THE CHEMISTRY OF URANIUM FLUORIDES

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CONTENTS

1. Introduction 654
2. Uranium trifluoride 654
A. Physical properties 654
B. Chemical properties 654
3. Uranium tetrafluoride 655
A. Preparation 655
B. Physical and physicochemical properties 657
C. Chemical properties 658
4. Double fluorides 659
5. Intermediate fluorides 660
A. Physical and physicochemical properties 661
B. Chemical properties 661
6. Uranium hexafluoride 662
A. Methods of preparation 662
B. Physical properties 662
C. Thermochemical properties 663
D. Mechanical properties 663
E. Chemical properties 664
7. Uranyl fluoride 666
A. Physical properties 667
B. Chemical properties 667

1. INTRODUCTION

Uranium fluorides were prepared in the 19th and at the beginning of the 20th centuries [1,2], but little attention was paid to their properties, since they had no practical applications. The use of uranium for atomic fuel led to the problem of separating its isotopes. This was achieved in various ways, including a diffusion method based on the use of uranium hexafluoride [3]. The technology of the production of uranium hexafluoride and of metallic uranium enriched in the light isotope (^{235}U) is associated with the preparation of the lower fluorides, particularly the tetrafluoride. Atomic reactors do not achieve complete combustion of the fuel in the sense that the fissile material is not completely utilised; to achieve complete utilisation it is necessary to carry out several combustion cycles with intermediate regeneration cycles. Uranium hexafluoride is used in this field [4]. Methods for the extraction of uranium as UF_6 by dissolving the spent fuel in fused salts with subsequent fluorination by gaseous fluorine [5,6] are also being studied. This does not exhaust the applications of the fluorides, as their direct use as atomic fuel is at present being examined; for this they can be used either in molten [7] or in gaseous [8,9] form. These applications show the part which uranium fluorides play in the atomic energy industry. It is for this reason that the last twenty years have seen a marked increase in the study of their chemistry and technology.

2. URANIUM TRIFLUORIDE

Uranium trifluoride can be obtained by reducing anhydrous uranium tetrafluoride with hydrogen [10]. Traces of moisture and oxygen, which lead to contamination of the product with uranium oxides, must be completely absent.

A new method has recently been proposed [11] for preparing uranium trifluoride by reducing UF_4 with aluminium at high temperatures *in vacuo*. Uranium tetrafluoride, prepared by hydrofluorination of UO_2 at 650°, was mixed with aluminium filings and heated in a graphite crucible. The reaction

$$UF_4 + Al = UF_3 + AlF$$

begins at 800°, proceeds rapidly at 900°, and is complete in one and a half hours. Chemical analysis and X-ray diffraction showed that the reaction product is UF_3, containing less than 2% uranium dioxide. The AlF sublimed onto the walls of the apparatus. The residues contained ~90% UF_3.

A. Physical Properties

Uranium trifluoride is a violet-red crystalline substance with melting point 1495°. [12] At high temperatures disproportionation takes place:

$$4UF_3 = 3UF_4 + U.$$

D'Eye and Martin found the disproportionation slow at 1500° (~20% in 1 h).

From X-ray powder patterns, Zachariasen [13] found the uranium atoms in this compound to be hexagonal close-packed, with $a_0 = 4.146 \pm 0.003$ Å, $c_0 = 7.348 \pm 0.004$ Å, space group $P6_3/mmc$, with two UF_3 molecules in the unit cell. Uranium trifluoride is isomorphous with the fluorides of lanthanum, praseodymium, cerium, and neodymium [14]. Later, Staritzky and Douglas [15] determined the lattice parameters of UF_3 from X-ray oscillation photographs: $a = 7.179$ Å, $c = 7.345$ Å (±0.001 Å); $c/a = 1.023$, ρ (calc.) = = 8.965, $Z = 6$, space group $P6_3/mcm$. Isomorphism of uranium trifluoride with the fluorides of the rare-earth elements has been confirmed [14] and the data of Zachariasen [13], who proposed a different structure for UF_3, have been refuted.

B. Chemical Properties

Uranium trifluoride is not hygroscopic, but is affected by moist air. When heated in air it is oxidised to oxide fluoride and at 900° is converted to U_3O_8. Disproportionation takes place on heating in an inert atmosphere.

It is insoluble in water but is oxidised appreciably to U^V, the rate of this reaction increasing considerably with increasing temperature. UF_3 is sparingly soluble in acids,

but in the presence of oxidising agents it goes into solution as UO_2F_2. The ability of acids to dissolve UF_3 increases in the order $HCl < H_2SO_4 < HNO_3$. The presence of boric acid facilitates dissolution. The reaction of uranium trifluoride with chlorine at 350° yields $UClF_3$.[16,17] Fluorine and other fluorinating agents (ClF_3, BrF_3, etc.) react readily with UF_3 to form uranium hexafluoride.

The reaction of UF_3 with metal fluorides has been studied. Thus the UF_3–BaF_2 system has been studied by X-ray diffraction, thermal analysis, and density measurement[12]. The solid solution of UF_3 in BaF_2 contains up to ~50 mole % UF_3, the lattice parameter a for BaF_2 decreasing from 6.189 kX to 6.034 kX†. The conjugate solid solution of BaF_2 in UF_3 contains ~20 mole % BaF_2. The densities found for the solid solutions indicate random distribution of the U^{3+} and Ba^{2+} cations in the cationic positions of the UF_3 lattice, the anionic lattice being incomplete. Pure UF_3 is hexagonal, a = 4.131 kX, c = 7.335 kX. The melting point of BaF_2 increases on formation of the solid solutions. A peritectic appears to exist at 1400°. UF_3 can also form solid solutions with SrF_2; for the specimen with 33 mole % UF_3 in SrF_2, a = 5.821 ± 0.005 kX

3. URANIUM TETRAFLUORIDE

A. Preparation

The existing methods can be reduced to three main types. The first is based on preparation of uranium tetrafluoride from aqueous solutions of tetravalent uranium by the addition of fluoride ions to the solution. The second is based on direct fluorination of various tetravalent uranium compounds with hydrogen fluoride, and the third on preparation of uranium tetrafluoride from the hexafluoride.

The first papers elucidating the conditions for the preparation of uranium tetrafluoride were those of Bolton[1], who established that addition of hydrofluoric acid to uranium tetrachloride solution precipitates the tetrafluoride, and that the action of hydrofluoric acid on U_3O_8 yields a mixture of tetrafluoride and uranyl fluoride

$$U_3O_8+8HF=UF_4+2UO_2F_2+4H_2O.$$

Bolton later showed that a precipitate of the tetrafluoride can be obtained by reducing a boiling solution of uranyl fluoride with stannous chloride or by reducing ammonium uranate with ammonium carbonate in the presence of hydrofluoric acid.

Allen *et al.*[18,19] studied a number of reducing agents: $SnCl_2$, CuCl, $CrCl_3$, $TiCl_3$, and SO_2, for the preparation of U^{IV}. They found that all these compounds are effective, except sulphur dioxide, which does not reduce uranium, even when excess fluoride is present. It was found, however, that in the presence of Cu^{2+} ions at high temperatures, SO_2 reduces U^{VI} to U^{IV} as a result of the preliminary reduction of Cu^{2+} to Cu^{+}, which then reduces the uranium.

Methods based on the direct reduction of various uranium salts in the presence of fluoride ions are of particular interest. Thus the passage of SO_2 through a solution of uranyl nitrate in the presence of HCOOH and NH_4F (or NaF) leads to reduction of the uranyl nitrate[20] according to the equation:

$$UO_2(NO_3)_2+2SO_2+HCOOH+5NH_4F=NH_4UF_5+2NH_4NO_3+2NH_4HSO_3+CO_2.$$

† 1 kX = 1.002 Å.

The rate of reaction increases with increase in temperature. The resulting NH_4UF_5 precipitate, when heated to 450°, decomposes to UF_4 and NH_4F.

A method has been proposed for preparing uranium tetrafluoride from solutions of uranyl nitrate in the presence of HF.[21] Rongalite ($NaHSO_2.CH_2O.2H_2O$) is recommended as reducing agent. Rongalite reduces hexavalent uranium in uranyl nitrate solution even at room temperature, but the reaction is slow in the absence of acid. Hydrogen ions accelerate the reaction, probably as a result of the process:

$$UO_2^{2+}+2H^++2e \longrightarrow UO^{2+}+H_2O.$$

Tetravalent uranium is precipitated quantitatively from solution as the fluoride. Reducing agents similar in character to sulphoxylate include thiourea dioxide, $(NH_2)_2CSO_2$, which has been used for the quantitative separation of platinum from solution[22]. Thionyl chloride and fluoride belong to the same group. A feature of all these compounds which distinguishes them from sulphoxylate is that reduction takes place without liberation of sulphur, and the solution is not contaminated by alkali metals.

Electrolytic methods for the reduction of U^{VI} solutions have recently been developed. Their chief advantage is that reduction takes place without introduction of foreign substances into the solution. Uranium can be precipitated from the reduced solutions in different hydrated forms, depending on the temperature: as $UF_4.\frac{3}{4}H_2O$ at 95°–100°, and as $UF_4.2\frac{1}{2}H_2O$ at room temperature. This method can also be used to prepare double fluorides of uranium[23]; the double fluoride is precipitated in the cathode compartment by adding hydrofluoric acid and ammonium fluoride. Thermal decomposition of the resulting ammonium salt yields pure uranium tetrafluoride.

Most organic compounds do not reduce uranyl compounds under ordinary conditions, but reduction is possible in sunlight. Photo-reactions take place in, for example, solutions of methyl or ethyl alcohols, ethers, and glycol. In the presence of fluoride ions the reduction takes place with formation of tetrafluoride[24,25].

Uranium tetrafluoride is also obtained by electrolysis of a solution of the hexafluoride in water[26]. When UF_6 is dissolved in water, hydrolysis takes place with the formation of UO_2F_2 and HF. This solution contains sufficient fluoride ions for the formation of UF_4. Technological methods for the preparation of UF_4 and NH_4UF_5 or $NaUF_5$, based on electrolytic reduction in cells with diaphragms of ion-exchange membranes, have been described[27–30].

The most popular methods in uranium tetrafluoride technology are those in which purified U_3O_8[31–33] or uranates[34] are dissolved in mineral acids. The resulting solutions are reduced (for example with $SnCl_2$) and the UF_4 is precipitated with hydrofluoric acid. Methods based on the direct reaction of uranium dioxide with hydrofluoric acid[35–37] have recently found extensive application. They provide for the use of UO_2 obtained from UO_3 by reduction with hydrogen. The uranium dioxide, in either tablet or powder form, is fluorinated with 40% hydrofluoric acid. Uranium tetrafluoride can be obtained by heating a suspension of U_3O_8 in aqueous hydrofluoric acid solution to boiling, and then adding a reducing agent ($SnCl_2$).[38]

Methods of the second type are based on the preparation of uranium tetrafluoride from uranium dioxide and hydrogen fluoride. A number of papers[39–43] describe the fluorination of uranium dioxide with gaseous hydrogen fluoride at high

temperature. At the Second International Conference on the Peaceful Uses of Atomic Energy, brief details were given of methods which can be used under industrial or laboratory conditions for the preparation of UF_4 by the action of gaseous hydrogen fluoride on uranium dioxide at 600°–700°.[44-48] The most important feature of the proposed methods is the design of the apparatus for the fluorination, which can be carried out in a suspended layer, with tablets, or in a vibratory apparatus. Ammonium hydrogen fluoride can also be used as fluorinating agent[49,50].

