI) [7] has been studied and found to be uneconomical because of long equilibration times. It therefore seemed worthwhile to search for systems in which exchange of uranium between two chemically different uranium containing species was rapid.

Rapid exchange between free and complexed hexafluorides has been observed with Lewis base complexes of tungsten and molybdenum hexafluorides [8]. Uranium hexafluoride has a similar chemical reactivity to these hexafluorides so it is reasonable to look for rapid exchange with uranium hexafluoride

complexes [9]. Rapid fluorine exchange has been observed in mixtures of bromine trifluoride and uranium hexafluoride [10].

In a system containing two compounds of uranium, the difference in enthalpy for compound -1 containing U-238 and that containing U-235 can be given as ΔH_1 . Similarly, the enthalpy difference for compound -2 will be ΔH_2 . It then follows that the distribution of, say U-235, between compounds 1 and 2 will follow the Boltzmann distribution, $N_2 = N_1 \cdot \exp \frac{(\Delta H_1 - \Delta H_2)}{RT}$. This means that, provided the enthalpy differences do not change greatly with temperature, the theoretically possible enrichment by selective distribution between compounds 1 and 2 will increase markedly with decrease in temperature. It would therefore be advantageous to choose a system for isotopic enrichment where exchange is fast and solubility is high at as low a temperature as feasible.

EXPERIMENTAL

All manipulations of reagents were done on a hybrid glass-metal vacuum system with careful exclusion of water, as with tungsten and molybdenum hexafluorides [8]. Uranium hexafluoride was used directly as supplied by Var-Lac-Oid Chemical Co. Solvents and other reagents were purified in the usual manner [11,12]. Samples for fluorine resonance studies were prepared as previously described [8]. Fluorine resonance spectra were obtained at 94.1 MHz on a Varian Associates HA100D spectrometer modified for a wide sweep range. Chemical shifts are reported in ppm relative to CFC_2Cl_3 . Uranium isotopic analyses were performed on a Varian MAT UF_5 mass spectrometer.

In the distribution studies known quantities of CF_2Cl_2 , SO_2 , and UF_6 were added to the reactor and the two phases separated at the given temperature. Each phase was weighed and passed into an excess of concentrated sodium hydroxide solution. The sulfite was converted to sulfate and this and the

uranium were analyzed gravimetrically. In every case a satisfactory material balance was obtained compared with the initial quantities of material used. For the solvents alone, known quantities of each were condensed into a container and the consolute temperature was determined visually.

In the enrichment studies a manual cascade of a few stages at -60°C was normally employed to improve the accuracy of the enrichment ratio per stage, α ; where

$$\alpha = \frac{\text{Final isotope ratio} - \text{Initial isotope ratio}}{\text{Initial isotope ratio}}$$

The UF_6 for the isotope ratio measurements was separated from the solvent in the CF_2Cl_2 phase by fractional distillation and stored, for analysis, in stainless steel containers closed by stainless steel bellows valves.

RESULTS AND DISCUSSION

The very low field, but sharp, fluorine resonance signal in uranium hexafluoride has been explained by low lying excited states which contribute a paramagnetic term to the shielding [13,14]. Since certain of the fluorines in vanadium pentafluoride also exhibit very large chemical shifts to low field [15], and low lying excited states are unlikely for this compound, it is possible that the low field chemical shift does not derive from a specific paramagnetic term. Complex formation is suggested by broadening and some displacement of the UF_6 fluorine resonance upon addition of an electron donor. The minimum in chemical shift for a ratio of 0.5:1 in the system UF_6 -acetonitrile, which is listed in Table 1, suggests that a complex $\text{UF}_6 \cdot 2\text{CH}_3\text{CN}$ is formed. This complex is insoluble in CFC_l_3 at low temperature but is soluble in $\text{SO}_2\text{Cl}_l\text{F}$. The complex dissociates upon pumping under vacuum and cannot be isolated. It is also thermally unstable, quickly reacting to give reduced uranium species at room temperature [9], and therefore is

unsuitable for enrichment studies. Fluorine exchange between UF_6 and (^{18}F)-labelled BF_3 has been observed in acetonitrile solution [16]. Fluorine exchange, by ^{19}F nmr, has been observed in the present study between UF_6 and AsF_5 or BF_3 , but not PF_5 , in SO_2 and SO_2Cl_2 as solvents, without any evidence of complex formation. There is no fluorine exchange nor complex formation with tetrabutylammonium (TBA) PF_6 or TBA TaF_6 , but complex formation is observed with TBA AsF_6 , TBA SbF_6 , TBA NbF_6 and TBA BF_4 .

