## Chapter 16

URANIUM OXYHALIDES

The oxyhalides of sexivalent uranium of the type of UO_2^{++} were among the earliest compounds of uranium to be studied. Despite this, few physical constants have been determined with any degree of accuracy, and the chemistry of these compounds is still fragmentary. Until 1940, oxyhalides of uranium(IV) were unknown; but now the compounds $UOCl_2$ and $UOBr_2$ are readily available, and a considerable amount of information about them has been accumulated. Evidence for the probable existence of oxyhalides of uranium(VI) of the type of UO^{+4} and of uranium(V) of the type of UOX_3 has already been discussed in Chap. 14.

Here, attention will be directed to the uranyl halides and to the uranium(IV) oxyhalides. Questions relating to ionic equilibria and the physical properties of aqueous solutions of these compounds are discussed in the second portion of this volume.

1. URANYL FLUORIDE, UO_2F_2

Uranyl fluoride was first prepared by reaction of hydrofluoric acid and uranium oxide. Berzelius (1824) treated UO_3 with hydrofluoric acid and obtained a white amorphous solid on evaporation. Bolton (1866a) prepared solutions of uranyl fluoride by treating U_3O_8 with hydrofluoric acid.

$$U_3O_8 + 8HF \rightarrow UF_4 + 2UO_2F_2 + 4H_2O \qquad (1)$$
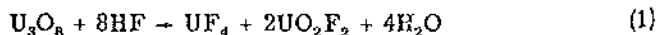
He was unable to obtain crystalline uranyl fluoride from the solution. Smithells (1883), on repeating the work of Bolton, found that uranyl fluoride could be obtained as a bright-yellow soapy substance by evaporation of the aqueous solution; on one occasion a partially crystalline material with a mother-of-pearl luster was obtained. Smithells

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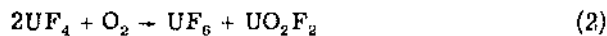
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1.2 Preparation o
Anhydrous uranyl flu
oxide with HF vapor:

designated the hydrated amorphous material, obtained by evaporation of aqueous UO$_2$F$_2$ solutions, as the β form, to distinguish it from the compound that he obtained in very small yield by heating uranium tetrafluoride in a closed crucible and designated as the α form. The latter probably is anhydrous UO$_2$F$_2$, formed by the reaction

$$2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2 \tag{2}$$

Ditte (1884) erroneously formulated the compound obtained by ignition of uranium tetrafluoride in a limited supply of air as UOF$_4$.

1.1 Preparation of Uranyl Fluoride from Aqueous Solution. Uranyl fluoride has a tendency to form acid and basic salts of ill-defined composition. To prepare pure neutral uranyl fluoride (Montreal 1) a known weight of oxide (UO$_3$ or UO$_4$·2H$_2$O) is dissolved in the calculated quantity of hydrofluoric acid, and the solution is then evaporated to dryness. The product is usually found to contain a higher percentage of uranium than calculated for the neutral salt. An amount of hydrofluoric acid equivalent to the excess uranium is then added, with enough water to dissolve the salt, and the resulting product is allowed to crystallize from solution. Crystals obtained in this way appear to be the dihydrate UO$_2$F$_2$·2H$_2$O.

Uranyl fluoride is difficult to crystallize, very viscous syrups being formed on concentration. Even if uranyl fluoride dihydrate crystals can be induced to form, separation of the crystals from the mother liquor is usually very difficult. The crystals of uranyl fluoride dihydrate are soft thin plates, pale yellow, and so hygroscopic that it is difficult to dry them. Consequently, solutions are often evaporated to dryness at 150 to 200°C without attempting to achieve crystallization. At 200°C products with a composition corresponding to that of the neutral salt and containing less than 0.1 per cent water can be obtained.
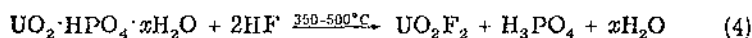
Anhydrous uranyl fluoride has also been prepared by reaction of uranyl acetate with hydrofluoric acid (von Unruh, 1909). The acetate is repeatedly evaporated with hydrofluoric acid in a platinum crucible on a water bath to volatilize acetic acid. The residue is then evaporated to dryness to remove water and excess hydrofluoric acid. On prolonged drying in a vacuum desiccator, an anhydrous product is obtained. This method was used by British workers to prepare UO$_2$F$_2$ (British 1).

1.2 Preparation of UO$_2$F$_2$ by High-temperature Hydrofluorination. Anhydrous uranyl fluoride is readily prepared by reaction of uranium oxide with HF vapor:

$$UO_3 + 2HF \rightarrow UO_2F_2 + H_2O \tag{3}$$
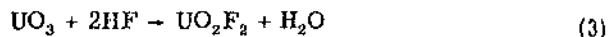
A temperature of 350 to 500°C appears suitable (MP Chicago 1). On a commercial scale, temperatures as high as 550°C have been recommended (Du Pont 1). Other workers prefer temperatures in the vicinity of 400°C (British 2; SAM Columbia 1) to avoid formation of U_3O_8 from the UO_3 and consequent contamination of the product with uranium tetrafluoride. The type of UO_3 used will determine the optimum temperature. This is probably the most convenient method for preparing anhydrous uranyl fluoride.
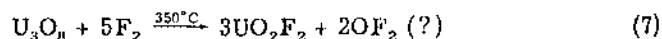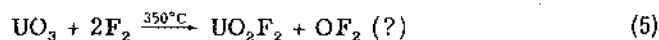
Although not of particular value as a method of preparation, the following reaction can be mentioned as also yielding anhydrous uranyl fluoride:

$$UO_2 \cdot HPO_4 \cdot xH_2O + 2HF \xrightarrow{350-500°C} UO_2F_2 + H_3PO_4 + xH_2O \tag{4}$$

Above 500°C reduction occurs and uranium tetrafluoride begins to form (CEW-TEC 1).

Uranyl fluoride can be readily prepared by the reaction of anhydrous uranyl chloride with liquid anhydrous hydrogen fluoride at room temperature (Brown 1). The reaction is best carried out in a platinum-lined nickel reactor; the reaction mixture is allowed to stand overnight, and the hydrogen chloride and fluoride are removed by distillation in vacuum at 450°C. A completely water-soluble chlorine-free product results.

Miscellaneous Reactions Yielding Uranyl Fluoride as a Product. Although not especially desirable as methods of preparation, the following reactions give uranyl fluoride as a product (MP Chicago 1):

$$UO_3 + 2F_2 \xrightarrow{350°C} UO_2F_2 + OF_2 \ (?) \tag{5}$$

$$UO_2 + F_2 \xrightarrow{350°C} UO_2F_2 \tag{6}$$

$$U_3O_8 + 5F_2 \xrightarrow{350°C} 3UO_2F_2 + 2OF_2 \ (?) \tag{7}$$

Uranyl fluoride is one of the products of the reaction (MP Chicago 2)

$$2UF_4 + O_2 \rightarrow UF_6 + UO_2F_2 \tag{8}$$
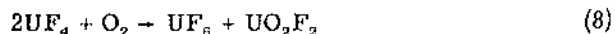
It has been reported that when uranium hexafluoride is treated with water vapor a complex compound of uranyl fluoride, hydrogen fluoride, and water results, from which uranyl fluoride can be prepared by heating to 180°C (British 3). The existence of this complex requires confirmation.

1.3 Physical Properti
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the melting point is unkn

(a) Crystal Structures
structure of UO_2F_2 has b
Zachariasen, 1948). The
with one molecule per un

$$a = 5.755$$

The space group is $R\bar{3}m$.

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2 O ir
2 F ir

To each uranium atom a
U-O = 1.91 A and six flu
structure consists of lay
of the uranyl groups are
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O-O and O-F bonds hold
all show varying degree
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The density as comput
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British workers report a
density of 2.55 g/cc (Bri

(b) Optical and Photoc
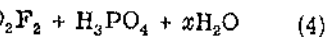absorption and fluoresce
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(c) Specific Heat. Enth
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was calculated to be 63
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₂F₂ + H₃PO₄ + xH₂O (4)

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OF₂ (?) (7)

e reaction (MP Chicago 2)

₂ (8)

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fluoride, hydrogen fluo-
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1.3 Physical Properties of Uranyl Fluoride. Anhydrous uranyl fluoride is a pale-yellow solid; no other physical constants have been determined. Since uranyl fluoride undergoes thermal decomposition, the melting point is unknown.

(a) Crystal Structures of Anhydrous Uranyl Fluoride. The crystal structure of UO_2F_2 has been studied by Zachariasen (MP Chicago 3; Zachariasen, 1948). The ideal structure of UO_2F_2 is rhombohedral with one molecule per unit cell. The unit cell has the dimensions

$$a = 5.755 \pm 0.003 \text{ A} \qquad \alpha = 42° \, 47' \pm 3'$$

The space group is $R\bar{3}m$, with the atomic positions

$$1 \text{ U in } (0 \ 0 \ 0)$$
$$2 \text{ O in } \pm(u \ u \ u) \quad \text{with } u = 0.122$$
$$2 \text{ F in } \pm(v \ v \ v) \quad \text{with } v = 0.294$$

To each uranium atom are bonded two oxygen atoms at a distance U-O = 1.91 A and six fluorine atoms at a distance U-F = 2.50 A. The structure consists of layers of uranium atoms 5.22 A apart; the axes of the uranyl groups are perpendicular to these planes. The fluorine atoms are 0.61 A above and below the uranium atom planes, and weak O-O and O-F bonds hold the layers together. Actual samples of UO_2F_2 all show varying degrees of stacking disorder with the planes displaced relative to each other.

The density as computed from the x-ray data is 6.37 g/cc. A direct measurement by displacement in benzene gave 5.8 g/cc, but this value was thought to be low owing to entrapped air (SAM Columbia 2). British workers report a pouring density of 2.95 g/cc and a packing density of 2.55 g/cc (British 2).

(b) Optical and Photochemical Properties of Uranyl Fluoride. The absorption and fluorescence spectra of uranyl fluoride will be discussed in the second portion of this volume.