Another group of methods involves preparation of uranium tetrafluoride from the trioxide by simultaneous reduction and fluorination. The freons CCl_2F_2,[51,52] $CFCl_3$,[52] $C_2Cl_4F_2$, $CClF_3$, $C_2Cl_3F_3$, and $CHCl_2F$[53] are used for this purpose. For freon-12 (CCl_2F_2) the process is:

$$UO_3+2CCl_2F_2 \xrightarrow{360°-380°} UF_4+CO_2+COCl_2+Cl_2.$$

Fluorination with freon-12 [54,55] has been proposed for a technological scheme in which the uranium in solution is separated from impurities by means of hydrogen peroxide. This is also possible in the presence of fluoride ions; a sparingly soluble peroxofluoro compound of the type $3NH_4F.4UO_4$ or $(NH_4)_3U_4O_{16}F_3$ is formed. This compound is dried at 110° and heated at 450°–550° in a current of freon to yield the tetrafluoride:

$$3NH_4F\cdot4UO_4+{}^{13}/_3CCl_2F_2=4UF_4+3NH_3+2O_2+4CO_2+4Cl_2+{}^5/_2COCl_2+{}^3/_2H_2O.$$

NH_3, CO_2, and other volatile compounds are liberated, leaving the UF_4 as a crystalline mass. Pure uranium tetrafluoride can also be obtained by an analogous method from the double ammonium compounds (for example NH_4UF_5) by decomposing them at 400°–600°, when ammonium fluoride sublimes away[56].

The third type of method for preparing uranium tetrafluoride is based on reduction of the hexafluoride. Hydrogen can be used[57], reduction taking place at 250°–400°. It occurs at a measurable rate[58]. At 25° the reaction is ~30% complete after 30 min. The quantity of hydrogen taken for the reaction corresponds to a calculated $H_2:UF_6$ ratio of 3:1. Uranium hexafluoride can be reduced to tetrafluoride by heating with gaseous HCl, HBr, or HI.[59,60] The reaction with HBr takes place at 100°, and that with HCl at 300°. Ethylene, trichloroethylene, propane, ammonia, $SiCl_4$, PCl_3, etc. can be used for the reduction. Smiley and Brater[57] studied direct reduction of UF_6 to UF_4 with trichloroethylene, carrying it out in both the liquid and gaseous phases in the range 74°–480°. The uranium hexafluoride was completely reduced, but the resulting tetrafluoride was contaminated with carbon, hexachlorobenzene, and other impurities.

The most efficient reducing agent for uranium hexafluoride is carbon tetrachloride, which reduces it to UF_4 rapidly at 100°–200°.[61] The reaction was carried out in an autoclave at 150°:

$$UF_6+2CCl_4=UF_4+Cl_2+2CCl_3F.$$

The concentration of intermediate fluorides UF_5, U_2F_9, and U_4F_{17} was reduced to a minimum (~1%) by removing the volatile products before the end of the reaction by reheating to the initial temperature. The optimum ratio of uranium hexafluoride to carbon tetrachloride was 1:4. The reaction involves formation of chlorofluoromethanes as intermediate products and is apparently autocatalytic; traces of UF_4 accelerate the reaction. The resulting uranium tetrafluoride was kept in a current of air at 120° to remove adsorbed gases. The authors established that the reaction takes place sufficiently rapidly at atmospheric pressure and can be used in industry for the continuous treatment of large quantities of UF_6 enriched in the light isotope.

Crystal hydrates of uranium tetrafluoride. A number of hydrates of uranium tetrafluoride have been described. Bolton[1] found that addition of hydrofluoric acid to uranyl chloride solution yielded a precipitate which after drying *in vacuo* or in air at 100° had the composition $UF_4.H_2O$. Khlopin and Gerling[62] prepared $UF_4.2H_2O$ by electrochemical reduction of uranyl sulphate in hydrofluoric acid. When this hydrate was dried over $CaCl_2$ or concentrated sulphuric acid, or by heating to constant weight at 100°–105°, $UF_4.\frac{1}{2}H_2O$ was obtained. Khlopin and Yashchenko[63] studied the physicochemical properties of the tetrafluoride prepared under various conditions and established that the air-dried tetrafluoride obtained by the electrochemical reduction of UO_2SO_4 solution in hydrofluoric acid solutions of concentrations from 4 to 20% always has the composition $UF_4.2\frac{1}{2}H_2O$, irrespective of the method of preparation. When this hydrate is dried to constant weight at 100°–105°, a compound of composition $UF_4.\frac{1}{2}H_2O$ is obtained.

Popov and Gagarinskii[64] established that the stable crystal hydrate is $UF_4.2\frac{1}{2}H_2O$, and that all crystal hydrates of lower water content are gradually converted to this form. Dawson *et al.*[65] found that UF_4 forms two hydrates: a higher hydrate $UF_4.2\frac{1}{2}H_2O$ with orthorhombic structure and a lower hydrate $UF_4.nH_2O$ with $0.5 < n < 2$ and a pseudo-cubic structure. The higher hydrate $UF_4.2\frac{1}{2}H_2O$ is stable *in vacuo* at 25° and in air up to 100°. Above this temperature it loses water rapidly to yield UF_4. With increase in temperature the hydrate $UF_4.2\frac{1}{2}H_2O$ loses water to give $UF_4.\frac{1}{2}H_2O$. The dehydration of $UF_4.\frac{1}{2}H_2O$ is much slower than the initial loss of water. Part of the water can be removed from the pseudo-cubic hydrate with dry methanol, whereas under the same conditions only adsorbed water can be removed from $UF_4.2\frac{1}{2}H_2O$. The hydrate $UF_4.2\frac{1}{2}H_2O$ is formed from the lower hydrate by placing it in 2–10% hydrofluoric acid.

There are reports on the relationship between the temperature of precipitation of UF_4 from solution and the composition of the resulting hydrates[26]. $UF_4.2\frac{1}{2}H_2O$ is formed below 40° and the monohydrate above 60°. Between 40° and 60° a mixture of the two hydrates is formed. Allen *et al.*[18,19] obtained $UF_4.\frac{3}{4}H_2O$ at 95°. The quantity of hydrate water in the uranium tetrafluoride molecule decreases with increase in the temperature of precipitation.

From X-ray diffraction, calorimetric, and tensimetric studies, Gagarinskii and Mashirev[66] concluded that the lower crystal hydrate of uranium tetrafluoride, with pseudo-cubic structure, previously assumed[65] to be $UF_4.nH_2O$ ($0.5 < n < 2$) has the composition $UF_4.0.4H_2O$. The water in excess of 0.4 molecules is not chemically combined with the UF_4 and does not form part of the composition of the crystal hydrate. When the lower crystal hydrate of uranium tetrafluoride is dehydrated *in vacuo* below 225°, the resulting phase retains a structure similar to that of the original compound. Hydration of the dehydrated salts obtained from various uranium tetrafluoride crystal hydrates gives the crystal hydrate from which the anhydrous salt was obtained. Thus, dehydration of $UF_4.2\frac{1}{2}H_2O$ yields a phase which retains a structure similar to that of the original hydrate, and this ensures that introduction of water into the lattice (the reverse process) gives the original compound. Anhydrous UF_4 prepared at high temperatures is not hydrated.

Dawson *et al.*[65] found from the thermogravimetric curve that the conversion of $UF_4 \cdot \frac{1}{2}H_2O$ to UF_4 takes place more slowly than the conversion of $UF_4 \cdot 2\frac{1}{2}H_2O$ to $UF_4 \cdot \frac{1}{2}H_2O$. A similar observation was made by Gagarinskii and Mashirev[66], who established that in the dehydration of $UF_4 \cdot 2\frac{1}{2}H_2O$, only that fraction of the water in excess of 0.4 moles per mole of UF_4 is removed fairly rapidly. As the water content is reduced to approximately 0.4 moles per mole of uranium tetrafluoride, almost no further dehydration takes place at 95°. Aqueous vapour pressures were measured at different water contents for specimens of partially dehydrated $UF_4 \cdot 2\frac{1}{2}H_2O$ at 95°. The hydrate $UF_4 \cdot 0.4H_2O$ is very stable, and a temperature of 400°–500° is required for its decomposition. Dehydration of crystal hydrates of uranium tetrafluoride is complicated by the two side reactions[18]:

$$UF_4 + 2H_2O \rightleftarrows UO_2 + 4HF,$$

$$2UF_4 + O_2 + 2H_2O \rightleftarrows 2UO_2F_2 + 4HF.$$

Both these reactions take place readily at the high temperatures necessary to dehydrate uranium tetrafluoride crystal hydrates. It is thus very important to know the course of each individual reaction.

B. Physical and Physicochemical Properties

Uranium tetrafluoride is a crystalline solid, usually green, which is precipitated from aqueous solutions in two modifications, a coarse-grained green form and a finer pale blue form[63,64], which can be readily separated by elutriation.

The vapour pressure of uranium tetrafluoride was measured by Popov *et al.*[67] by a flow method. The carrier gas was argon, previously purified from oxygen and water vapour. Spectroscopic analysis showed that the uranium tetrafluoride specimen contained 0.01% iron and up to 0.001% each of silicon, magnesium, and calcium. They established that the vapour pressure of uranium tetrafluoride in equilibrium with the solid salt at 875°, 900°, and 950° satisfies the equation:

$$\log P_{mm} = 12.945 - 16\,140/T$$

The discrepancies between experimental and calculated values of the pressure at 875°, 900°, and 950° were +2.0%, -2.5%, and +4.5% respectively. The vapour pressures of UF_4 in equilibrium with the liquid at 975° and 1000° lie on the straight line given by:

$$\log P_{mm} = 8.003 - 10\,000/T.$$

The intersection of the two straight lines gives 969° for the melting point of uranium tetrafluoride, which agrees satisfactorily with the value 960° ± 5°, found from the heating curve[10].

The structure of UF_4 was studied by Zachariasen[13]. X-Ray single-crystal diffraction patterns for uranium tetrafluoride showed that it is monoclinic with twelve molecules in the unit cell, $a = 12.79 \pm 0.06$ kX, $b = 10.72 \pm 0.05$ kX, $c = 8.39 \pm 0.05$ kX, $\beta = 126°10' \pm 30'$, space group $C2/c$.