The phase diagram for the system $SO_2-CF_2Cl_2$ is shown in Figure 1. Also included on the diagram are measurements made when UF_6 , or UF_6 -tetraethylammonium (TEA) fluoroborate are dissolved in the system. The partition of UF_6 between the two solvent phases is listed in Table 2 on the basis of grams/gram of solvent. The TEA salt remains almost exclusively in the sulfur dioxide rich phase. The solubility of UF_6 in the pure solvents is presented in Figure 2. Assuming that the solubilities in the pure solvents are a measure of the preference of UF_6 for that solvent, the distribution co-efficient between the two phases in the binary solvent system was calculated and is listed in Table 2 along with the experimental values. The above assumption seems to be reasonable since there is moderate agreement between the calculated and observed values. Similar measurements were also made at lower temperatures with one half an equivalent of TEA UF_6 for each equivalent of UF_6 . There is no appreciable change in distribution, as listed in Table 2, indicating that complex formation is at best very slight.

For a 3 stage enrichment cascade with $TBABF_4$ in the SO_2 rich phase, the average value of α is 1.0009 with U-235 enrichment in the CF_2Cl_2 rich phase. With TEA BF_4 as the added salt, α is 1.0014 per stage in a 2 stage cascade with U-235 depletion in the CF_2Cl_2 rich phase. It is therefore concluded that this procedure does not produce significant isotopic enrichment for uranium.

TABLE 1

Fluorine resonance results for the UF_6 -acetonitrile complex

Concentration Ratio $\text{UF}_6/\text{CH}_3\text{CN}$	T°C	Chemical Shift	Line Width Hz
0.3	- 80	753	1200
0.3	-120	742	300
0.5	- 80	747	620
0.5	-120	738	240
1.0	- 80	756	260
1.0	-120	746	90
2.0	- 80	757	210
2.0	-120	751	
3.0	- 80	758	320
∞	- 80	764	2

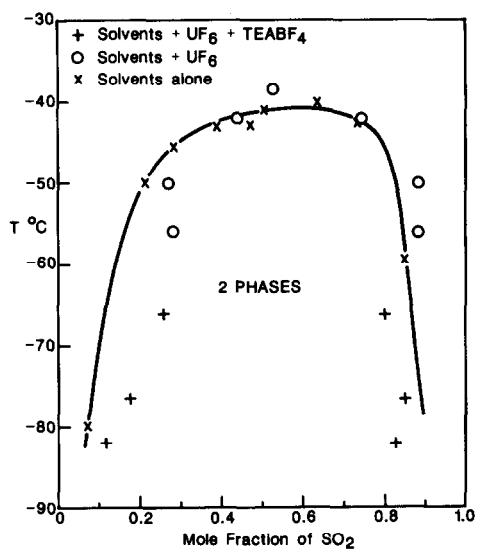
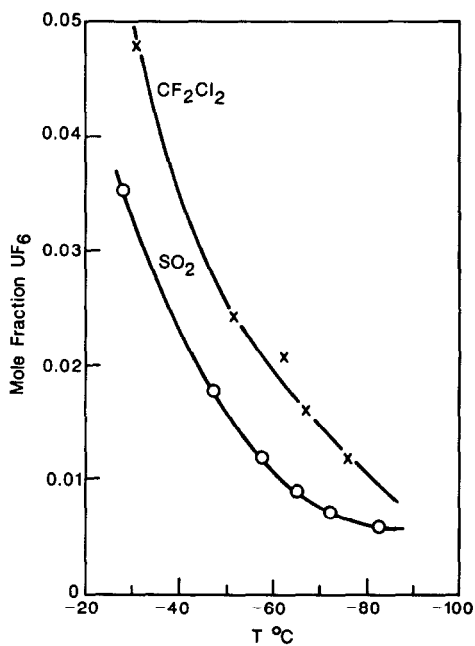
Fig. 1. Consolute temperatures and phase compositions for the system SO_2 - CF_2Cl_2 .

TABLE 2

Partition of UF_6 between the two phases in the system $\text{SO}_2\text{-CF}_2\text{Cl}_2$

T °C	UF_6 in CF_2Cl_2 Phase		Found (Solvents alone)	Found with TEA UF_6
	UF_6 in SO_2 Phase Calculated			
-42	.80		1.11	
-50	.92		0.62	
-57	.93		0.94	
-66	1.00			1.00
-77	0.96			0.78
-82	0.88			1.22

Fig. 2. The solubility of UF_6 in SO_2 and CF_2Cl_2 .

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