(c) Specific Heat, Enthalpy, and Entropy of Uranyl Fluoride. (Natl. Bur. Standards 1; Wacker and Cheney, 1947.) The heat capacity of uranyl fluoride was measured from 13 to 418°K. The enthalpy $H° - H_0°$ was calculated to be 63.96, 77.62, and 108.15 int. joules per gram at 298.16, 338.16, and 423.16°K, respectively, and the entropy was calculated to be 0.4400, 0.4830, and 0.5635 int. joules per degree-gram at the same temperatures. No evidence of a transition was found. The values of the specific heat, enthalpy, entropy, and free energy are

tabulated at temperature intervals of 5°K in Table 16.1. The probable error is of the order of a few tenths of 1 per cent.

Table 16.1—Heat Capacity, Enthalpy, Entropy, and Free Energy of Uranyl Fluoride
(In International Joules)

Temp., °K	$C°$, J/g °C	$H°-H°_0$, J/g	$S°$, J/g °C	$-(F°-H°_0)$, J/g	Temp., °K	$C°$, J/g °C	$H°-H°_0$, J/g	$S°$, J/g °C	$-(F°-H°_0)$, J/g
0	0	0	0	0	215	0.2949	37.626	0.33687	34.802
5	0.00051	0.00064	0.00017	0.00021	220	0.2979	39.107	0.34368	36.503
10	0.00493	0.01014	0.00135	0.00339	225	0.3008	40.604	0.35041	38.238
15	0.01231	0.0492	0.00440	0.01690	230	0.3037	42.116	0.35705	40.006
20	0.02333	0.1378	0.00943	0.0508	235	0.3064	43.641	0.36361	41.808
25	0.03386	0.2803	0.01575	0.1133	240	0.3090	45.179	0.37009	43.643
30	0.04478	0.4768	0.02288	0.2096	245	0.3116	46.731	0.37649	45.510
35	0.05567	0.7280	0.03060	0.3431	250	0.3142	48.295	0.38281	47.408
40	0.06637	1.0331	0.03874	0.5163	255	0.3166	49.872	0.38905	49.337
45	0.07747	1.3925	0.04719	0.7310	260	0.3190	51.462	0.39523	51.298
50	0.08909	1.8086	0.05595	0.9887	265	0.3214	53.063	0.40133	53.290
55	0.10191	2.2855	0.06503	1.2910	270	0.3237	54.676	0.40735	55.310
60	0.11549	2.8292	0.07448	1.6396	275	0.3259	56.300	0.41331	57.362
65	0.12713	3.4371	0.08420	2.0363	280	0.3280	57.934	0.41920	59.443
70	0.13573	4.0951	0.09395	2.4817	285	0.3300	59.579	0.42503	61.555
75	0.14362	4.7933	0.10358	2.9756	290	0.3320	61.235	0.43079	63.694
80	0.15261	5.5333	0.11313	3.5174	295	0.3339	62.900	0.43648	65.862
85	0.16310	6.3220	0.12269	4.1070	300	0.3357	64.574	0.44210	68.058
90	0.17378	7.1647	0.13232	4.7443	305	0.3374	66.256	0.44767	70.284
95	0.18226	8.0500	0.14196	5.4302	310	0.3390	67.947	0.45317	72.536
100	0.18847	8.9834	0.15147	6.1638	315	0.3406	69.647	0.45860	74.814
105	0.19439	9.9404	0.16081	6.9446	320	0.3422	71.354	0.46398	77.121
110	0.2007	10.928	0.16999	7.7713	325	0.3438	73.069	0.46930	79.454
115	0.2070	11.947	0.17905	8.6440	330	0.3454	74.792	0.47456	81.814
120	0.2132	12.998	0.18800	9.5620	335	0.3470	76.523	0.47976	84.199
125	0.2193	14.079	0.19682	10.524	340	0.3486	78.262	0.48492	86.612
130	0.2252	15.190	0.20554	11.530	345	0.3502	80.009	0.49002	89.049
135	0.2308	16.331	0.21415	12.579	350	0.3517	81.764	0.49507	91.512
140	0.2362	17.498	0.22264	13.671	355	0.3532	83.526	0.50007	94.000
145	0.2413	18.692	0.23102	14.806	360	0.3546	85.296	0.50502	96.512
150	0.2463	19.911	0.23928	15.981	365	0.3560	87.072	0.50992	99.050
155	0.2510	21.154	0.24743	17.198	370	0.3572	88.855	0.51477	101.611
160	0.2556	22.421	0.25547	18.455	375	0.3584	90.645	0.51957	104.196
165	0.2598	23.710	0.26340	19.752	380	0.3596	92.440	0.52433	106.806
170	0.2640	25.019	0.27122	21.089	385	0.3607	94.241	0.52904	109.440
175	0.2679	26.349	0.27893	22.464	390	0.3617	96.046	0.53370	112.098
180	0.2717	27.698	0.28653	23.878	395	0.3627	97.858	0.53831	114.776
185	0.2753	29.066	0.29403	25.330	400	0.3638	99.674	0.54288	117.480
190	0.2788	30.451	0.30141	26.818	405	0.3648	101.495	0.54741	120.206
195	0.2822	31.854	0.30870	28.343	410	0.3658	103.321	0.55189	122.954
200	0.2854	33.273	0.31589	29.906	415	0.3668	105.153	0.55633	125.725
205	0.2886	34.708	0.32297	31.502	420	0.3678	106.989	0.56073	128.518
210	0.2917	36.159	0.32997	33.135	425	0.3688	108.831	0.56508	131.330

1.4 Chemical Properties of Uranyl Fluoride. (a) Water. Anhydrous uranyl fluoride is soluble in water, methanol, and ethanol; un-

like the other uranyl h[ ]
(von Unruh, 1909). The [ ]
temperatures (SAM Co[ ]

The solubility of ur[ ]
SAM Carbide and Carb[ ]
16.3 (SAM Carbide an[ ]

Table 16.2[ ]

Temp., °C
25.0
75.0
99.9

Table 16.3—Solub[ ]

Temp., °C
1
25
60
100

uranyl fluoride vs. th[ ]
heat of the reaction

$UO_2F_2 \cdot H_2O$ (so[ ]

is found to be 1.0 kcal [ ]
water increases with t[ ]
in hydrofluoric acid h[ ]
crystallization of uran[ ]

Uranyl fluoride prep[ ]
but uranyl fluoride o[ ]
exhibits no deliquescen[ ]
fluoride can be dehyd[ ]
(British 2; SAM Colun[ ]
appear to be unstable [ ]
cess of UO_3 requires [ ]
(up to 250°C). At 250 [ ]
becomes pink but doe[ ]
real 1).

X in Table 16.1. The probable
per cent.

! Free Energy of Uranyl Fluoride

les)

C°, J/g °C	H°−H$_0$°, J/g	S°, J/g °C	−(F°−H$_0$°), J/g
0.2949	37.626	0.33687	34.802
0.2979	39.107	0.34368	36.503
0.3008	40.604	0.35041	38.238
0.3037	42.116	0.35705	40.006
0.3064	43.641	0.36361	41.808
0.3090	45.179	0.37009	43.643
0.3116	46.731	0.37649	45.510
0.3142	48.295	0.38281	47.409
0.3166	49.872	0.38905	49.337
0.3190	51.462	0.39523	51.298
0.3214	53.063	0.40133	53.290
0.3237	54.676	0.40735	55.310
0.3259	56.300	0.41331	57.362
0.3280	57.934	0.41920	59.443
0.3300	59.579	0.42503	61.555
0.3320	61.235	0.43079	63.694
0.3339	62.900	0.43648	65.862
0.3357	64.574	0.44210	68.058
0.3374	66.256	0.44767	70.284
0.3390	67.947	0.45317	72.536
0.3406	69.647	0.45860	74.814
0.3422	71.354	0.46398	77.121
0.3438	73.069	0.46930	79.454
0.3454	74.792	0.47456	81.814
0.3470	76.523	0.47976	84.199
0.3486	78.262	0.48492	86.612
0.3502	80.009	0.49002	89.049
0.3517	81.764	0.49507	91.512
0.3532	83.526	0.50007	94.000
0.3546	85.296	0.50502	96.512
0.3560	87.072	0.50992	99.050
0.3572	88.855	0.51477	101.611
0.3584	90.645	0.51957	104.196
0.3596	92.440	0.52433	106.806
0.3607	94.241	0.52904	109.440
0.3617	96.046	0.53370	112.098
0.3627	97.858	0.53831	114.776
0.3638	99.674	0.54288	117.480
0.3648	101.495	0.54741	120.206
0.3658	103.321	0.55189	122.954
0.3668	105.153	0.55633	125.725
0.3678	106.989	0.56073	128.518
0.3688	108.831	0.56508	131.330

Fluoride. (a) Water. Anhy-
methanol, and ethanol; un-

like the other uranyl halides it is insoluble in ether or amyl alcohol
(von Unruh, 1909). The solubility in water has been studied at various
temperatures (SAM Columbia 2); the data are given in Table 16.2.

The solubility of uranyl fluoride has also been determined at the
SAM Carbide and Carbon laboratory. Their data are given in Table
16.3 (SAM Carbide and Carbon 1). By plotting the mole fraction of

Table 16.2—Solubility of Uranyl Fluoride in Water

Temp., °C	UO$_2$F$_2$, wt. %	Molality	ρ, g/cc
25.0	67.3	5.18	2.405
75.0	69.6	5.59	2.472
99.9	72.4	6.08	2.588

Table 16.3—Solubility of Uranyl Fluoride at Various Temperatures

Temp., °C	UO$_2$F$_2$, %	UO$_2$F$_2$, mole fraction
1	61.4	0.0862
25	65.6	0.100
60	71.0	0.125
100	74.1	0.143

uranyl fluoride vs. the reciprocal of the absolute temperature, the
heat of the reaction

$$UO_2F_2 \cdot H_2O \text{ (solid)} + H_2O \rightarrow UO_2F_2 \text{ (saturated solution)} \qquad (9)$$
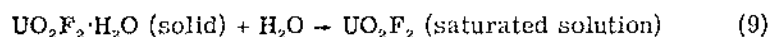
is found to be 1.0 kcal per mole. The solubility of uranyl fluoride in
water increases with temperature, but the solubility of uranyl fluoride
in hydrofluoric acid has a negative temperature coefficient so that
crystallization of uranyl fluoride occurs on heating.