The higher crystal hydrate $UF_4 \cdot 2\frac{1}{2}H_2O$ is orthorhombic and contains eight molecules in the unit cell, $a = 12.75 \pm 0.04$ Å, $b = 11.12 \pm 0.04$ Å, $c = 7.05 \pm 0.03$ Å, space group $Pnam$. $UF_4 \cdot nH_2O$ ($n = 0.75$–2) has a pseudo-cubic lattice with $a = 5.69 \pm 0.01$ kX, space group $Fm3m(O_h^5)$.[65]

The heat capacity, enthalpy, and entropy of uranium tetrafluoride have been determined[68] at temperatures from 20° to 350°K. The UF_4 specimen contained 2% UO_2F_2. It was assumed that the heat capacity of this impurity does not differ greatly from that of uranium tetrafluoride and introduces no serious error. The values of C_p were calculated from a smooth curve drawn through the experimental points. The enthalpies were calculated by integrating the function $dH = C_{sat}\,dT + V dP$, where C_{sat} is the heat capacity of the condensed phase in equilibrium with the saturated vapour, using Simpson's rule, with the values obtained for C. The entropies were obtained by the same method, integrating the function $dS = (C/T)dT$. Measurements of the heat capacity of uranium tetrafluoride were repeated by Osborne *et al.*[69], using uranium tetrafluoride containing 0.05% UO_2F_2. The heat capacity was measured from 5° to 300°K in an adiabatic calorimeter. C_p, $H^0 - H_5^0$, and $S^0 - S_5^0$ at 298.16°K are 27.37 ± 0.03 cal deg^{-1} mole^{-1}, 5389 ± 6 cal × × mole^{-1}, and 36.13 ± 0.04 cal deg^{-1} mole^{-1} respectively.

Lohr *et al.*[70] determined the magnetic entropy of uranium tetrafluoride from the difference between the entropies of UF_4 and ThF_4 assuming that, owing to diamagnetism, the entropy of ThF_4 is determined entirely by the lattice vibrations. The isomorphism, the slight (2.5%) difference in the unit cell volumes, and the small difference between the molecular weights of UF_4 and ThF_4 suggest that for these substances the entropies due to lattice vibrations should be close to one another. The magnetic entropy was found to be 2.17 e.u. at 298.16°K, that is, very close to the value of the spin magnetic entropy: $R\log(2S + 1) = R\log 3 = 2.18$.

The heat of hydration of uranium tetrafluoride

$$UF_4(\text{solid}) + 2\tfrac{1}{2}H_2O(\text{liquid}) = UF_4 \cdot 2\tfrac{1}{2}H_2O(\text{solid}) + \bar{Q},$$

was determined by an adiabatic method[71] for two specimens, obtained by dehydrating $UF_4 \cdot 2\frac{1}{2}H_2O$ *in vacuo* with gradual heating to 225°. The first specimen contained 0.28% H_2O, corresponding to the presence of 2.23% $UF_4 \cdot 2\frac{1}{2}H_2O$, and the second specimen was anhydrous. The heat of hydration was found to be 8.21 ± 0.02 kcal mole^{-1} UF_4 at 20°. The authors checked this heat of hydration with two specimens of salt containing 2.5 and 2.43 moles H_2O respectively. In the first case the heat was found to be zero, while in the second case it corresponded to the heat evolved for hydration of $UF_4 \cdot 2.43H_2O$ to $UF_4 \cdot 2.5H_2O$. The dissociation pressure of $UF_4 \cdot 2\frac{1}{2}H_2O$ was measured by Popov and Gagarinskii[64], who showed that the average dissociation pressure (mm Hg) of $UF_4 \cdot 2\frac{1}{2}H_2O$ in the temperature range 20°–35° satisfies the equation:

$$\log P_{mm} = 10.035 \pm 0.003 - \frac{2920 \pm 3}{T}.$$

The dissociation pressure of the lower hydrate $UF_4 \cdot 0.4H_2O$ is small[66], even at 95°, and much less than that of $UF_4 \cdot 2\frac{1}{2}H_2O$. The heat of hydration of UF_4 with liquid water, calculated from the dissociation pressure of $UF_4 \cdot 2\frac{1}{2}H_2O$ at various temperatures[64], was found to be 7.23 kcal mole^{-1}. Direct determination of the heat of hydration of UF_4 (obtained by dehydrating $UF_4 \cdot 0.4H_2O$) on hydration to $UF_4 \cdot 0.4H_2O$, gave 6.09 ± 0.01 kcal mole^{-1}.[66] The heat of hydration of UF_4 to $UF_4 \cdot 2\frac{1}{2}H_2O$ is 8.21 ± 0.02 kcal mole^{-1}. The authors consider that in this case the phases being hydrated have different structures. The discrepancy between the calorimetric heat of hydration of UF_4 to $UF_4 \cdot 2\frac{1}{2}H_2O$ (8.21 kcal mole^{-1}) and the same heat of hydration calculated from the dissociation pressure of the crystal hydrate $UF_4 \cdot 2\frac{1}{2}H_2O$ (7.23 kcal mole^{-1}) arises because the latter refers not to the hydration of UF_4 but of a solid solution containing water.

C. Chemical Properties

Uranium tetrafluoride is sparingly soluble in water. The solubility in water, found by different authors, ranges from 1×10^{-4} M to 1.9×10^{-3} M. The most reliable value, obtained by Khlopin and Yashchenko[63] at 25° under conditions precluding oxidation, is 1.7×10^{-4} M.

A solution of $UF_4.2\frac{1}{2}H_2O$ in water gives an acid reaction. This has been attributed[63] to part of the water being not simply water of crystallisation but directly coordinated to the uranium. Thus it has been suggested that $UF_4.2\frac{1}{2}H_2O$ in aqueous solution is an acid capable of losing a proton. The pH was the same for different crystal hydrates and corresponded very closely to the presence in solution of two hydrogen ions per g-atom of uranium, agreeing with the coordination formula $H_2[UF_4(OH)_2]$. This formula was not considered to be proved conclusively. The equilibrium constants for the reactions

$$U^{4+} + HF \rightleftarrows UF^{3+} + H^+,$$

$$U^{4+} + 2HF \rightleftarrows UF_2^{2+} + 2H^+,$$

were estimated by Day *et al.*[72] as 10^6 and 10^8 respectively.

Uranium tetrafluoride is sparingly soluble in acids, the solubility increasing with increasing temperature. The solubility in 2 *N* H_2SO_4 is 2.9 g litre^{-1}. It is less in concentrated sulphuric acid than in dilute. Uranium tetrafluoride dissolves in sulphuric acid, when it is heated to fumes of SO_3 and subsequently diluted with water.

It is readily soluble in mineral acids in the presence of boric acid, owing to formation of the BF_4^- ion, and in a mixture of dilute sulphuric acid and silica, in which case $U(SO_4)_2$ and H_2SiF_6 are formed. It also dissolves in hot phosphoric acid. Nitric acid dissolves uranium tetrafluoride with oxidation of U^{4+} to UO_2^{2+}. The addition of boric acid, as with other acids, increases the solvent action of nitric acid.

Uranium tetrafluoride is soluble in certain electrolytes, for example, aluminium salts. This is due to the formation of the stable AlF_2^+ complex ion, which binds the fluoride ion and thus reduces its concentration. Uranium tetrafluoride prepared by the high-temperature method and containing no hydrate water is chemically inactive.

The sensitivity of uranium tetrafluoride to water vapour was studied in the temperature range 100°–500°.[73] It was shown that water vapour acts on uranium tetrafluoride above 100°. The constant for the reaction

$$UF_4 + 2H_2O \rightleftarrows UO_2 + 4HF,$$

and the heat of this reaction (-30 kcal) have been determined. The decomposition of UF_4 by water vapour is widely used in its analysis[74].

The reaction between uranium tetrafluoride and a current of dry oxygen[75] at 600°–900° can be used to prepare uranium hexafluoride under laboratory conditions. An interesting feature is that the preparation of UF_6 in this way does not require free fluorine. The main reaction

$$2UF_4 + O_2 = UF_6 + UO_2F_2,$$

starts above 750° and is accompanied by side reactions, for example, $UF_4 + UF_6 \rightleftharpoons 2UF_5$. The latter leads to an increased consumption of UF_4, condensation of UF_4 and UF_5 in the colder zones, and contamination of the uranium hexafluoride with UF_5. The rate of vaporisation of uranium tetrafluoride at 600°–900° is very low (1/50th of the rate of the main reaction). The rate constant for the decomposition of uranyl fluoride:

$$3UO_2F_2 = UF_6 + {}^2/_3U_3O_8 + {}^1/_3O_2,$$

is 7.6×10^{-5}–6.7×10^{-5} min^{-1} at 700° and 7.7×10^{-4}–$7.8 \times \times 10^{-4}$ min^{-1} at 800°. The rate constant for this reaction is fairly low at temperatures below 800° and is 1/50th of the rate constant for the reaction of uranium tetrafluoride with oxygen. The activation energy calculated from these data is 50 kcal mole^{-1}.

The kinetics of oxidation of uranium tetrafluoride with oxygen have been studied[76]. The rate of the reaction of uranium tetrafluoride with dry oxygen was determined by a thermogravimetric method in the temperature range 550°–815°. The reaction is first order. The reaction rate depends on the partial pressure of oxygen, and the rate constant is given by the expression $k = 8.31 \times 10^6 \times \times \exp(-45\,900/RT)$, where k has units of moles min^{-1} m^{-2}. For the reaction of UF_4 with dry air, the rate constant is given by $k_a = 8.24 \times 10^6 \times \exp(-47\,000/RT)$, which satisfies the relationship $k_a = 0.55\ k$ at each temperature. In calculating the rate constants, sublimation of uranium tetrafluoride and decomposition of uranyl fluoride were neglected. At each temperature[75], the rate of sublimation was 50 times less than the rate of the reaction with oxygen. The rate of decomposition of uranyl fluoride is also insignificant in the temperature range studied. Thus at temperatures where UF_5 is not formed the only reaction is

$$2UF_4 + O_2 = UF_6 + UO_2F_2.$$

The side reaction $UF_4 + UF_6 = 2UF_5$ was detected only above 750°. The quantity of uranium tetrafluoride taking part in this reaction increases from 1% at 750° to 30% at 815°. The standard heat of the reaction, estimated from the equation $\Delta H^0 = 22\,060 + 27.1\,T - 17.1 \times 10^{-3}\,T^2 + 158.3 \times \times 10^4\,T^{-1}$, was found to be ~ -5 kcal (mole UF_4)$^{-1}$ between 550° and 815°.

Uranium tetrafluoride reacts with elementary fluorine. Labaton and Johnson[77] established that the preparation of UF_6 from the tetrafluoride involves formation of intermediate fluorides, which undergo further fluorination but at a lower rate than the rate of fluorination of the tetrafluoride.

Halogen fluorides, such as ClF_3 and BrF_3, react with uranium tetrafluoride. Its reaction with chlorine trifluoride was studied at temperatures from 17° to 193° by the change in weight of the solid phase[78]. The reaction rate passed through a maximum at 105°, decreased to a minimum at 148°, and subsequently increased. The decrease in rate between 100° and 150° arises because the reaction of chlorine trifluoride with the intermediate fluorides is probably slower than the reaction with uranium tetrafluoride, as was observed with fluorine.

At 17°–58° and 156°–194°, the Arrhenius equation relating rate constants and reaction temperature is applicable within the limits of experimental error. The activation energies of the fluorination reaction found for uranium tetrafluoride obtained by hydrofluorination are 5.6 kcal × × mole^{-1} and 3.4 kcal mole^{-1}. It was shown that close to room temperature a linear relationship exists between the reaction rate and the partial pressure of chlorine trifluoride. In the range of gas velocities studied, the linear velocity of the gas did not influence the rate of reaction. Comparison of the results for the reaction between uranium tetrafluoride and chlorine trifluoride with those for the reaction with fluorine shows that the former takes place at

much lower temperatures than the latter. For a given specimen, the activation energy is also lower than that for the reaction with fluorine (5.6 kcal mole^{-1} and 3.4 kcal mole^{-1} compared with 19.1 kcal mole^{-1}). Comparison of the rate constants after reduction of the values to the same partial pressure shows that at 265°, fluorination by chlorine trifluoride is 160 times faster than fluorination by fluorine. At higher temperatures the difference between the rates would be less, because the reaction of uranium tetrafluoride with fluorine increases more rapidly than that of the reaction with chlorine trifluoride.

The reaction of uranium tetrafluoride with bromine trifluoride was shown by Sharpe and Emeléus[79] to take place rapidly and quantitatively with formation of uranium hexafluoride. Uranium tetrafluoride reacts with CCl_4 [17] at 420° in an inert atmosphere. The reaction yields uranium monochlorotrifluoride $UClF_3$, which is also obtained by heating uranium tetrafluoride and tetrachloride in an inert atmosphere.

When a mixture of UF_4 and $CaSO_4$ in the molar ratio 1 : 2 is heated in a graphite crucible in an atmosphere of helium to 715° – 730°, a vigorous reaction takes place and is complete in 3 h.[80] The main products are CaF_2, U_3O_8, SO_2, and SO_3, identified by X-ray diffraction and chemical analysis. The loss in weight corresponds to the equation:

$$6CaSO_4+3UF_4=6CaF_2+U_3O_8+2SO_2+4SO_3.$$

The quantity of SO_2 evolved in the reaction exceeds that required by this equation. This is apprently due to reduction of the SO_3 by the crucible material. The reaction products were, moreover, found to contain a small quantity of $CaUO_4$ and traces of UO_2F_2. The presence of these compounds is probably due to reaction of the intermediate product UO_3 with $CaSO_4$ and CaF_2 to form $CaUO_4$ and UO_2F_2:

$$CaSO_4+UO_3=CaUO_4+SO_3,$$

and

$$CaF_2+2UO_3=CaUO_4+UO_2F_2.$$

The importance of the tetrafluoride in the atomic energy industry is due to the fact that metallic uranium is obtained by a metallothermic process using calcium or magnesium[81]. Dubrovin and Evseev[82] concluded, on the basis of thermodynamic calculations, that the reduction of uranium tetrafluoride by magnesium at 1400° would take place almost completely to form metallic uranium and MgF_2, since the equilibrium vapour pressure of magnesium at this temperature is very low (0.8 mm Hg). The higher the magnesium vapour pressure, the more rapid the reduction, estimated to be complete in a few tenths of a second.

4. DOUBLE FLUORIDES

Double fluorides are obtained by precipitating uranium tetrafluoride from aqueous solution in the presence of metal fluorides or by fusing UF_4 with a metal fluoride. The ammonium, sodium, and potassium double fluorides have been most studied.

Khlopin and Gerling[62] and Khlopin and Yashchenko[63] synthesised the salt $UF_4.NH_4F$ by the electrochemical reduction of a solution of uranyl fluoride in hydrofluoric acid in the presence of ammonium fluoride. The composition of the air-dried precipitate $NH_4UF_5.\frac{1}{2}H_2O$ remained almost unchanged on heating up to 105°. The electrical conductivity and pH of solutions of this compound were determined and used to calculate the molar conductance and solubility in water at 25° (1.4 M). The authors consider that the electrical conductivity and solution pH indicate that in aqueous solution NH_4UF_5 breaks down to ammonium fluoride and uranium fluoride. Alkalis readily decompose solutions of this compound. It dissolves slowly in hydrochloric, sulphuric, and nitric acids, and readily in concentrated solutions of Na_2CO_3, $NaHCO_3$, and $(NH_4)_2CO_3$.[83] Determination of the solubility is made difficult by the ready oxidation of U^{IV} to UO_2^{2+}; the presence of uranyl fluoride in solution prevents the double fluoride dissolving. Similar phenomena are observed for dissolution of NH_4UF_5 in solutions of ammonium and sodium carbonates. The solubilities for saturated solutions of NH_4UF_5 (calculated as anhydrous UF_4) in concentrated solutions of Na_2CO_3, $NaHCO_3$ (9.5%), and $(NH_4)_2CO_3$ are 6.6, 2.4, and 5.0 g per 100 ml of solution respectively. It was also observed that dilution of these solutions leads to hydrolysis with precipitation of hydrated uranium dioxide. Dilution with 6 to 12 times the volume of cold water yields a pale green precipitate which gradually becomes black. Dilution with hot water yields an immediate black precipitate. The reason for the different colours of the precipitate has not been established. The action of acetic acid on a carbonate solution of NH_4UF_5 yields a precipitate insoluble in excess acid. Oxalic acid does not yield a precipitate, owing to the formation of a readily soluble oxalate complex. On heating, carbonate solutions of the double fluoride undergo complete [in the case of $(NH_4)_2CO_3$] or partial (in the case of Na_2CO_3, etc.) decomposition with precipitation of uranium(IV) hydroxide.

Double compounds of the type $UF_4.nMF$ have been detected in a number of systems[5,6,84-89] studied in connection with the use of a mixture of molten fluorides for the extraction of uranium from spent fuel elements.

The $NaF-UF_4$ and $LiF-UF_4$ systems[88] have been studied by straightforward and differential thermal analysis, quenching, optical identification of solid phases, X-ray diffraction, and visual observation of polytherms. The $LiF-UF_4$ system (Fig. 1) contains only incongruently-melting compounds with peritectic points: $4LiF.UF_4$ with 26 mole % UF_4 at 500°; $7LiF.6UF_4$ with 40 mole % UF_4 at 610°, and $LiF.4UF_4$ with 57 mole % UF_4 at 775°. The eutectic of $4LiF.UF_4$ and $7LiF.6UF_4$ is formed at 27 mole % UF_4 at 490°. At 470° $4LiF.UF_4$ breaks down to LiF and $7LiF.6UF_4$. When specimens with 20–32 mole % UF_4 were quenched from temperatures > 490°, a metastable phase assumed to have the composition $3LiF.UF_4$ was formed.

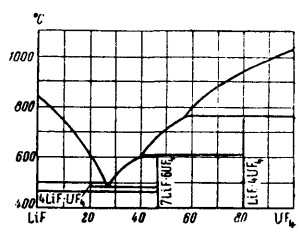


Fig. 1. The $LiF-UF_4$ system[88].

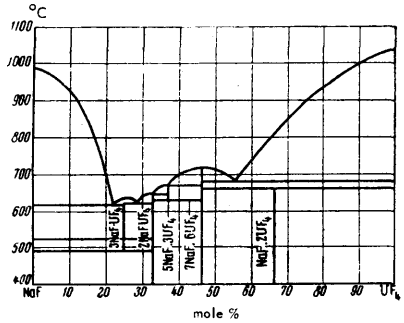


Fig. 2. The $NaF-UF_4$ system [88].

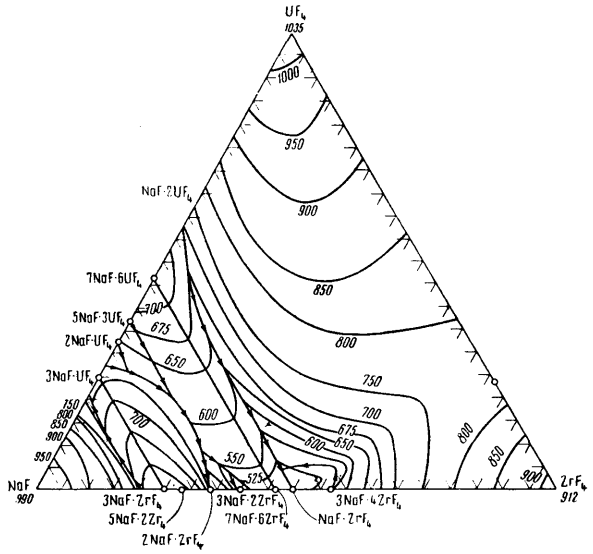


Fig. 3. The $NaF-ZrF_4-UF_4$ system [89].

The $NaF-UF_4$ system (Fig. 2) shows formation of the congruently-melting compounds $3NaF.UF_4$ at 625° and $7NaF.6UF_4$ at 718°, and incongruently-melting compounds with peritectic points, $2NaF.UF_4$ with 32.5 mole % UF_4 at 648° and $5NaF.3UF_4$ with 37 mole % UF_4 at 673°. Eutectics were found at 21.5 mole % UF_4 (618°), 28 mole % UF_4 (623°), and 56 mole % UF_4 (680°). The solid phase contains the compound $NaF.2UF_4$, which breaks down at 660° to $7NaF.6UF_4$ and UF_4. The compound $3NaF.UF_4$ undergoes a polymorphic transformation at 528°, and at 497° breaks down to NaF and $2NaF.UF_4$. The compound $5NaF.3UF_4$ breaks down at 630° to $2NaF.UF_4$ and $7NaF.6UF_4$. The α-$2NaF.UF_4$ phase described by Zachariasen [87] is in fact the compound $5NaF.3UF_4$, and the γ-$2NaF.UF_4$ phase is metastable. Barton *et al.* [88] deny the existence of the compound $NaF.UF_4$, the polymorphism of $2NaF.UF_4$, and the existence of solid solutions in the range 33.3–40 mole % UF_4, which were reported previously [87].

Phase equilibrium has been studied in the UF_4-ZrF_4 and $NaF-ZrF_4-UF_4$ systems [89]. Thermal, differential-thermal, microscope, optical, and X-ray diffraction studies, with chemical analysis of the phases isolated from the melt by filtration at high temperature, have been used to construct equilibrium diagrams for the UF_4-ZrF_4 and $NaF-ZrF_4-UF_4$ systems (Fig. 3). The UF_4-ZrF_4 system forms a continuous series of solid solutions with a minimum melting point of 765° at 77% ZrF_4. Sections of the ternary $3NaF.ZrF_4-3NaF.UF_4$ system and of the $7NaF.6ZrF_4-7NaF.6UF_4$ system consist of continuous solid solutions. The regions of primary deposition of the solid solutions $3NaF.U(Zr)F_4$, $7NaF.6U(Zr)F_4$, and $U(Zr)F_4$ occupy ~90% of the liquidus surface. No ternary eutectics or ternary compounds were detected.

The solubility of the inert gases He and Xe in an $NaF-ZrF_4-UF_4$ melt (50/46/4 mole %) was studied in the pressure range 0.5–2.0 atm at 600°, 700°, and 800°. [90] The dissolved gas was displaced from the fluoride melt by another inert gas and its concentration in the latter was measured by mass-spectrometry. It was found that the solubility increases linearly with pressure, decreases with decrease in atomic weight, and increased with temperature. The Henry constants $10^8 K$, in mole (cm of melt)$^{-3}$, at atmospheric pressure and 600°, 700°, and 800° are respectively 20, 27, and 41 for He, and 2.0, 4.0, and 6.5 for Xe.