Uranyl fluoride prepared at low temperatures is very hygroscopic,
but uranyl fluoride obtained by high-temperature hydrofluorination
exhibits no deliquescence even on long standing in air. Hydrated uranyl
fluoride can be dehydrated at 120°C without serious decomposition
(British 2; SAM Columbia 3). Hydrates of uranyl fluoride generally
appear to be unstable above 100°C. Uranyl fluoride containing an ex-
cess of UO$_3$ requires higher temperatures for complete dehydration
(up to 250°C). At 250°C uranyl fluoride undergoes a color change; it
becomes pink but does not appear to be changed chemically (Mont-
real 1).

Aqueous solutions of neutral uranyl fluoride do not attack glass even at the boiling point. Solutions of 2M uranyl fluoride have been heated in pyrex tubes to 200°C for ten days without formation of any precipitate (Montreal 1). Superheated steam at 900°C removes all the fluorine, leaving a residue of U_3O_8. At 450°C the residue is largely UO_3 (MP Ames 1).

(b) The UO_2F_2-HF-H_2O System. (SAM Carbide and Carbon 1.) A phase study of this system has been made by the solubility method.

Table 16.4—Composition of the Liquid and Solid Phases in Equilibrium in the UO_2F_2-HF-H_2O System at 25°C

Liquid phase				Solid phase		
HF, %	UO_2F_2, %	H_2O, %	D^{25}_{25}	HF, %	UO_2F_2, %	H_2O, %
0.00	65.55	34.45	2.224	...	...	...
11.88	31.88	56.24	1.440	8.52	51.95	39.53
20.70	22.99	57.01	...	18.20	32.50	49.30
25.75	18.19	56.01	...	14.51	51.25	34.24
32.51	1.35	56.14	1.231	12.06	64.47	23.47
				3.50*	83.76*	12.74*
41.70	6.10	52.20	...	8.77	75.2	16.03

*Partially dried.

(The uranyl fluoride used was prepared by reaction of UO_3 with hydrogen fluoride.) The various mixtures were allowed to come to equilibrium at 25°C in two to three weeks' time. The results obtained are presented in Table 16.4.

The data indicate a marked decrease in solubility with increasing concentration of hydrofluoric acid. In the region investigated, only one solid phase appears. On extrapolating the tie lines joining points corresponding to the compositions of the solution phases and the equilibrium solids, the composition of the equilibrium solid phase is found to be $UO_2F_2 \cdot H_2O$ (Fig. 16.1).

(c) Thermal Decomposition of Uranyl Fluoride. The compound appears to be stable in air to 300°C. Above 300°C decomposition to U_3O_8 occurs (CEW-TEC 2; British 4). The thermal decomposition has been studied in some detail at Ames (MP Ames 2). Decomposition is found to occur even at 200°C, but most of it occurs at 850 to 900°C (in vacuum). The substance does not melt. A black cokelike residue of U_3O_8 remains in the furnace; a yellow substance, UO_2F_2(?), and a green substance, impure UF_4, distill out of the furnace. There is also evidence for the evolution of fluorine (or perhaps UF_6), since a deposit of mercurous fluoride is usually found in the mercury vapor
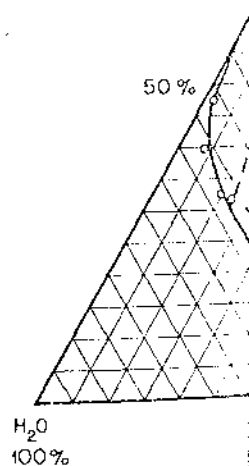
:ANIUM

uoride do not attack glass
uranyl fluoride have been
s without formation of any
m at 900°C removes all the
0°C the residue is largely

Carbide and Carbon 1.) A
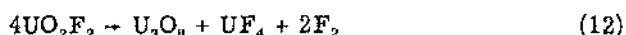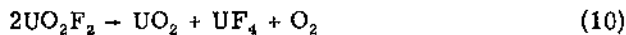e by the solubility method.

Phases in Equilibrium in the
25°C

	Solid phase		
F, %	UO$_2$F$_2$, %	H$_2$O, %	
.	. . .	. . .	
52	51.95	39.53	
20	32.50	49.30	
51	51.25	34.24	
06	64.47	23.47	
50*	83.76*	12.74*	
77	75.2	16.03	

reaction of UO$_3$ with hy-
were allowed to come to
ime. The results obtained

solubility with increasing
region investigated, only
he tie lines joining points
solution phases and the
quilibrium solid phase is

ride. The compound ap-
)°C decomposition to U$_3$O$_8$
l decomposition has been
es 2). Decomposition is
t occurs at 850 to 900°C
A black cokelike residue
stance, UO$_2$F$_2$(?), and a
e furnace. There is also
erhaps UF$_6$), since a de-
d in the mercury vapor

pump. The Ames workers postulated a number of concurrent reactions to account for the observed products of thermal decomposition.

$$2UO_2F_2 \rightarrow UO_2 + UF_4 + O_2 \tag{10}$$

$$UO_2F_2 \rightarrow UO_2 + F_2 \tag{11}$$

$$4UO_2F_2 \rightarrow U_3O_8 + UF_4 + 2F_2 \tag{12}$$

The evidence is still too meager to permit drawing any definite conclusions as to the predominant reaction. A primary reaction which
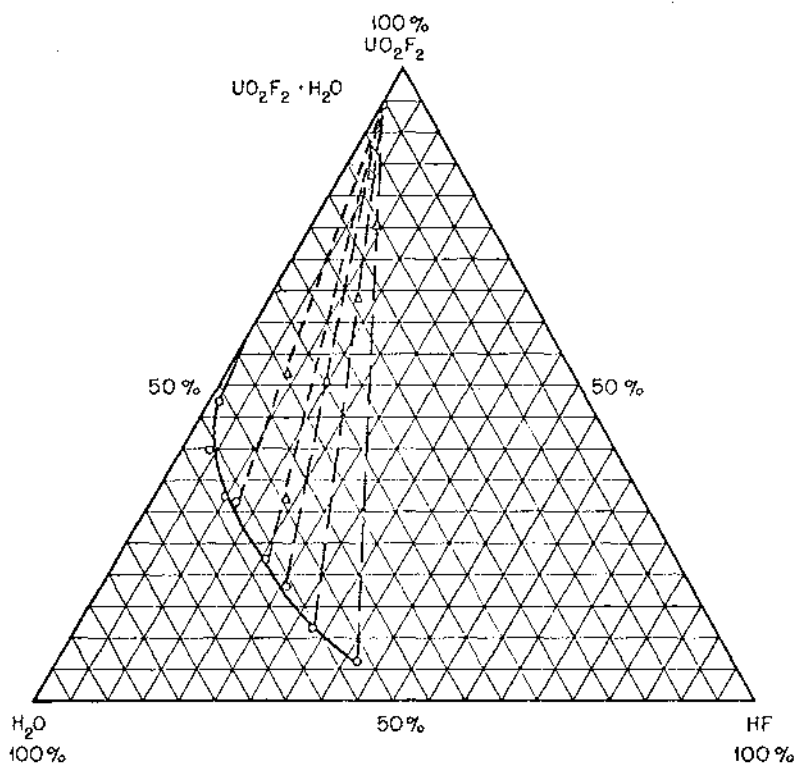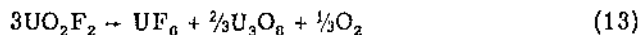

Fig. 16.1—The uranyl fluoride—hydrogen fluoride—water system at 25°C.

could perhaps account for the observed result (at least in part) is

$$3UO_2F_2 \rightarrow UF_6 + \tfrac{2}{3}U_3O_8 + \tfrac{1}{3}O_2 \tag{13}$$

Fried and Davidson have estimated the ΔF of this reaction; from

their computations it appears that a temperature of at least 1300°K would be necessary for it to proceed (MP Chicago 2). However, a number of arbitrary assumptions were involved in computing the free energy of reaction 13, and the possibility that UF_6 actually is formed according to this equation need not be excluded. More work is desirable since formation of UF_6 by decomposition of uranyl fluoride would have some interest.

(d) Some Chemical Reactions of Uranyl Fluoride. Uranyl fluoride undergoes reduction with hydrogen.

$$UO_2F_2 + H_2 \rightarrow UO_2 + 2HF \tag{14}$$
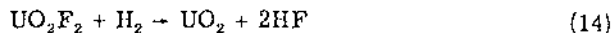
This reaction proceeds rapidly at 600°C, rather slowly at 500°C (MP Chicago 1; Du Pont 2). The uranium dioxide so produced is very reactive. Fluorine converts uranyl fluoride to UF_6.

$$UO_2F_2 + 4F_2 \rightarrow UF_6 + 2F_2O \tag{15}$$
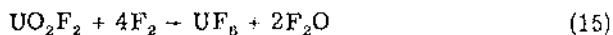
A reaction which is typical of all solutions containing UO_2^{++} but which has been applied particularly to uranyl fluoride is reduction with stannous chloride (see Chap. 12).

$$UO_2F_2 + 4HF + SnCl_2 \rightarrow UF_4 + SnCl_2F_2 + 2H_2O \tag{16}$$
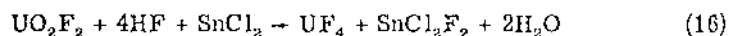
Solutions of uranyl fluoride containing glucose or alcohol are reduced by direct sunlight to uranium tetrafluoride. Fusion with alkali, e.g., NaOH or CaO, converts uranyl fluoride to a mixture of sodium (or calcium) uranate and sodium (or calcium) fluoride (Aloy and Rodier, 1922)

(e) Complex Salts of Uranyl Fluoride. Uranyl fluoride is coordinatively unsaturated and forms extensive series of double salts. Double salts of the following types are formed with metal fluorides:

A. MUO_2F_3 or $MF \cdot UO_2F_2$ (M = Na)

B. $M_3UO_2F_5$ or $3MF \cdot UO_2F_2$ (M = K, NH_4, ½Ba)

C. $M_3(UO_2)_2F_7$ or $3MF \cdot 2UO_2F_2$ (M = K)

D. $M_5(UO_2)_2F_9$ or $5MF \cdot 2UO_2F_2$ (M = K)

Ditte (1884) described compounds of the series $M_4UO_2F_6$ (M = Li, Na, K, Rb, Tl), which he obtained by fusion of U_3O_8 and potassium fluoride with a small amount of carbonate. He also described compounds of

the type $M_4UOF_8 \cdot nH_2O$
Smithells to be in all p
simply uranates (Smit
pounds $Cs_4UO_2F_6$ and
but no details of prep
compound forms mono
appear to be any obvio
$4MF \cdot UO_2F_2$ should no
probably not by the me

Although the UO_2F_2
Bolton (1866b), it was
tions. When potassium
or uranyl fluoride, K_3
from pure water (or a
cent KHF_2), $K_5(UO_2)_2$
$K_5(UO_2)_2F_9$ is recrysta
is formed.