5. INTERMEDIATE FLUORIDES

The intermediate fluorides are compounds of formula UF_n, where $4 < n \leq 5$. U_4F_{17} ($UF_{4.25}$), U_2F_9 ($UF_{4.5}$), and UF_5 have been reported as distinct compounds. Besides these, there exist substances with more arbitrary fluorine : :uranium ratios; this casts doubt on their individuality and suggests that fluoride ions have been introduced into the crystal structure of the tetrafluoride.

There are few references to methods of preparing these compounds. The earliest papers include a report by Ruff and Heinzelman [2] on the reaction between anhydrous liquid hydrogen fluoride and uranium pentachloride. The uranium pentafluoride obtained disproportionates to UF_6 and UF_4. This method was subsequently developed by Carignan [91], who treated the chlorides UCl_5 and UCl_6 with anhydrous HF at temperatures from -33° to +25°. The pentafluoride, was obtained and volatile reaction products were removed by heating *in vacuo*. The reaction involves halide conversion and reduction:

$$2UCl_6 + 10HF \rightarrow 2UF_5 + 10HCl + Cl_2.$$

Agron and Weller [92] reported conditions for the formation of U_4F_{17} by the reaction between UF_4 and UF_6. These conditions are defined by: $12.75\ T - T \log P \leq 7143$ and $13.68\ T - T \log P \geq 7315$, where T is expressed in °K and P is pressure of UF_6 vapour in mm Hg. Under other conditions, U_2F_9 and UF_5 in α- and β-modifications are formed.

A similar reaction can be carried out between the liquid hexafluoride and tetrafluoride. Reaction for 1 week at 100°–125° yields β-UF_5, but if the duration of reaction is insufficient for equilibrium to be reached, the product is U_2F_9.

Intermediate fluorides are formed on fluorination of the tetrafluoride, $UF_4 + \frac{1}{2}F_2 \rightarrow UF_5$. This reaction takes place at a temperature lower than that at which chiefly the hexafluoride is obtained (350°–360°). More details are being obtained. Labaton and Johnson[77] approached the chemistry of fluorination from the kinetic viewpoint. At 220°, no reaction takes place between fluorine and the tetrafluoride; at 300° and a hexafluoride pressure of 42 mm Hg, the reaction between UF_6 and UF_4 yields intermediate fluorides. Fluorides of composition $UF_{4.52}$–$UF_{4.12}$ were obtained, depending on the method of preparing the specimens used (dehydration of $UF_4.2\frac{1}{2}H_2O$, hydrofluorination of the dioxide). The same compositions were obtained in fluorination of UF_4 with fluorine. The formation of intermediate fluorides during the preparation of the hexafluoride is due to the concentration of fluorine being lower in the bulk of the tetrafluoride layer than at the surface, whereas the UF_6 concentration is sufficient for formation of intermediate fluorides by the reaction between UF_6 and UF_4. The rate of the reaction depends on the temperature. In accordance with the Arrhenius equation, the rate constants lie on a straight line plot of $\ln k$ *vs.* $1/T$, where k is the rate constant and T is in °K. The activation energies for three specimens of UF_4 lay in the range 15.5–19.9 kcal mole^{-1}, the higher value corresponding to specimens of greater crystalline complexity, as shown by X-ray diffraction. The formation of intermediate fluorides in the preparation of hexafluoride from tetrafluoride is, at first, the result of adsorption of fluorine on the surface of the particles of the substance being fluorinated and then penetration of the fluorine into the tetrafluoride lattice. The compositions of these compounds may not correspond to stoichiometric ratios.

TABLE 1. Crystal-chemical and thermodynamic characteristics of intermediate uranium fluorides.

Compound	Structure[93,94]	Thermodynamic characteristics[10]			Remarks
		$\Delta H_{298°}$, kcal mole^{-1}	$S_{298°}$, e.u.	$\Delta H_{298°}$, kcal mole^{-1}	
α-UF_5	tetragonal $a = 6.512 \pm 0.001$ Å $c = 4.463 \pm 0.001$ Å	-483.7 ± 1.3	48.0 ± 0.4	-458.2 ± 1.4	$\alpha \rightarrow \beta$ change not known
β-UF_5	tetragonal $a_1 = 11.450 \pm 0.002$ Å $c = 5.198 \pm 0.001$ Å	-485.2 ± 1.4	43.3 ± 0.5	-458.7 ± 1.5	$\alpha \rightarrow \beta$ change takes place at $t° > 125°$ with disproportionation pressure 1.76 mm Hg
U_2F_9	cubic, mixed $(U^{4+}_{0.5}, U^{5+}_{0.5})F_{4.5}$ or $(U^{4+}_{0.75}, U^{6+}_{0.25})F_{4.5}$ $a = 8.454 \pm 0.002$ Å	-933.8 ± 3	75.3 ± 0.6	-884.0 ± 3	
U_4F_{17}	not known	-1820 ± 4	149 ± 0.6	-1727.5 ± 4	black product; all uranium atoms structurally equivalent, indicating intermediate valency 4.5

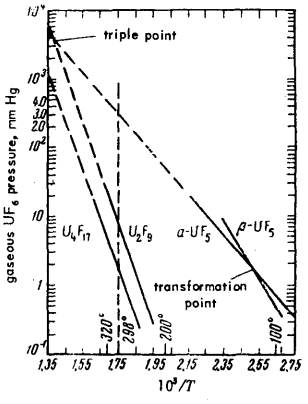


Fig. 4. Disproportionation pressure of U_4F_{17}, U_2F_9, α-UF_5, and β-UF_5[10].

A. Physical and Physicochemical Properties

This review of their preparation shows that intermediate fluorides should be regarded as comprising U_4F_{17} (probably), U_2F_9 (also obtained in a black modification), and UF_5 (α- and β-forms). Their crystal-chemical and thermodynamic data are given in Table 1.

B. Chemical Properties

A characteristic chemical property of the intermediate fluorides is disproportionation, which takes place on heating and in solution:

$$2UF_5 \rightleftarrows UF_4 + UF_6 \text{— thermal disproportionation,}$$

$$2UF_5 \xrightarrow{+2H_2O} UF_4 + UO_2F_2 + 4HF \text{— hydrolytic disproportionation.}$$

Both processes are connected with the uranium in the intermediate fluorides being present in both the hexavalent and tetravalent states. The thermal disproportionation has a definite pressure of volatile component (UF_6). Agron and Weller's results[92] lie on a straight line for log P *vs.* $1/T$ (Fig. 4). The diagram shows that the most stable compound is U_4F_{17}; at 300° its disproportionation pressure is ~1.5 mm, whereas that of α-UF_5 is ~400 mm.

Hydrolytic disproportionation takes place at different rates for different intermediate fluorides; U_4F_{17} is less reactive than U_2F_9 and UF_5, the hydrolytic disproportionation reaction in this case being:

$$2U_4F_{17} + 2H_2O \longrightarrow 7UF_4 + UO_2F_2 + 4HF.$$

Black U_2F_9 is affected by water only on boiling. Intermediate fluorides have been detected in the reduction of uranium hexafluoride to tetrafluoride, for example, by hydrogen or CCl_4. They thus take part in these processes and may be reduced to UF_4. These are all the available data on the chemical properties of these compounds.

6. URANIUM HEXAFLUORIDE

A. Methods of Preparation

The methods of preparing uranium hexafluoride can be classified according to the fluorinating agents employed. These include: 1) gaseous fluorine; 2) halogen fluorides, either liquid or gaseous (ClF_3, BrF_3, BrF_5, IF_7, etc.); 3) certain metal fluorides; 4) hydrogen fluoride.

Various uranium-containing materials are used for the preparation of the hexafluoride by means of gaseous fluorine. Ruff and Heinzelman[2] fluorinated metallic uranium or its carbide. Almost any uranium compound is fluorinated by fluorine under appropriate conditions to yield the hexafluoride, for example U_3O_8, UO_2, UF_4,[46,48,95,96] intermediate fluorides, uranyl fluoride[97], and sodium diuranate. Other uranium compounds proposed as starting materials include double salts of the type KUF_5 and K_2UF_6. Fluorination is carried out at 200°–400°.[98]

The next most important methods of fluorination are those based on the use of halogen fluorides. These reactions can be used in the condensed phase. For this reason liquid halogen fluorides have been widely used in fluorination technology[99–105]. Fluorination can be carried out both in the gaseous phase [for example ClF_3 (gas) + U(solid)] and in the condensed phase [for example BrF_3 (liquid) + U (solid)]. Chlorine trifluoride and bromine trifluoride and pentafluoride have been used for fluorination of metallic uranium.

Halogen fluorides are used chiefly for extracting uranium from the irradiated uranium heat-producing blocks of nuclear reactors[4,84,105–108]. Dissolution of the irradiated uranium in halogen fluorides yields volatile and non-volatile fluorides of the fission elements and plutonium tetrafluoride. The uranium fluoride is distilled from the non-volatile fluorides and the residue is brought into solution by treating with aluminium nitrate. This is based on the reaction proposed by one of the authors of this article[109]:

$$Al^{3+}+RF_n \longrightarrow AlF_2^+ + R^{n+} + (n-2)\,F^-,$$

where R is a fission element. Further extraction of this solution for plutonium and fission elements is possible using extracting agents stable to irradiation.

Halogen fluorides are used to prepare fluorides of a number of elements[110–114]. Their role as fluorinating agents is increasing as they have considerable advantages over elementary fluorine. The writers have synthesised a number of higher fluorides of transition elements by means of chlorine and bromine trifluorides and have shown the advantages of this method[115–117].

The reaction between certain higher metal fluorides and the compound to be fluorinated, for example UF_4, is also of interest. The addition of 2 moles of CoF_3 to 1 mole of UF_4 heated to 400° yields UF_6:

$$UF_4+2CoF_3=UF_6+2CoF_2.$$

The uranium hexafluoride is distilled off and the CoF_2 is regenerated by treatment with fluorine. Silver difluoride, palladium trifluoride, and platinum hexafluoride can be used in the same way.

The preparation of uranium hexafluoride using only hydrogen fluoride (without subsequent use of fluorine) is based on double decomposition with subsequent disproportionation. Ruff and Heinzelman[2] first prepared UF_6 in this way from uranium pentachloride:

$$UCl_5+5HF=UF_5+5HCl,$$
$$3UF_5 \xrightarrow{175^\circ} U_2F_9+UF_6,$$
$$2U_2F_9 \overset{200^\circ}{\rightleftarrows} 3UF_4+UF_6.$$

The uranium hexafluoride can readily be separated from the uranium tetrafluoride by heating, and from excess hydrogen fluoride by fractional distillation.

B. Physical Properties

Under ordinary conditions uranium hexafluoride is a white crystalline volatile substance which sublimes without melting. The known actinide hexafluorides UF_6, NpF_6, and PuF_6 have similar chemical and physical properties, but uranium hexafluoride is also the analogue of the higher fluorides of the chromium subgroup elements, MoF_6 and WF_6. A characteristic feature of the actinide hexafluorides is their lower stability and higher reactivity[118–122]. Weinstock and Malm's[121] physical properties for these compounds are given in Table 2.