Of these salts, K_3U
at red heat with dece
and the compound is c
composed by warm co
hydroxide precipitate
ates yield water-solu
uranium is not held i
gives no precipitate w
inum salts; but bariu
complex salts of the
oxalic or formic acid
K_2UF_6. All the compl
ing in air or on fusion
of course, converted
fluoride.

Hydrogen peroxide
$K_3UO_2F_5$ to insoluble
$NaUO_4F \cdot 5H_2O$ and K
sidered as firmly est
100°C with evolution
tivity of aqueous so
studied (Miolati and
the existence of stabl
evidence below). The
preparation and crys

nperature of at least 1300°K
MP Chicago 2). However, a
nvolved in computing the free
' that UF_6 actually is formed
excluded. More work is de-
mposition of uranyl fluoride

l Fluoride. Uranyl fluoride

2HF (14)

rather slowly at 500°C (MP
ide so produced is very re-
to UF_6.

2F₂O (15)

lutions containing UO_2^{++} but
uranyl fluoride is reduction

nCl₂F₂ + 2H₂O (16)

glucose or alcohol are re-
luoride. Fusion with alkali,
ide to a mixture of sodium
alcium) fluoride (Aloy and

Uranyl fluoride is coordi-
ve series of double salts.
med with metal fluorides:

Na)

K, NH₄, ½Ba)

K)

K)

ries $M_4UO_2F_6$ (M = Li, Na,
U₃O₈ and potassium fluoride
so described compounds of

the type $M_4UOF_8 \cdot nH_2O$ (M = K, Rb). The latter have been shown by Smithells to be in all probability of type B, whereas the former were simply uranates (Smithells, 1883). The preparation of the two compounds $Cs_4UO_2F_8$ and $K_4UO_2F_6$ has been reported (SAM Columbia 4), but no details of preparation or analysis were given. The cesium compound forms monoclinic prismatic crystals. Since there does not appear to be any obvious reason that complex compounds of the type $4MF \cdot UO_2F_2$ should not exist, they may well be obtainable although probably not by the methods of Ditte.

Although the UO_2F_2 complexes were discovered and studied by Bolton (1866b), it was Baker (1879) who first elucidated their relations. When potassium fluoride is added to a solution of uranyl nitrate or uranyl fluoride, $K_3UO_2F_5$ precipitates. If this salt is recrystallized from pure water (or an aqueous solution containing less than 13 per cent KHF_2), $K_5(UO_2)_2F_9$ is formed. Further, if either $K_3UO_2F_5$ or $K_5(UO_2)_2F_9$ is recrystallized from uranyl nitrate solution, $K_3(UO_2)_2F_7$ is formed.

Of these salts, $K_3UO_2F_5$ has been studied in some detail. It melts at red heat with decomposition. On heating in air, fluorine is lost, and the compound is converted to uranate. The salt is completely decomposed by warm concentrated sulfuric acid. Ammonia and sodium hydroxide precipitate diuranates, but ammonium and sodium carbonates yield water-soluble complexes. This reaction indicates that the uranium is not held in a very tight complex. A solution of $K_3UO_2F_5$ gives no precipitate with copper, silver, zinc, mercury, iron, or platinum salts; but barium, calcium, and lead ions precipitate insoluble complex salts of the type $Ba_3(UO_2)_2F_{10} \cdot 2H_2O$. Photoreduction of an oxalic or formic acid solution of $K_3UO_2F_5$ results in precipitation of K_2UF_6. All the complex salts undergo conversion to uranates on heating in air or on fusion with sodium carbonate; the ammonium salt is, of course, converted to U_3O_8 on ignition, with loss of ammonium fluoride.

Hydrogen peroxide oxidizes aqueous solutions of $NaUO_2F_3$ or of $K_3UO_2F_5$ to insoluble per-compounds which have been formulated as $NaUO_4F \cdot 5H_2O$ and $K_4U_4O_{15}F_6 \cdot 4H_2O$. These formulas cannot be considered as firmly established. The per-compounds decompose above 100°C with evolution of oxygen (Lordkipanidze, 1900). The conductivity of aqueous solutions of $K_3UO_2F_5$ and $(NH_4)_3UO_2F_5$ has been studied (Miolati and Alvisi, 1897), and the results purport to show the existence of stable $(UO_2F_5)^{-3}$ ions (compare with crystallographic evidence below). Table 16.5 summarizes some pertinent data on the preparation and crystallographic properties of these complex salts.

Table 16.5 — Preparation and Properties of Complex Compounds of Uranyl Fluoride and Metal Fluorides

Compound	Ratio of metal fluoride to UO_2F_2	Crystal habit*	Crystallographic* data	Density* at 20°C, g/cc	Solubility	Preparation
$NaUO_2F_3 \cdot 4H_2O$	1/1	Monoclinic	a:b:c = 1.0270:1:0.5222 β = 94° 51'			Crystallizes by slow evaporation of a solution of uranyl nitrate and NaF or a solution of sodium uranate in HF; exact conditions are unknown; the dihydrate is obtained on recrystallization from H_2O†
$K_3UO_2F_5$	3/1	Tetragonal; no appreciable fluorescence	a:c = 0.992	4.263	12.5 g/100 g H_2O at 21°C;† precipitates by addition of alcohol	Ppts. as a yellow crystalline solid on addition of a slight excess of KF to $UO_2(NO_3)_2$ solution; this is the primary reaction product of KF and UO_2F_2 or $UO_2(NO_3)_2$ solutions*†‡
$(NH_4)_3UO_2F_5$	3/1	Tetragonal; strongly fluorescent in x-ray or ultra-violet light	Refractive index = 1.4955	3.186	10.11 g/100 g solution at 27°C; 20.70 g/100 g solution at 81.3°C;§ insol. in C_2H_5OH	Addition of NH_4F to a solution of uranyl nitrate*†
$Ba_3(UO_2)_2F_{10} \cdot 2H_2O$	3/1				Very sparingly sol. in hot water	$BaCl_2$ + $K_3UO_2F_5$ solution; the dihydrate is obtained by drying at 100°C; Ca and Pb compounds are obtained in the same way†
$K_3(UO_2)_2F_7 \cdot 2H_2O$	3/2	Monoclinic; distinct green fluorescence	a:b:c = 0.918:1:0.978 β = 114° 0'	4.108	Sol. in warm water	Prepared by adding to a solution of UO_2F_2 an amount of KF insufficient to cause a permanent precipitate and then evaporating or by crystallizing $K_3UO_2F_5$ or $K_3(UO_2)_2F_9$ from $UO_2(NO_3)_2$ or UO_2F_2 solution*
$K_5(UO_2)_2F_9$	5/2	Triclinic; large crystals show distinct fluorescence	a:b:c = 0.6222:1:0.568 α = 72° 38' β = 116° 23' γ = 111° 57'	4.379		Prepared by recrystallization of $K_3UO_2F_5$ from water or from a less than 13% KHF_2 solution*

*Baker, 1879.
†Bolton, 1866a.
‡Smithells, 1883.
§Bolland, 1910.
¶Bürger, 1904.

Base	
Pyridonium	C
Pyridonium	C
Pyridonium	C
Quinolonium	C
Quinolonium	C
Trimethyl-p-tolyl ammonium	(C
Trimethyl-p-tolyl ammonium	(C
Tetramethylammonium	(C
Tetramethylammonium	(C
Tetraethylammonium	(C
Trimethyl-p-tolyl ammonium	(C
Trimethyl-p-tolyl ammonium	(C
Tetramethyl pyridonium	(C
Tetramethyl pyridonium	(C
Triethyl sulfonium	(C
Diethyl anilonium	(C
Diethyl anilonium	(C
Trimethylammonium	(C
Propyl ammonium	(C
Propyl ammonium	C
Tetrapropyl ammonium	(C
Methyl ethyl propyl phenyl ammonium	(C
Anilonium	(C
Dimethyl anilonium	(C

concentrated uranyl nitr phase, anhydrous K_3UO_2 with a body-centered tr sions

a_1 = 9.05

UR

The crystal structure of $K_3UO_2F_5$ has been studied recently (MP Chicago 4). Material prepared by addition of potassium fluoride to a

Table 16.6—Complex Compounds of Uranyl Fluoride with Organic Bases

Base	Compound	Solubility in H_2O at 20°C, g/100 ml
Pyridonium	$C_5H_8NHUO_2F_3\cdot H_2O$	1.289
Pyridonium	$C_5H_5NH(UO_2)_2F_6\cdot 3H_2O$	1.952
Quinolonium	$C_9H_8NHUO_2F_3\cdot H_2O$	0.126
Quinolonium	$C_8H_8NHUO_2F_5\cdot 2H_2O$	0.979
Tetramethylammonium	$(CH_3)_4N(UO_2)_2F_5\cdot 2H_2O$	0.143
Tetraethylammonium	$(C_2H_5)_4NUO_2F_3$	0.716
Tetraethylammonium	$(C_2H_5)_4NUO_2F_3\cdot 2H_2O$	0.771
Trimethyl-p-tolyl ammonium	$(CH_3C_6H_4)(CH_3)_3NUO_2F_3\cdot 2H_2O$	1.645
Trimethyl-p-tolyl ammonium	$(CH_3C_6H_4)(CH_3)_3N(UO_2)_2F_5\cdot H_2O$	3.091
Tetramethyl pyridonium	$(C_5H_2)(CH_3)_4NH(UO_2)_3F_7\cdot 6H_2O$	0.708
Diethyl anilonium	$C_6H_5N(C_2H_5)_2HUO_2F_3\cdot 2H_2O$	1.759
Diethyl anilonium	$C_6H_5N(C_2H_5)_2H(UO_2)_2F_5\cdot 2H_2O$	3.896
Triethyl sulfonium	$(C_2H_5)_3S(UO_2)_2F_5\cdot 2H_2O$	0.897
Trimethylammonium	$(CH_3)_3NH(UO_2)_2F_5\cdot 2H_2O$	
Propyl ammonium	$C_3H_7NH_3UO_2F_3\cdot 2H_2O$	
Propyl ammonium	$C_3H_7NH_3(UO_2)_3F_7\cdot 6H_2O$	
Tetrapropyl ammonium	$(C_3H_7)_4N(UO_2)_3F_7\cdot 2H_2O$	
Methyl ethyl propyl phenyl ammonium	$(CH_3)(C_2H_5)(C_3H_7)(C_6H_5)N\cdot(UO_2)_3F_7\cdot 6H_2O$	
Anilonium	$C_6H_5NH_3UO_2F_3\cdot 3H_2O$	
Dimethyl anilonium	$C_6H_5N(CH_3)_2H(UO_2)_2F_5\cdot H_2O$	

concentrated uranyl nitrate solution was found to consist of a single-phase, anhydrous $K_3UO_2F_5$. The compound has a tetragonal structure with a body-centered translation group. The unit cell with the dimensions

$$a_1 = 9.05 \pm 0.05 \text{ A} \qquad a_3 = 18.10 \pm 0.10 \text{ A}$$

[left margin, rotated text:]

hot water

Sol. in warm water

hydrate is obtained by drying at 100°C; Ca and Pb compounds are obtained in the same way†
Prepared by adding to a solution of UO_2F_2 an amount of KF insufficient to cause a permanent precipitate and then evaporating or by crystallizing $K_3UO_2F_5$ or $K_3(UO_2)_2F_9$ from $UO_2(NO_3)_2$ or UO_2F_2 solution*
Prepared by recrystallization of $K_3UO_2F_5$ from water or from a less than 13% KHF_2 solution*

4.106

4.379

Monoclinic; distinct green fluorescence

Triclinic; large crystals show distinct fluorescence

$a:b:c = 0.918:1:0.978$
$\beta = 114°\,0'$

$a:b:c = 0.6222:1:0.568$
$\alpha = 72°\,38'$
$\theta = 116°\,23'$
$\gamma = 111°\,57'$

3/2

5/2

§Bolland, 1910.
¶Bürger, 1904.

$K_3(UO_2)_2F_7\cdot 2H_2O$

$K_3(UO_2)_2F_9$

*Baker, 1879.
†Bolton, 1866a.
‡Smithells, 1883.

contains eight molecules. The calculated density is 4.29 g/cc, and the probable space group is I4/amd. An approximate structure has been deduced; an interesting feature is the existence of $(UO_2F_4)^{--}$ units in the lattice with the fifth fluorine bound only to potassium.

Uranyl fluoride forms a series of addition compounds with ammonia (von Unruh, 1909). Liquid ammonia reacts with uranyl fluoride (or lower ammoniated complexes) to give $UO_2F_2 \cdot 4NH_3$, a deep orange-red substance which is more stable than the corresponding derivatives of uranyl bromide and uranyl chloride. Gaseous ammonia reacts with uranyl fluoride to give $UO_2F_2 \cdot 3NH_3$ (orange-yellow), which on warming is converted to $UO_2F_2 \cdot 2NH_3$ (yellow).

Complex compounds with organic bases have also been prepared (Olsson, 1930). A solution of the appropriate base (in dilute hydrofluoric acid) is added to a solution of uranyl nitrate (containing F^-). The precipitate is removed, washed first with dilute hydrofluoric acid, then with water, and finally dried on filter paper. Most of the compounds are stable in air for long periods; heat converts them to U_3O_8. They are somewhat soluble in water, and the solubility usually increases as the temperature is raised. The complexes dissolve in acids; bases such as sodium hydroxide or ammonia precipitate uranates and carbonates form soluble complexes. No solubility is observed in organic solvents, such as glacial acetic acid, alcohol, ether, or acetone. Table 16.6 lists a number of these compounds and their solubilities in water.

The compounds are of three types:

A. $MUO_2F_3 \cdot nH_2O$ or $MF \cdot UO_2F_2$

B. $M(UO_2)_2F_5 \cdot nH_2O$ or $MF \cdot 2UO_2F_2$

C. $M(UO_2)_3F_7 \cdot nH_2O$ or $MF \cdot 3UO_2F_2$

where M is a univalent organic base.

2. URANIUM(IV) OXYFLUORIDE, UOF_2

Giolitti and Agamennone (1905) have claimed preparation of the compound $UOF_2 \cdot 2H_2O$. Giolitti (1904) had developed an analytical method for uranium based on the precipitation of uranium tetrafluoride. The results he obtained by this procedure were very erratic, and in seeking the reason for this he came to the rather surprising conclusion that uranium tetrafluoride does not exist at all and that uranium(IV) oxyfluoride is the compound that precipitates when hydrofluoric acid is added to a uranium(IV) solution.

There can be little d
very inadequate analyti
easily have been in erro

In the course of this
observations of the reac
been confirmed by mor
cago 5). When U_3O_8 is to
appear which can be re
ference in density. The
dense material is gre
doubt.

The Brown Universit
fluoride by treating un
hydrogen fluoride at r
was the only product ob
by fusing UO_2 with UF_4

3.

Anhydrous uranyl chl
ture vapor-phase reac
chloride can be readily
without formation of bas

3.1 Preparation of A

was employed by Péligo
ride. The reaction is c
usually incomplete. Reg
separate the uranyl chlc
the ether cannot then be
group found that the rea
rine proceeds at 500
(Brown 2). With UO_3, c
U_3O_8 is formed (MP A
UO_3 with methane (cf. C
on treatment with chlori
rine, reaction occurs at
be sublimed away in a
of yellow anhydrous ura

A number of other re
chloride is formed. W

RANIUM

ensity is 4.29 g/cc, and the
ximate structure has been
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$F_2 \cdot 4NH_3$, a deep orange-red
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have also been prepared
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eat converts them to U_3O_8.
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he complexes dissolve in
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acetic acid, alcohol, ether,
ese compounds and their

E, UOF₂

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n of uranium tetrafluo-
lure were very erratic,
to the rather surprising
not exist at all and that
t precipitates when hy-
tion.

There can be little doubt that Giolitti's conclusions were based on very inadequate analytical methods. His fluorine determinations could easily have been in error by several hundred per cent.

In the course of this work, Giolitti and Agamennone made several observations of the reaction of hydrofluoric acid and U_3O_8, which have been confirmed by more recent investigators (MP Ames 3; MP Chicago 5). When U_3O_8 is treated with hydrofluoric acid, two solid phases appear which can be readily separated by flotation because of the difference in density. The less dense material is blue-green; the more dense material is green. The nature of these two phases is still in doubt.

The Brown University group attempted to prepare uranium(IV) oxyfluoride by treating uranium(IV) oxychloride with liquid anhydrous hydrogen fluoride at room temperature, but uranium tetrafluoride was the only product obtained (Brown 1). An attempt to prepare UOF_2 by fusing UO_2 with UF_4 also failed (MP Ames 13).

3. URANYL CHLORIDE, UO₂Cl₂

Anhydrous uranyl chloride can be prepared only by high-temperature vapor-phase reactions. Although aqueous solutions of uranyl chloride can be readily obtained, they have not as yet been dehydrated without formation of basic salts.

3.1 Preparation of Anhydrous Uranyl Chloride. The reaction

$$UO_2 + Cl_2 \rightarrow UO_2Cl_2 \qquad (17)$$

was employed by Péligot (1842a,b) to prepare anhydrous uranyl chloride. The reaction is carried out at red heat with dry chlorine but is usually incomplete. Regelsberger (1885) employed ether extraction to separate the uranyl chloride from the unreacted oxide. Unfortunately, the ether cannot then be completely removed. The Brown University group found that the reaction between UO_2 and commercial dry chlorine proceeds at 500°C, to give a product containing some U_3O_8 (Brown 2). With UO_3, chlorine does not react at 400°C; above 400°C U_3O_8 is formed (MP Ames 4). Active UO_2, prepared by reduction of UO_3 with methane (cf. Chap. 11), was reported to yield uranyl chloride on treatment with chlorine (UCRL 1). With $U_3O_2S_2(UO_2 \cdot 2US)$ and chlorine, reaction occurs at 60°C. After it is over, the UCl_4 formed can be sublimed away in a stream of chlorine at 600°C, leaving a residue of yellow anhydrous uranyl chloride (MP Ames 5).

A number of other reactions are known in which anhydrous uranyl chloride is formed. When carbon tetrachloride reacts with various

uranium oxides, some uranyl chloride is formed which presumably could be separated from concurrently produced uranium tetrachloride either by vacuum sublimation at elevated temperatures or by sublimation in a stream of chlorine (see Chap. 14). Thus when UO_3 is treated with carbon tetrachloride vapor at 290°C, a product containing 23 per cent UO_2Cl_2 and 77 per cent UCl_4 is obtained (UCRL 2). If carbon monoxide or, better, chloroform is introduced with the carbon tetrachloride, the yield of uranyl chloride is increased (UCRL 3). However, these are not particularly convenient preparative reactions.

Hydrogen chloride reacts readily with uranium trioxide to form uranyl chloride. The reaction is exothermic and proceeds spontaneously at room temperature. Moisture must be present, for if anhydrous UO_3 is used, the reaction is extremely slow. A closed system, containing partially hydrated UO_3, is evacuated without heating in order to remove air but leave as much water as possible. Hydrogen chloride is then introduced at a rate sufficient to maintain a pressure of 1 atm in the reaction system. Approximately 18 to 24 hr at room temperature is required for completion of the reaction. Material so prepared has the formula $UO_2Cl_2 \cdot H_2O$. The hydrated uranyl chloride can be dried without decomposition in a current of dry hydrogen chloride gas at 300°C (Brown 3). It has been reported (without detail) that UO_3 suspended in ethanol or carbon tetrachloride gives uranyl chloride on treatment with hydrogen chloride (Purdue 1). The preparative value of this reaction is unknown.