The melting and boiling points of uranium hexafluoride have been determined many times[2,123–125] and, allowing for the difficulty of measurement, all the reported values agree well except the original data of Ruff and Heinzelman[2]. The vapour pressure of uranium hexafluoride over a wide range of temperature, for both liquid and solid states, has been determined by many authors[121–128]. On the whole the results show good agreement. The vapour pressures of solid and liquid uranium hexafluoride at different temperatures are expressed by the equations given in Table 3, which cover the whole temperature range studied. The critical temperature (230° ± 0.2°) and pressure (45.5 ± ± 0.5 atm) have been determined by Oliver *et al.*[126] and Llewellyn[128]. Llewellyn's value for the critical temperature is 245° ± 5°.

TABLE 2. Physical properties of the hexafluorides[121].

Hexafluoride	M.p., °C	B.p., °C	Vapour pressure at 0°, mm Hg	Vapour pressure at the m.p., mm Hg
MoF_6	17.4	35.0	—	—
WF_6	2.3	17.06	370.7	414.9
UF_6	64.0*	56.5	17.5	1137.9**
NpF_6	54.4*	55.2	20.8	754.9**
PuF_6	50.8*	62.2	17.6	533.0**

* Triple point.

** Vapour pressure at triple point.

TABLE 3.

Equation	Temperature range, °C	Reference
Solid UF_6		
$\log P_{mm} = \frac{2751}{T} - 75.0e^{2560/T} - 1.01 \log T + 13.797$	−15—+65	160
$\log P_{mm} = 10.023 - \frac{2486}{T} + 0.0012\,T$	0—+34.6	159
$\log P_{mm} = 6.38363 + 0.0075377\,t - 942.76\,(t - 183.416)$		158
$\log P_{mm} = -(3123.479/T) + 21.87103 - 3.77962 \log T$		157
Liquid UF_6		
$\log P_{mm} = -1946/T - 0.00492T + 0.934 \log T + 8.1$	65—100	160
$\log P_{mm} = 6.99464 - 1126.288\,(t + 221.963)$	64—116	158
$\log P_{mm} = 7.69069 - 1683.165\,(t + 302.148)$	>116	158
$\log P_{mm} = -(2065.679/T) + 18.600033 - 3.72662 \log T$		157

TABLE 4. Heats of sublimation and vaporisation of UF_6.

Temperature, °K	Heat, kcal mole^{-1}	Reference	Temperature, °K	Heat, kcal mole^{-1}	Reference
Heat of sublimation			Heat of vaporisation		
223	12.145	128	337	6.820	126
253	12.075	128	338	6.920	128
273	12.220	125	340	6.859	129
273	11.980	128	343	6.890	128
273.16	12.023	129	348	6.487	125
293	11.870	128	350	6.671	129
298	11.970	125	363	6.670	128
298	11.800	126	370	6.404	129
298.16	11.872	129	383	6.310	128
313	11.730	128			
323	11.580	125			
329.56	11.500	126			
330	11.537	129			
333	11.530	128			
337	11.380	126			

C. Thermochemical Properties

The heat of formation:

$$U(metal) + 3F_2(gas) = UF_6(gas)$$

is 505 ± 3 kcal mole^{-1}.

According to Llewellyn's data [128] the heat of sublimation of solid UF_6 is given by the equation

$$\lambda_T = 12\,600 - 875\,600e^{-2560/T} - 2T \text{ cal mole}^{-1}$$

and the heat of vaporisation of liquid UF_6 by the equation

$$\lambda_T = 8890 - 0.0225\,T^2 + 1.85\,T \text{ cal mole}^{-1}.$$

The author points out that the latter equation does not satisfy the condition $\lambda_T = 0$ at the critical temperature. The empirical equation

$$\lambda_T = 6920 - 5.3(t - 65) - 0.134(t - 65)^2 \text{ cal mole}^{-1}.$$

satisfying the condition $\lambda_T = 0$, has been put forward. Numerical values of the heat of sublimation and vaporisation [125,126,128,129] are given in Table 4. The heats of sublimation and vaporisation at the triple point are 11.38 kcal × × mole^{-1} and 6.82 kcal mole^{-1} respectively, so that the heat of fusion is $\lambda_{fus} = \lambda_{sub} - \lambda_{vap} = 4.56$ kcal mole^{-1}. [125] Direct calorimetric determination of the heat of fusion gives the same value.

The heat of hydrolysis according to

$$UF_6(solid) + 2H_2O \longrightarrow (UO_2F_2 + 4HF)(liquid)$$

was determined by Popov *et al.* [71] as 50.22 ± 0.051 kcal × mole^{-1}.

The thermal conductivity of gaseous UF_6 corresponds to the equation $k = (1.459 + 0.00614\,t) \times 10^{-5}$ cal cm^{-1} sec^{-1} × × deg^{-1}, and individual values are 1.42×10^{-5} at 5° and 1.94×10^{-5} at 105°. [128] The thermal conductivity of liquid UF_6 is known for one temperature (72°), 3.83×10^{-4} (±3%) cal cm^{-1} sec^{-1} deg^{-1}.

D. Mechanical Properties

The density of liquid uranium hexafluoride at the triple point is 3.624 g cm^{-3}, [128] which agrees with the value found earlier [130]. Determination of the density of gaseous UF_6 has confirmed that it consists of non-associated molecules. The viscosity of liquid and gaseous UF_6 has been measured in the range 0°–200°. [128]

The structure of UF_6. The problem of the structure of the uranium hexafluoride molecule has not yet been finally solved. Some authors [131,132] interpret the electron diffraction data for uranium hexafluoride on the basis of a rhombic bipyramid model, but others [133,134] suggest that the molecule may be an irregular octahedron with three short (1.87 Å) and three long (2.17 Å) bonds. The possibility of a molecule with an inversion centre and two short (1.87 Å), two intermediate (2.12 Å), and two long (2.22 Å) bonds is not excluded. It has been suggested [135] that the electronic configuration of uranium permits a regular octahedral structure and development of the theory of electron diffraction has shown that the uranium hexafluoride molecule corresponds more to this type [136]. The U–F distance in uranium hexafluoride is 1.994 Å. [121] From the number of active lines in the infra-red, Raman, and absorption spectra, it can be concluded that uranium hexafluoride has a completely symmetrical structure [137,138]. The dipole moment, equal to zero [139], is not consistent‡ with a regular octahedral model. A number of papers [123,140] have been devoted to study of the absorption spectra of uranium hexafluoride in the visible and ultra-violet.

Sheremet'ev [141] has shown that the absorption spectrum of gaseous and solid UF_6 in the visible and near ultra--violet consists of overlapping absorption bands. From this he concludes that the electronic vibrational energy levels of the UF_6 molecule are diffuse and change little

‡ This should probably read *is consistent* (Ed. of Translation).

on passing from room temperature to 88°K. The structure of the 407–347 mμ absorption band is identical for gaseous and solid UF_6, confirming that uranium hexafluoride crystals are of the molecular type [141,142]. If we assume the point group symmetry O_h (regular octahedron) for the UF_6 molecule, its six fundamental vibrations are distributed as follows: three to the valency vibrations and three to the deformational vibrations [143,144]. Sheremet'ev's experimental data [141] do not agree completely with earlier calculations [138]. On the basis of the absorption spectra frequency data, the author suggests that the sturcture of the UF_6 molecule is not exactly a regular octahedron.

Weinstock and Malm [121] have reviewed the structures of a number of hexafluorides, including PuF_6 and NpF_6. From a study of the infra-red absorption spectrum, magnetic susceptibility, and electron diffraction, they concluded that the UF_6, and PuF_6 and NpF_6, molecules are regular octahedra (point group O_h). That being so, it is possible to explain the absence of association in UF_6.

E. Chemical Properties

Uranium hexafluoride is an extremely reactive substance. Its chemical properties are in many respects analogous to those of the higher fluorides of the actinides and of the chromium subgroup elements. Those hexafluorides can be arranged in the following order of stability towards dissociation into fluorine and lower fluorides [120]: PuF_6, NpF_6, UF_6, MoF_6, WF_6. Bromine trifluoride fluorinates compounds of uranium, molybdenum, and tungsten with formation of the hexafluorides, but plutonium hexafluoride acts towards BrF_3 as a fluorinating agent:

$$PuF_6+BrF_3=PuF_4+BrF_5.$$

Plutonium hexafluoride is able to fluorinate the lower fluorides of all the elements standing to its right in the above series, giving the higher fluorides. For example, uranium tetrafluoride is fluorinated to UF_6: [121]

$$4UF_4+PuF_6=2U_2F_9+PuF_4,$$

$$U_2F_9+1.5PuF_6=2UF_6+1.5PuF_4.$$

Neptunium hexafluoride only partially fluorinates BrF_3 to BrF_5. The latest quantitative studies suggest two possible (but not certain) ionisation processes for the hexafluorides:

$$2MF_6 \rightleftarrows MF_5^+ + MF_7^-,$$

and

$$2MF_6 \rightleftarrows MF_4^{2+} + MF_8^{2-}.$$

Both processes produce ions, which may, to a certain degree, be stable. Proof that ionisation of this type is possible is provided by preparation of salts containing these ions. At present, however, such salts have been obtained only for uranium: $2RbF.UF_6$, $3AgF.UF_6$, $3NaF.UF_6$, and $3KF.UF_6$.

Uranium hexafluoride reacts with highly-dispersed sodium fluoride at 100° to yield the complex $3NaF.UF_6$; [5,145–147] between 80° and 320° the dissociation pressure of this complex (to UF_6 and NaF) is given by $\log P_{mm} = 10.88 - 50.90/T$, and ΔH = -23.2 kcal mole^{-1}. The vapour pressure reaches 760 mm Hg at 363°. When $3NaF.UF_6$ is heated to 400° in a current of nitrogen or fluorine, almost all the uranium hexafluoride present is liberated. When it is heated to 245°–345° under an excess pressure of UF_6 the reaction

$$3NaF.UF_6=UF_5.3NaF+0.5F_2$$

takes place. Further reduction to the tetravalent state takes place on heating under excess UF_6 pressure to 550°.

A fundamental property of UF_6 is its tendency to undergo hydrolysis to uranyl fluoride and hydrogen fluoride:

$$UF_6+2H_2O=UO_2^{2+}+2F^-+4HF_{aq}.$$

The UF_6–HF system has been studied [148,149] by the polythermal method and the equilibrium diagram has been constructed (Fig. 5). Pressure was measured, so that it was possible to plot isobars on the equilibrium diagram. The system has a region corresponding to the formation of immiscible solutions, starting at 61.2°, in the concentration range 10 ± 5 formula % UF_6 to 80 ± 3 formula % UF_6. The highest temperature of separation into layers (101°) occurs at 40–50 formula %. In the low-temperature region a eutectic is formed at -85° and less than 0.5 formula % UF_6. No chemical compound of UF_6 and HF was detected. in the system, so they can be separated by simple distillation. Hydrogen fluoride dissolves up to 10 formula % of the hexafluoride, and the hexafluoride up to 20% hydrogen fluoride (the concentration limits for separation into layers).