Probably the best method for the preparation of anhydrous uranyl chloride is the reaction of uranium tetrachloride with oxygen at 300 to 350°C.

$$UCl_4 + O_2 \rightarrow UO_2Cl_2 + Cl_2 \tag{18}$$
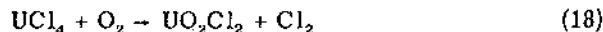
There is a tendency for the reaction mass to sinter, preventing complete conversion; it can be counteracted by agitating the reaction tube. Mixtures of UCl_5, UCl_6, and UCl_3 also react with oxygen to give uranyl chloride, but UCl_4 appears to be the best starting material (MP Ames 4).

Acetyl chloride, CH_3COCl, reacts with various oxides to give halides or oxyhalides (Chrétien and Oechsel, 1938). With UO_3 and liquid CH_3COCl at room temperature, $UO_2Cl_2 \cdot (CH_3CO)_2O$, a pale-yellow crystalline powder, is obtained. Whether pure uranyl chloride could be obtained from this complex is not stated. Further work would be interesting.

3.2 Preparation of Uranyl Chloride Hydrates. Aqueous solutions of uranyl chloride have been prepared by careful oxidation of a solution of uranium tetrachloride with nitric acid (Arfvedson, 1824), by

solution of $UO_3 \cdot H_2O$ in (Mylius and Dietz, 1901). amount of barium chlor 1909a). Solid hydrates solutions. Usually, amor oration in a desiccator fluorescent, easily decom Dietz, 1901). Crystalliz into a concentrated solut prepared by treating som centrated hydrochloric a ously by slow evaporation

The monohydrate, UO 1909a) to be formed by air. Evaporation of a uran also been stated to yield with hydrogen chloride of ride at −10°C gives UO_2Cl (Aloy, 1901a).

All the above-mentioned uranyl chloride could not tion. Mylius and Dietz rep at room temperature when form basic salts is great isolated in the form of sma from the syrupy evapora This substance is probably by Lecanu (1825). It is m water of crystallization is

3.3 Physical Properties (MP Ames 6.) X-ray di uranyl chloride powder a uranyl chloride from the v as the needles show many diagram. The crystal is cell. The lattice constant

Needles: $a_0 = 8.71 \pm 0.01$

Powder: $a_0 = 8.69 \pm 0.01$

The density calculated fro measurement of the densi (MP Ames 5).

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solution of UO$_3$·H$_2$O in an equivalent amount of hydrochloric acid (Mylius and Dietz, 1901), and also by the addition of the stoichiometric amount of barium chloride to a solution of uranyl sulfate (de Coninck, 1909a). Solid hydrates can be prepared by evaporation from such solutions. Usually, amorphous products are obtained, but slow evaporation in a desiccator yields yellowish-green, doubly refracting, fluorescent, easily decomposed crystals of UO$_2$Cl$_2$·3H$_2$O (Mylius and Dietz, 1901). Crystallization can sometimes be induced by introducing into a concentrated solution of uranyl chloride a few seed crystals, prepared by treating some of the semiamorphous material with concentrated hydrochloric acid and allowing it to crystallize spontaneously by slow evaporation in a desiccator.

The monohydrate, UO$_2$Cl$_2$·H$_2$O, has been reported (de Coninck, 1909a) to be formed by slow evaporation of an aqueous solution in dry air. Evaporation of a uranyl chloride solution at 120°C to dryness has also been stated to yield UO$_2$Cl$_2$·H$_2$O (SAM Columbia 5). Saturation with hydrogen chloride of a saturated aqueous solution of uranyl chloride at −10°C gives UO$_2$Cl$_2$·HCl·2H$_2$O as yellow, very unstable crystals (Aloy, 1901a).

All the above-mentioned workers were of the opinion that hydrated uranyl chloride could not be dehydrated without serious decomposition. Mylius and Dietz reported that hydrogen chloride is evolved even at room temperature when evaporation is attempted. The tendency to form basic salts is great. A compound, UO$_2$(OH)Cl·2H$_2$O, has been isolated in the form of small yellow needles (Mylius and Dietz, 1901) from the syrupy evaporation product of a uranyl chloride solution. This substance is probably identical with that described much earlier by Lecanu (1825). It is more stable than uranyl chloride hydrate; the water of crystallization is lost at 150°C without further decomposition.

3.3 Physical Properties of Uranyl Chloride. (a) Crystal Structure. (MP Ames 6.) X-ray diagrams have been obtained for anhydrous uranyl chloride powder and for the needles obtained by condensing uranyl chloride from the vapor (500°C). The two forms are different, as the needles show many maxima that are absent from the powder diagram. The crystal is orthorhombic with four molecules per unit cell. The lattice constants are

Needles: $a_0 = 8.71 \pm 0.01$ A $\qquad b_0 = 8.39 \pm 0.01$ A $\qquad c_0 = 5.72 \pm 0.01$ A

Powder: $a_0 = 8.69 \pm 0.01$ A $\qquad b_0 = 8.39 \pm 0.01$ A $\qquad c_0 = 5.70 \pm 0.01$ A

The density calculated from the x-ray data is 5.426 g/cc. A direct measurement of the density by benzene displacement gave 5.28 g/cc (MP Ames 5).

(b) Volatility. Uranyl chloride was described as somewhat volatile in a stream of chlorine or oxygen above 500°C. It has been found, however, that uranyl chloride will not markedly volatilize at 630°C in a chlorine atmosphere in 7 hr (Purdue 2). The volatility has been studied by tracer techniques with results that indicated no substantial volatility below 775°C. These results require confirmation (Mp Berkeley 1). Decomposition renders interpretation of the volatility data difficult. Anhydrous uranyl chloride has been reported to melt at a relatively low temperature (red heat). The vapor was reported to be orange-yellow in color (Péligot, 1842a,b).

(c) Miscellaneous. Crystals of anhydrous uranyl chloride show no triboluminescence (Trautz, 1905). Molten uranyl chloride conducts an electric current; chlorine is evolved and uranium dioxide separates out of the melt (Hampe, 1888).

3.4 Chemical Properties of Uranyl Chloride. Anhydrous uranyl chloride is a bright-yellow crystalline substance. The hydrates have a greenish cast and appear to be fluorescent. Both anhydrous and hydrated uranyl chloride are very hygroscopic and rapidly form viscous solutions on exposure to air. In dry air the compounds are stable indefinitely.

(a) Solubility in Water and the Stability of Aqueous Solutions. Uranyl chloride, its hydrates, and basic salts are very soluble in water. The trihydrate is soluble to the extent of 746 parts per 100 parts of water at 18°C and even more at higher temperatures (Mylius and Dietz, 1901), but this seems strange. The solubility is reported to be higher in hydrochloric acid solution (Aloy, 1901b). The density of the saturated aqueous solution at 18°C is 2.740 g/cc, which is sufficiently high to float glass or quartz. The density of solutions containing between 1 and 10 per cent uranyl chloride at 13 to 16°C lies between 1.0056 and 1.0517 g/cc (de Coninck, 1904). The molar heat of solution of $UO_2Cl_2 \cdot H_2O$ (in 2,500 moles of H_2O) has been determined as 6.05 kcal (at 18 to 20°C) (Aloy, 1896). This value is uncertain because of the indefinite composition of the salt used.

Aqueous solutions of uranyl chloride are thermally and photochemically unstable (Mylius and Dietz, 1901). Solutions are usually acid to litmus, indicating appreciable hydrolysis. Although de Coninck (1909b) was unable to verify the existence of $UO_2(OH)Cl \cdot 2H_2O$ (which has been found by other workers), the formation of such basic salts as a result of hydrolysis seems fairly well established.

(b) Nonaqueous Solutions of Uranyl Chloride. Uranyl chloride is said to dissolve in methyl acetate, ethyl acetate, acetone, and pyridine, but whether reaction occurs is not stated (Naumann, 1904, 1909).

Anhydrous uranyl lene, and benzene. chloroform. It is dioxane, but react Uranyl chloride tri

Von Unruh (1909 amyl alcohol by re drochloric acid an chloride in amyl al alcohol.

(c) Thermal Sta undergo decomposi converted to U_3O_8 ports that uranyl chlorine at tempei U_3O_8 (Brown 4). Ames (MP Ames 5 and chlorine occui stream of chlorine at about 500°C. A sition to UO_2 and chloride and of U the uranyl chlori studies have show ferent from ordin

(d) Reducing Ag and potassium cl Magnesium at red metal (Seubert an ings fail to do so uranyl chloride to

(e) Alkalis. (D hydroxide or sod with a small am some $CaUO_4$ form Barium hydroxide air give some U_3(also, whereas Ba strontium oxide k

(f) Acids. (De rine and nitrogen sulfuric acid con

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(Naumann, 1904, 1909).

Anhydrous uranyl chloride is insoluble in carbon tetrachloride, xy-lene, and benzene. It does not dissolve in, but reacts with, ethers and chloroform. It is soluble in alcohols, acetophenone, pyridine, and dioxane, but reaction occurs with all these solvents (MP Ames 4). Uranyl chloride trihydrate is soluble in alcohol and ether.

Von Unruh (1909) prepared anhydrous uranyl chloride solutions in amyl alcohol by repeatedly evaporating uranyl acetate, first with hy-drochloric acid and then with water, dissolving the hydrated uranyl chloride in amyl alcohol, and distilling the water off with some of the alcohol.

(c) Thermal Stability. Uranyl chloride and its hydrates readily undergo decomposition at elevated temperatures. Uranyl chloride is converted to U$_3$O$_8$ by ignition in air. The Brown University group re-ports that uranyl chloride decomposes in vacuum with evolution of chlorine at temperatures above 450°C, leaving a mixture of UO$_2$ and U$_3$O$_8$ (Brown 4). The thermal stability has been further studied at Ames (MP Ames 5). In a stream of nitrogen, decomposition to UO$_2$ and chlorine occurs above 400°C. In vacuum it begins at 300°C. In a stream of chlorine, uranyl chloride melts to a reddish-brown liquid at about 500°C. As the temperature is increased to 900°C, decompo-sition to UO$_2$ and chlorine occurs, with some sublimation of uranyl chloride and of UCl$_5$ formed by reaction with chlorine. The bulk of the uranyl chloride is converted to black crystalline UO$_2$. X-ray studies have shown that the UO$_2$ obtained in this way is slightly dif-ferent from ordinary brown UO$_2$.

(d) Reducing Agents. Anhydrous uranyl chloride is reduced to UO$_2$ and potassium chloride by metallic potassium (Péligot, 1842a,b). Magnesium at red heat partially reduces uranyl chloride to uranium metal (Seubert and Schmidt, 1892). Hydrogen, zinc, or copper turn-ings fail to do so (de Coninck, 1904, 1909c). Hydrogen sulfide reduces uranyl chloride to UO$_2$, sulfur, and hydrogen chloride.

(e) Alkalis. (De Coninck, 1904, 1909a,c.) Fusion with potassium hydroxide or sodium hydroxide in air gives a mixture of diuranate with a small amount of uranate. With calcium hydroxide, U$_3$O$_8$ and some CaUO$_4$ form; if air is excluded, UO$_2$ is formed instead of U$_3$O$_8$. Barium hydroxide acts similarly. Calcium oxide and barium oxide in air give some U$_3$O$_8$ and, in the case of CaO, some CaUO$_4$ and CaU$_2$O$_7$ also, whereas BaO gives principally BaU$_2$O$_7$. Strontium hydroxide and strontium oxide behave similarly to the barium compounds.

(f) Acids. (De Coninck, 1903, 1904.) Uranyl chloride evolves chlo-rine and nitrogen oxides on warming with nitric acid. Concentrated sulfuric acid converts uranyl chloride to uranyl sulfate with evolution

of hydrogen chloride. Selenic acid dissolves uranyl chloride; on warming, chlorine is evolved and a solution of uranyl selenite is formed.

(g) Reactions in Aqueous Solutions. Aqueous solutions of uranyl chloride exhibit all the reactions characteristic of the uranyl ion.

(h) Complex Compounds of Uranyl Chloride with Ammonia and Organic Bases. An extensive series of uranyl chloride ammoniates is known. Vacuum-dried uranyl chloride absorbs two molecules of ammonia to form an orange compound, $UO_2Cl \cdot 2NH_3$; of the two NH_3 molecules, one is bound so strongly as to be retained in vacuum (Peters, 1909, 1912). An ether solution of uranyl chloride, when treated with ammonia, forms a precipitate, $UO_2Cl_2 \cdot 2NH_3 \cdot (C_2H_5)_2O$, from which the ether can be removed in vacuum (Regelsberger, 1885). The same etherate can also be obtained from an amyl alcohol solution of uranyl chloride by treatment with ammonia and treatment of the dried precipitate with ether (von Unruh, 1909). The diammoniate is decomposed by warming to 100°C with the formation of ammonium chloride; on ignition in air it is converted to U_3O_8. It is reduced at elevated temperatures by hydrogen or ammonia to UO_2 (Regelsberger, 1885). A triammoniate is also known but only in the form of an etherate, $UO_2Cl_2 \cdot 3NH_3 \cdot (C_2H_5)_2O$ (Regelsberger, 1885). This compound is obtained by treatment of the diammoniate etherate with gaseous ammonia; it is an orange material, stable in air at room temperature, but loses ammonia on heating. An unstable tetraammoniate is formed by treating uranyl chloride with liquid ammonia at 5°C. The orange-red amorphous solid begins to decompose at 10°C (von Unruh, 1909). Rosenheim and Jacobsohn (1906) observed the formation of a gray-green precipitate when uranyl chloride was treated with liquid ammonia, but its composition was not established.

The most precise work on the uranyl chloride–ammonia system is that of Spacu (1936), who studied the reaction of liquid ammonia and uranyl chloride at −78°C. Under these conditions uranyl chloride is found to form decaammoniate, $UO_2Cl_2 \cdot 10NH_3$. As the temperature is raised ammonia is evolved, and vapor pressure measurements have indicated the existence of the complexes $UO_2Cl_2 \cdot 5NH_3$, $UO_2Cl_2 \cdot 4NH_3$, $UO_2Cl_2 \cdot 3NH_3$, $UO_2Cl_2 \cdot 2NH_3$, and $UO_2Cl_2 \cdot NH_3$. Figure 16.2 illustrates the results from which these conclusions were drawn. The temperatures of the isothermal lines in Fig. 16.2 indicate the thermal stability ranges of the various compounds. The pentaammoniate is particularly unstable, even at −44°C, whereas the monoammoniate is quite stable up to 130°C.

The heat of formation of the ammoniates varies from −9.63 kcal per mole for $UO_2Cl_2 \cdot 5NH_3$ to −18.03 kcal per mole for $UO_2Cl_2 \cdot NH_3$.

A number of organic bases uranyl chloride. It appears tha uranium in uranyl chloride c ammonia molecules, steric con organic groups to two. The p of such complexes are given i

Fig. 16.2—The uranyl chloride am Chem., 230: 183 (1936)].

also include, in addition to whose basic properties are

(i) Complex Compounds of Uranyl chloride forms a ser where M = a univalent metal pared anhydrous $K_2UO_2Cl_4$ an alkali halide with uranyl chlor are described as golden-yel heat without evolving any vap

Compounds of this type c tion, in which case the dihyd $K_2UO_2Cl_4 \cdot 2H_2O$ and $(NH_4)_2UO$ ing $K_2U_2O_7$ or $(NH_4)_2U_2O_7$ in by evaporation until cryst tallization of a uranyl chlor halide also is effective. W

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A number of organic bases also form complex compounds with uranyl chloride. It appears that, although the coordination sphere of uranium in uranyl chloride can accommodate a maximum of four ammonia molecules, steric considerations usually limit the number of organic groups to two. The preparation and properties of a number of such complexes are given in Table 16.7. The complexing groups
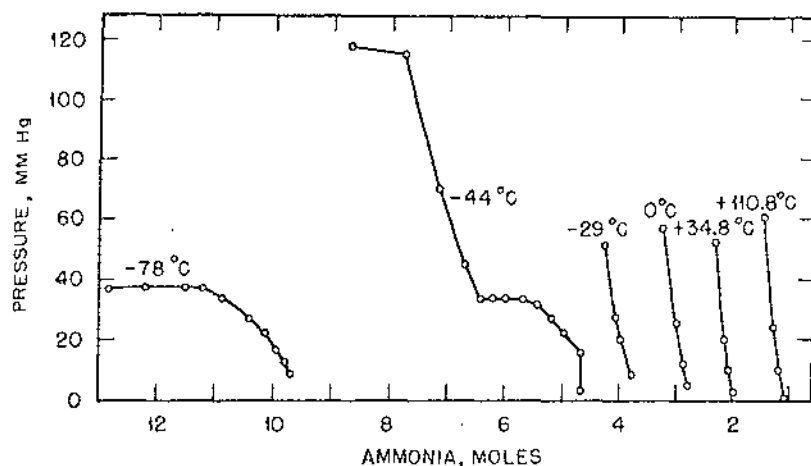

Fig. 16.2 — The uranyl chloride−ammonia system [from P. Spacu, Z. anorg. u. allgem. Chem., 230: 183 (1936)].

also include, in addition to basic nitrogen compounds, compounds whose basic properties are due to oxygen or sulfur.

(i) Complex Compounds of Uranyl Chloride and Metal Halides. Uranyl chloride forms a series of double salts of the type $M_2UO_2Cl_4$, where M = a univalent metal or an equivalent ion. Aloy (1901b) prepared anhydrous $K_2UO_2Cl_4$ and $Na_2UO_2Cl_4$ by treating the appropriate alkali halide with uranyl chloride vapors at red heat. The double salts are described as golden-yellow water-soluble solids that melt at red heat without evolving any vapors.

Compounds of this type can also be prepared from aqueous solution, in which case the dihydrate is usually obtained. The compounds $K_2UO_2Cl_4·2H_2O$ and $(NH_4)_2UO_2Cl_4·2H_2O$ were first prepared by dissolving $K_2U_2O_7$ or $(NH_4)_2U_2O_7$ in concentrated hydrochloric acid, followed by evaporation until crystallization occurred (Peligot, 1842b). Crystallization of a uranyl chloride solution containing the desired alkali halide also is effective. With M = potassium, it is necessary either

Table 16.7—Complex Compounds of Uranyl Chloride with Organic Bases

Organic base	Complex	Method of preparation	Properties	Solubility							
				Water	Ethanol	Amyl alcohol	Ether	Ethyl acetate	Acetone	Chloroform	Benzene
Ethyl ether[a]	$UO_2Cl_2 \cdot 2(C_2H_5)_2O$	Evaporation of a solution of UO_2Cl_2 in ether	Yellow needles; decomposes in moist air; ether cannot be removed								
2,3-Dimethyl chromone[b]	$UO_2Cl_2 \cdot 2C_{11}H_{10}O_2$	From conc. HCl solution of the components; recrystallized from conc. HCl	Long glistening bright-yellow prisms; decomposes without melting		Sl. sol.				Sl. sol.		
2,3-Dimethyl thiochromone[c]	$UO_2Cl_2 \cdot 2C_{11}H_{10}OS$	From conc. HCl solution of the components by evaporation			Sl. sol.				Sl. sol.		
Aniline[d]	$UO_2Cl_2 \cdot 2C_6H_5NH_2$	From an alcoholic solution of the components; recrystallized from alcohol	Small yellow needles		Sol.						
p-Toluidine[d]	$UO_2Cl_2 \cdot 2C_7H_7NH_2$	Evaporation of an alcoholic solution of the components	Yellow-green rhombic crystals								
Pyridine[e]	$UO_2Cl_2 \cdot 2C_5H_5N$	From solution of $UO_2Cl_2 \cdot xH_2O$ in amyl alcohol and $CHCl_3$ solution of pyridine, on cooling	Yellow, weak green fluorescence; very hygroscopic	Sol.	Sol. hot		In- sol.		In- sol.	In- sol.	In- sol.
p-Nitroso dimethyl aniline[f]	$UO_2Cl_2 \cdot 2(CH_3)_2NC_6H_4NO$	From a warm alcoholic solution of the components	Brick red; stable in air	Dif. sol.		In- sol.	Sl. sol.		In- sol.	Sl. sol.	
p-Nitroso diethyl aniline[g]	$UO_2Cl_2 \cdot 2(C_2H_5)_2NC_6H_4NO$	From a warm alcoholic solution of the components	Orange colored; amorphous	Dif. sol.		In- sol.	Sl. sol.		In- sol.	Sl. sol.	