Reduction reactions are characteristic. According to Ruff and Heinzelman's observations [2], uranium hexafluoride is reduced to UF_4 at room temperature by gaseous hydrogen. These observations have not been confirmed, however; attempts to reduce UF_6 with gaseous hydrogen between -78° and +100° using traces of water and technical UF_4 as catalysts did not give positive results [58]. Dawson *et al.* studied the reaction between uranium hexafluoride and hydrogen in detail, and concluded, from thermodynamic calculations, that the reduction of uranium hexafluoride by hydrogen should be complete, but that its extent depends on the temperature. Similar calculations for the reaction $UF_4 + 2H_2 = U + 4HF$ showed, however, that at 25° the equilibrium is displaced to the left, while near 1000° it is

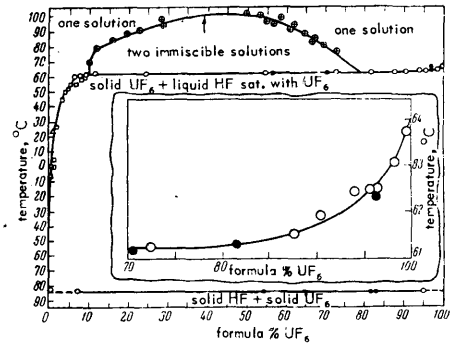


Fig. 5. Equilibrium diagram for the UF_6–HF system [149].

in the opposite direction. The authors confirmed experimentally the reaction between uranium hexafluoride and gaseous hydrogen for various temperatures, duration of reaction, and $H_2 : UF_6$ ratios in the gas mixture. It was established that at 430° the reduction of uranium hexafluoride is fairly complete; below 350° pure UF_4 was not obtained. The use of various catalysts for the reduction did not give positive results, only chlorides showing a significant effect.

Hydrogen halides are reductants for uranium hexafluoride[59,60]. The reaction between HCl and UF_6 at 200° yields a mixture of brown, green, and black products; owing to an incomplete reaction, both the tetrafluoride and intermediate uranium fluorides are formed. Hydrogen bromide reacts with uranium hexafluoride at 80° to yield pale green, friable uranium tetrafluoride powder. The use of carbon tetrachloride as reducing agent is of considerable interest. Nairn *et al.*[61] showed that the reduction of UF_6 by carbon tetrachloride takes place at 100°–200°. Other reducing agents include amorphous carbon[150], which reacts with UF_6 to form UF_4, CF_4, and other fluorocarbons, and also silicon, phosphorus, and sulphur. In the liquid phase UF_6 is reduced by PCl_3 and $SOCl_2$.

Systems based on uranium hexafluoride. A knowledge of systems in which UF_6 is a component is important for various technological reasons. UF_6–halogen fluoride–HF systems have been studied with the aim of setting up processes for fluorination of the metallic blocks obtained in the technology of irradiated uranium.

A study of the UF_6–ClF_3 system (liquid–solid equilibrium) was made by Wendolkowski and Barber[151] (Fig. 6) over a wide range of concentrations (0–100 mole % UF_6), ensuring experimentally that equilibrium was established while the melting and solidification curves were being recorded. With chlorine trifluoride, uranium hexafluoride forms a simple system with a eutectic point at -77.4°, 0.4 mole % UF_6. Enantiotropy was observed at -83.1°. The system shows positive deviation from ideal behaviour. The eutectic point could not be determined experimentally, since the heat of crystallisation of small quantities of uranium hexafluoride is insufficient for the accurate reproduction of the heating and cooling curves at a uranium hexafluoride content of ~0.4 mole %. The composition of the eutectic can be calculated, however, from the solubility data for ideal solutions and the experimental activity coefficients. Calculations carried out by the authors gave 0.4 mole % UF_6. The phase equilibrium in this system was also studied with allowance for pressure[152]. The liquid–vapour equilibrium diagram (Fig. 7) shows the absence of an azeotropic mixture. At 67° the components are completely miscible, but at 75° there exists a range of partial miscibility at 0.3–0.5 mole % UF_6.

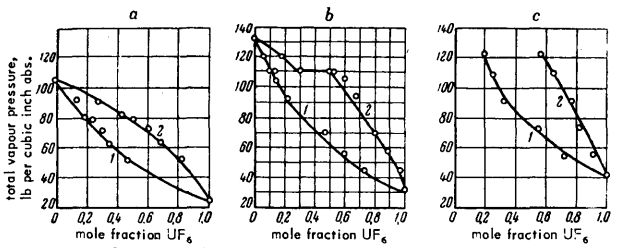


Fig. 7. ClF_3–UF_6 liquid–vapour equilibrium diagrams at various temperatures[152]:
a) 67°; *b*) 75°; *c*) 84°; 1) vapour; 2) liquid.

The equilibrium diagram of the ternary HF–UF_6–ClF_3 system is given by Rutledge and Davis[153] for the temperature range -100° to +100° (Fig. 8), from studies of the three binary systems HF–ClF_3,[154] UF_6–ClF_3,[151] and UF_6–HF.[149]

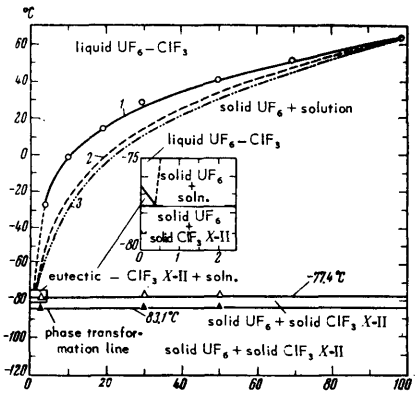


Fig. 6. Equilibrium diagram for the UF_6–ClF_3 system[151]:
1) experimental curve; 2) theoretical curve; 3) ideal curve.

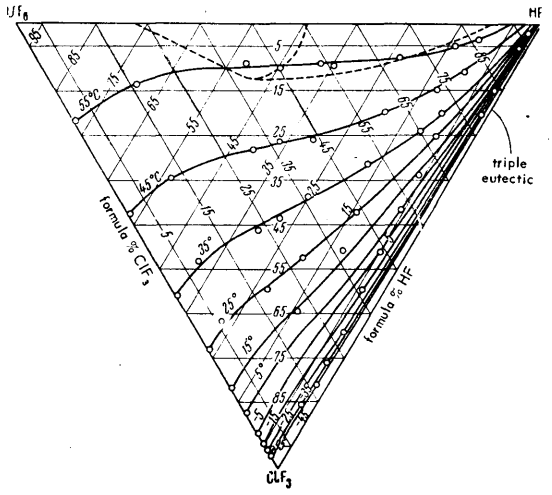


Fig. 8. The UF_6–ClF_3–HF system[153].

It was established that the ternary system, of simple eutectic type, contains pure components as solid phase. The ternary eutectic point of the HF–UF_6–ClF_3 system has the composition (formula %) 0.0–0.2 UF_6, 19.5 ClF_3, and 80.5 HF at -91°. The lower temperature limit at which two immiscible liquids saturated with solid uranium hexafluoride exist is 53° [composition (formula %) 49 UF_6, 13 ClF_3, and 38 HF]. Association of the components of the system and change in their association with temperature, pressure, and concentration made a theoretical discussion of this system, similar to that for the above binary system, difficult.

Study of the solid–liquid phase equilibrium in the condensed Br_2–UF_6 system[155] showed that this is a simple eutectic system. The solid phases are the pure components. The system shows positive deviation from ideal behaviour at concentrations > 15 mole % Br_2. The eutectic is at 99–100 mole % bromine, melting point -7.4° ± 0.1°.

The UF_6–BrF_3 and UF_6–BrF_5 systems[156] have been studied to obtain data on the solubility of uranium hexafluoride as a function of temperature and to determine the solid phases existing in equilibrium with the saturated solution. They are simple eutectic systems (Figs. 9 and 10). The solid in equilibrium with the saturated solution contains the pure component. Both solidification and fusion curves were recorded for the UF_6–BrF_3 system. The curves were identical, indicating that equilibrium was attained. The eutectic point is at 6.4° and 4.1 mole % UF_6.

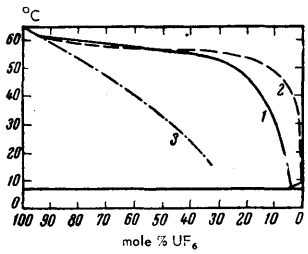


Fig. 9. Solubility curve for the UF_6–BrF_3 system[156]. 1) Experimental curve; 2) curve calculated according to Hildebrand; 3) ideal curve.

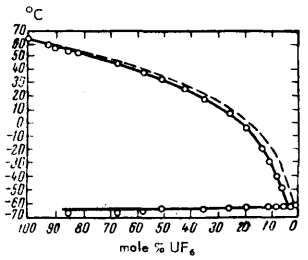


Fig. 10. Phase changes in the UF_6–BrF_5 system[156].

For the UF_6–BrF_5 system (Fig. 10), good agreement was obtained between the solidification and fusion curves. Because of the supercooling effect observed close to the eutectic point (-63.5°), the composition of the eutectic (3.2 ± 0.5 mole % UF_6) was obtained by extrapolation. The vapour pressure of BrF_5[152] was measured at 68° and 80° under conditions of complete miscibility of the components. These systems were also studied by the refraction method[157].

The data obtained in these studies have been used in the separation of uranium hexafluoride by distillation. Work has been carried out on the separation of binary mixtures of UF_6 with ClF_3, HF, Br_2, BrF_3, and BrF_5 and of the ternary mixture of UF_6 with ClF_3 and HF. For the HF–UF_6 system, a linear relationship between the composition of the azeotropic mixture and pressure was observed. The UF_6–Br_2 system could not be separated, but a UF_6–BrF_3 mixture is readily separated. The compositions of the azeotropic mixtures in the binary systems formed by HF with Br_2, BrF_3, and BrF_5 have been determined.

7. URANYL FLUORIDE

The fluorine compounds of uranium(VI) include uranium oxide fluorides containing the uranyl group, of which the simplest is uranyl fluoride UO_2F_2. Characteristic features of uranyl fluoride are its high solubility in water and its tendency to undergo reduction and to form various complex compounds.

Uranyl fluoride plays an important part in the technology of nuclear materials, as a product of the hydrolysis of uranium hexafluoride. Hydrolysis may be undesirable in gas-diffusion processes for separating uranium isotopes, since it yields solid components in the gas stream, leading to breakdown of the normal operation of the filtration assemblies. Hydrolysis of UF_6 with the production of uranyl fluoride solution is carried out to isolate uranium from the hexafluoride in a non-volatile form, as a stage in the technological preparation of metallic uranium. A uranyl fluoride solution can be used to prepare the tetrafluoride by reduction, either electrochemically or chemically.

In view of its high solubility and low effective cross-section for thermal neutrons, uranyl fluoride in solution has been suggested as a uranium-containing material for homogeneous nuclear reactors[158].

Uranyl fluoride was one of the first uranium compounds to be described. Methods for its preparation and its composition were reported as early as the beginning of last century by Berzelius[159], and later by Bolton[1]. Their syntheses were based on the reaction between uranium trioxide and hydrofluoric acid or on double decomposition reactions involving repeated treatment of other uranyl salts, for example uranyl acetate, with hydrofluoric acid. Evaporation of the solutions yielded the hydrate $UO_2F_2.nH_2O$.

Most work on the dissolution of uranium trioxide in HF solution has been done only recently, in collecting data on the UO_3–HF–H_2O system[160]. The reaction between uranium trioxide and hydrogen fluoride can also be carried out with gaseous HF at 300°–500°; anhydrous uranyl fluoride is then obtained. This can also be prepared from uranium ammonium phosphate, which lost first water and then ammonia at 60° and 450° respectively and was then treated with hydrogen fluoride at 500°. Pure UO_2F_2 was left as a non-volatile product[161].

The hydrolysis of uranium hexafluoride is another method of preparing uranyl fluoride. This has been studied in connection with the diffusion method for separating uranium isotopes. Thus Googin [162] hydrolysed liquid UF_6 by adding it to water in a closed vessel, the reaction mixture being cooled. The reverse process (addition of water to solid uranium hexafluoride) has also been used. The solid salt isolated was anhydrous uranyl fluoride. It is reported that hydrolysis of uranium hexafluoride by sulphuric acid solution (1 part of UF_6 to 2 parts of 70% H_2SO_4) yields uranyl sulphate.

A. Physical Properties

Anhydrous uranyl fluoride has a rhombohedral structure [163] with one molecule in the unit cell: $a = 5.755 \pm \pm 0.003$ Å, $\alpha = 42°47' \pm 3'$, space group $R\bar{3}m$.

The heat of formation of uranyl fluoride

$$U(solid) + O_2(gas) + F_2(gas) = UO_2F_2(solid)$$

was calculated by Popov *et al.* [71], who obtained 391.4 ± ± 3.6 kcal at 32°. The heat of solution of uranyl fluoride in aqueous HF has also been determined. The specimen of uranyl fluoride was prepared by dissolving uranium trioxide in the stoichiometric quantity of aqueous HF with subsequent evaporation to dryness. The dry residue was heated *in vacuo* to constant weight with gradual increase in temperature from 100° to 150°. The product contained 77.17 ± 0.09% uranium. The heat of solution of UO_2F_2 at 32° for component ratios $HF:H_2O = 1:400$, $UO_2F_2:HF = 1:4$ is 8.10 ± 0.01 kcal mole^{-1}.

The specific heat of uranyl fluoride has been measured [164] over the range 13° to 418°K by means of an adiabatic vacuum -type calorimeter. The specific heat, enthalpy, entropy, and free energy of uranyl fluoride in this temperature range have been given. The enthalpy and entropy at 298.16°K are 63.96 internat. J g^{-1} and 0.4400 internat. J g^{-1}deg^{-1}. No phase changes were observed.

B. Chemical Properties

The most important chemical properties of uranyl fluoride are its solubility and tendency to undergo hydrolysis and complex-formation.

The phase states of sexivalent uranium in aqueous solutions are described by the $HF-UO_3-H_2O$ system, which Marshall *et al.* studied at a constant $UO_3:F$ ratio of 1:2 over the temperature range from the ice eutectic (-13°) to the critical saturation temperature (+377°) [160] (Fig. 11).

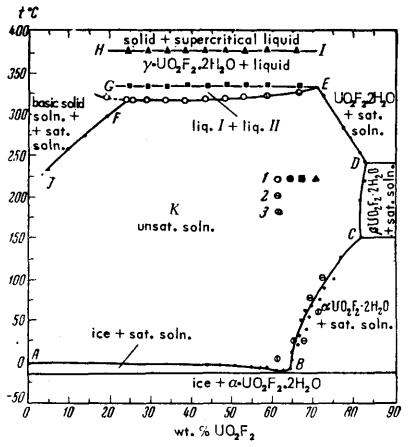


Fig. 11. Equilibrium diagram for the UO_3-HF-H_2O system, constructed from the data of various authors [160].
1) Marshall *et al.*; 2) *Dean; 3) *Kunin.

* See J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium", Part 1, First Edn., National Nuclear Energy Series, McGraw Hill, New York, 1951, p. 569 (Ed. of Translation).

The electrical conductivity of aqueous solutions of UO_2F_2 various concentrations (0.0001–6.0 N) has been measured at 0°, 25°, 50°, and 90°. [165] The conductance values and the form of the Λ *vs.* $C^{\frac{1}{2}}$ curves show that uranyl fluoride is a very weak electrolyte, whose dissociation shows almost no increase with change in temperature from 0° to 90°. The values of Λ for 25° were corrected for the conductivity of H^+ ions formed by hydrolysis. Extrapolation of the results gave $\Lambda = 87\ \Omega^{-1}\,cm^2$ from which $\lambda^0_{UO_2^{2+}} = 32\ \Omega^{-1}\,cm^2$ was calculated. Values of the dissociation constant for the reaction:

$$UO_2F_2 \rightleftarrows UO_2F^+ + F^-,$$

were calculated. Although at uranyl fluoride concentrations up to 0.01 N the dissociation constant remains almost unchanged (4.34×10^{-5}–4.85×10^{-5}), the authors suggest that the dissociation is more complex than this.

Johnson and Kraus [166] have measured the density and refractive index of aqueous solutions of uranyl fluoride in the range 1 to 62 wt.% at temperatures close to 25° and 30°. The results were extrapolated to 25.0° and 30.0°. Most of the density determinations were made by the pyknometric method and some with a gradient tube. The refractive indices were determined using an immersion refractometer (reproducibility ± 0.0004). The values found for the density can be expressed by:

$$1/d = 1/d_0 + aF_2 + bF_2^2,$$

where d and d_0 are the densities of the solution and pure solvent, F_2 the weight fraction of UO_2F_2 in the solution, and a and b are constants (at 25° a = -0.9120, b = 0.0567; at 30° a = -0.9126, b = 0.0569). The apparent molal volume of uranyl fluoride in solutions of different concentrations has been calculated: $\Phi_v = 28.0 + 17.5F_2$. The refractive index values can be expressed by:

$$n_D^t = n_D^{t^0} + \alpha c + \beta c^{3/2},$$

where n_D^t and $n_D^{t^0}$ are the refractive indices of the solution and water at temperature t, c the molar concentration of the solution, and α and β are constants (at 25° α = 0.02055, β = -0.00185; at 30° α = 0.02049, β = -0.00183). The n_D values were used to calculate the molar refraction of uranyl fluoride, $R = 17.1 \pm 0.1$ cm^3; this is independent of concentration.

The activity coefficients of uranyl fluoride have been determined from the freezing point depression [167]. They indicate that uranyl fluoride is essentially undissociated in

the range 0.1–5 mole % UO_2F_2. The activity coefficients were also determined by Johnson *et al.*[168] using an ultracentrifuge at 30°. The values obtained are close to those calculated from freezing point data, and indicate the existence of a dimerisation equilibrium in uranyl fluoride solutions. For dimerisation, $\Delta H \simeq 5$ kcal and $\Delta S \simeq 19$ e.u. Addition of KF to uranyl fluoride solution considerably increase the stability of the dimer.

When uranyl fluoride dissolves in hydrofluoric acid, fluoro-complexes $UO_2F_n^{(2-n)+}$ are formed. The number of fluoride ions coordinated around the UO_2^{2+} has been calculated[169] by the method of successive approximations from potentiometric measurements (with a quinhydrone electrode) in fluoride-containing buffer solutions in the presence and absence of UO_2^{2+}. The limiting value of the formation function found for the fluoride complex is four, that is, $[UO_2F_4]^{2-}$ is the highest member of the series of complexes formed at a fluoride concentration of 0.3 M. The formation functions of the complexes when the fluoride concentrations are not too high are found from the concentration equilibrium constants for the reactions

$$HF \rightleftarrows H^+ + F^-,$$

$$HF_2 \rightleftarrows H^+ + 2F^-,$$

which are calculated from the pH values. The fact that the formation functions are independent of the UO_2^{2+} concentration shows that in the concentration range studied (up to 0.025 M) the UO_2^{2+} ion does not form polynuclear complexes. The formation constants of the mono-, di-, tri-, and tetra-fluoro-complexes are (litre mole^{-1}): 3.9×10^4, 2.2×10^3, 3.6×10^2, and 23 respectively.

The polarographic behaviour of UO_2^{2+} in a hundredfold excess of fluoride ions has been studied[170] using as base electrolytes 0.1 M KCl and 0.1–0.2 M $NaClO_4$ at pH 1–7. The results were used to calculate the concentration of complex ions $UO_2F_n^{(2-n)+}$ ($n = 1-4$) and it was found that UO_2F^+ and UO_2F_2 are either reversibly reduced or dissociate rapidly to UO_2^{2+} ions, which are reversibly reduced.

TABLE 5. Genetic series of complex aquo-compounds derived from uranyl fluoride and an alkali fluoride[171].

Compound type	Moles U / Moles F	Example	Reference
$[(UO_2)_2F]^{3+}$	1 : 0.5	none obtained	
$[UO_2F]^+$	1 : 1.0	$Na\ [UO_2F(C_2O_4)_2(H_2O)]$	172
$[(UO_2)_2F_3]^+$	1 : 1.5	$K_2\ [(UO_2)_2F_3(O_2)(OOH)(H_2O)_4]$	173
$[UO_2F_2]^0$	1 : 2.0	$[UO_2F_2](H_2O)_2$	
$[(UO_2)_2F_5]^-$	1 : 2.5	$Na\ [(UO_2)_2F_5(H_2O)_4]$	
$[UO_2F_3]^-$	1 : 3.0	$Na\ [UO_2F_3(H_2O)_3].H_2O$	1
$[(UO_2)_2F_7]^{3-}$	1 : 3.5	$K_3\ [(UO_2)_2F_7(H_2O)_2]$	174
$[UO_2F_4]^{2-}$	1 : 4.0	exists in aqueous solution as the ion $[UO_2F_4]^{2-}$	169
$[(UO_2)_2F_9]^{5-}$	1 : 4.5	$K_5\ [(UO_2)_2F_9]$	174
$[UO_2F_3]^{3-}$	1 : 5.0	$Ba_3\ [UO_2F_5(H_2O)]_2$	1
$[UO_2]_2F_{11}]^{7-}$	1 : 5.5	non obtained	
$[UO_2F_6]^{4-}$	1 : 6.0	$Na_4\ [UO_2F_6]$	175

Note. The square brackets are placed arbitrarily, irrespective of other ligands in the coordination sphere of the complexes.

The rate constants for the pick-up of electrons and the transfer coefficient α have been calculated. It is suggested that the reaction:

$$UO_2F_n^{(2-n)+} + e = UO_2^+ + nF^-$$

takes place at the electrode. The rate of disproportionation of U^V depends on the F : U concentration ratio.

Complex aquo-compounds formed from uranyl fluoride and an alkali fluoride can be represented as a genetic series[171] (Table 5). Of the twelve theoretically possible types of fluoro-compound in the series, ten have been obtained. In complex compounds based on the uranyl ion, the fluoride ion may occupy either one or two coordination positions (the latter in binuclear compounds). Three types of binuclear complex in which fluorine acts as a bridging group have been discovered (Table 5). There are no indications of compounds containing more than two uranium nuclei[171].

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