Table 16.7—(Continued)

Organic base	Complex	Method of preparation	Properties	Solubility							
				Water	Ethanol	Amyl alcohol	Ether	Ethyl acetate	Acetone	Chloroform	Benzene
Diketopiperazine[h]	$UO_2Cl_2 \cdot C_4H_6N_2O_2 \cdot 1.5H_2O$		Yellow crystals; stable in air								
Acet-p-phenetidine[i]	$UO_2Cl_2 \cdot 2C_{10}H_{13}O_2N$	From a warm alcoholic solution	Yellow crystals with green fluorescence	Sol.	Sol. hot	Sol. hot	V. sol.		Sol.	V. sl.	
	$UO_2Cl_2 \cdot 3C_{10}H_{13}O_2N$	From a warm amyl									

Organic base	Complex	Method of preparation	Properties	Water	Ethanol	Amyl alcohol	Ether	Ethyl acetate	Acetone	Chloroform	Benzene
p-Toluidine[?]	$UO_2Cl_2 \cdot 2C_7H_7NH_2$	Evaporation of an alcoholic solution of the components	Yellow-green rhombic crystals								
Pyridine[e]	$UO_2Cl_2 \cdot 2C_5H_5N$	From solution of $UO_2Cl_2 \cdot xH_2O$ in amyl alcohol and $CHCl_3$ solution of pyridine, on cooling	Yellow, weak green fluorescence; very hygroscopic	Sol.	Sol. hot		Insol.		In-sol.	In-sol.	In-sol.
p-Nitroso dimethyl aniline[f]	$UO_2Cl_2 \cdot 2(CH_3)_2NC_6H_4NO$	From a warm alcoholic solution of the components	Brick red; stable in air	Dif. sol.	Insol.	Sl. sol.				In-sol.	Sl. sol.
p-Nitroso diethyl aniline[g]	$UO_2Cl_2 \cdot 2(C_2H_5)_2NC_6H_4NO$	From a warm alcoholic solution of the components	Orange colored; amorphous	Dif. sol.	Insol.	Sl. sol.				In-sol.	Sl. sol.

Table 16.7—(Continued)

Organic base	Complex	Method of preparation	Properties	Solubility							
				Water	Ethanol	Amyl alcohol	Ether	Ethyl acetate	Acetone	Chloroform	Benzene
Diketopiperazine[h]	$UO_2Cl_2 \cdot C_4H_6N_2O_2 \cdot 1.5H_2O$		Yellow crystals; stable in air								
Acet-p-phenetidine[i]	$UO_2Cl_2 \cdot 2C_{10}H_{13}O_2N$	From a warm alcoholic solution	Yellow crystals with green fluorescence; stable in air	Sol.	Sol. hot	Sol. hot	V. sl. sol.		Sol.		V. sl. sol.
	$UO_2Cl_2 \cdot 3C_{10}H_{13}O_2N$	From a warm amyl alcohol solution									
Methyl acetanilide[j]	$UO_2Cl_2 \cdot 2C_6H_5N(CH_3)COCH_3$	From an ethyl or amyl alcohol solution of the components	Shining tabular yellow crystals	Sol.	Sol.	Sl. sol.	Sl. sol.				
Phenyl dimethyl pyrazolone[k] (antipyrine)	$UO_2Cl_2 \cdot 2C_{11}H_{12}N_2O$	From an aqueous solution of the components	Stable in air even on heating	Sol.	Dif. sol.		Sol.			Sol.	
Bromantipyrine[l]	$UO_2Cl_2 \cdot 2C_{11}H_{11}BrN_2O$	From alcoholic solutions of the components at higher temperatures		Sol.	Sol. hot		In-sol.	V. sl. sol.	V. sl. sol.	In-sol.	
Dimethylamino antipyrine (pyramidon)[m]	$UO_2Cl_2 \cdot C_{11}H_{11}N(CH_3)_2N_2O$	From alcoholic solutions of the components at higher temperatures	Amorphous; yellow	Sol.	Sol.	Sl. sol.	In-sol.			Sl. sol.	Sl. sol.
	$UO_2Cl_2 \cdot 2C_{11}H_{11}N(CH_3)_2N_2O$	From alcoholic solutions of the components in the cold									

[a]Regelsberger, 1885.
[b]Simonis and Elias, 1915.
[c]Simonis and Elias, 1916.
[d]Leeds, 1881.
[e]Răscanu, 1930-1931a.
[f]Răscanu, 1931-1932a.
[g]Răscanu, 1931-1932b.
[h]Asahina and Dôno, 1930.
[i]Răscanu, 1930-1931b.
[j]Răscanu, 1931-1932c.
[k]Răscanu, 1930-1931c.
[l]Răscanu, 1932-1933.
[m]Răscanu, 1930-1931d.

Note: All references to the work of R. Răscanu are from "Gmelins Handbuch der anorganischen Chemie," System No. 55, pp. 135-136, Verlag Chemie, Berlin.

to use an excess of uranyl chloride or to work in concentrated hydrochloric acid solutions to prevent precipitation of potassium chloride. Thus $K_2UO_2Cl_4 \cdot 2H_2O$ was prepared by Rimbach (1904) by crystallizing an aqueous solution containing equimolecular quantities of the components, together with at least 15 per cent hydrochloric acid. $K_2UO_2Cl_4 \cdot 2H_2O$ forms yellow triclinic crystals with a:b:c = 0.607:1: 0.560, $\alpha = 80°\ 41'$, $\beta = 77°\ 42'$, and $\gamma = 91°\ 18'$. It is very soluble in water. Below 60°C dissolution occurs with decomposition, and the undissolved residue is mostly potassium chloride; above 60°C the solute and the undissolved solid have the same composition. The heat of dissolution is about 2 kcal per mole at 18°C, in infinitely dilute solution (1 mole in 2,500 moles) (Aloy, 1896). The compound can be dehydrated at 100°C but only with some decomposition. At red heat it melts with evolution of chlorine. Hydrogen reduces it. In contradistinction to $K_3UO_2F_5$, the compound $K_2UO_2Cl_4 \cdot 2H_2O$ is not reduced in sunlight by formic or oxalic acid solution (Bolton, 1866b).

$Rb_2UO_2Cl_4 \cdot 2H_2O$ and $Cs_2UO_2Cl_4$ are prepared similarly to $K_2UO_2Cl_4$ (Rimbach, 1904). The rubidium compound is isomorphous with the potassium and ammonium salts. The rubidium and cesium salts dissolve in water without decomposition. They are thus more stable than the complex with potassium chloride (and also that with NH_4Cl; cf. below), both of which dissociate upon dissolution at room temperature. A certain correlation appears to exist between stability of the complex and the size of the cation; the larger the latter, the stronger the complex. The cesium compound crystallizes in anhydrous form; the rubidium compound has been observed to do so occasionally. According to Wells and Boltwood (1895), who first studied these compounds, the cesium compound forms shiny rhombic crystals; but Nichols and Howes (1919) report the substance to be triclinic. The potassium, cesium, and ammonium salts have been grown as large crystals, and their absorption and fluorescence spectra studied; details are discussed elsewhere (SAM Columbia 4; Dieke and Duncan, 1949).

Quaternary ammonium salts form an analogous series of compounds. These differ from the complexes given in Sec. 3.4h in that the ligand is a salt rather than a free base. Rimbach (1904) has described compounds derived from ammonium chloride, trimethylammonium chloride, tetramethylammonium chloride, and tetraethylammonium chloride; efforts to prepare hydroxylamine and hydrazine derivatives were unsuccessful. Ammonium uranyl chloride, $(NH_4)_2UO_2Cl_4 \cdot 2H_2O$, can be prepared from a concentrated hydrochloric acid solution of uranyl chloride and ammonium chloride. It forms very unstable crystals isomorphic with the potassium compound. It dissolves in water, with decomposition, below 70°C. Mono-, di-, and trimethylamine hydrochlorides form unstable compounds of the type $[(CH_3)_3N]_2UO_2Cl_4 \cdot$

Tetramethylammonium pared from an aqueous strongly fluorescent. solve without decompos chloride, $[(C_2H_5)_4N]$ tion from an aqueous components. It forms morphic with the corr it dissolves in water uranyl chloride (Gr prepared by addition of ethylenediamine an chloride, forms very melt at 219°C (not sh prepared: pyridinium talline powder, solub lutidinium uranyl chl quinolinium uranyl c analogous oxonium s (Fosse and Lesage, 1

4. URANIUM(IV) O

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Aloy found that ev low temperatures in dissolution of this pr gives a product which in a desiccator, has t a bright-green cryst solutions decompose dioxide. These findin sity of California R uranium tetrachlorid hydrogen chloride, g and $UOCl_{2.02} \cdot 1.25H_2O$

Tetramethylammonium uranyl chloride, $[(CH_3)_4N]_2UO_2Cl_4$, can be prepared from an aqueous solution of the components as greenish-yellow, strongly fluorescent, tetragonal crystals (a:c = 1:0.9057) which dissolve without decomposition in water. Tetraethylammonium uranyl chloride, $[(C_2H_5)_4N]_2UO_2Cl_4$, is likewise prepared by slow crystallization from an aqueous solution containing equivalent proportions of the components. It forms yellow tetragonal crystals, a:c = 1:0.9094, isomorphic with the corresponding tetramethyl compound; like the latter, it dissolves in water without decomposition. Ethylenediammonium uranyl chloride (Grossman and Schuck, 1906), $C_2H_4(NH_3)_2UO_2Cl_4$, best prepared by addition of excess hydrochloric acid to a water solution of ethylenediamine and then addition of an equimolar amount of uranyl chloride, forms very hygroscopic, yellow, prismatic crystals that melt at 219°C (not sharp). The following compounds have also been prepared: pyridinium uranyl chloride, $(C_5H_6N)_2UO_2Cl_4$, yellow crystalline powder, soluble in water and alcohol (Kalischer, 1902); β-lutidinium uranyl chloride, $(C_7H_{10}N)_2UO_2Cl_4$ (Williams, 1881); and quinolinium uranyl chloride, $(C_9H_8N)_2UO_2Cl_4$ (Williams, 1856). The analogous oxonium salt, xanthylium uranyl chloride $[(C_{13}H_9O)_2UO_2Cl_4]$ (Fosse and Lesage, 1906), is also known.

4. URANIUM(IV) OXYCHLORIDE, UOCl$_2$ (URANOUS OXYCHLORIDE)

Several reports appear in the older literature purporting to describe this substance. Benrath (1917) claimed that anhydrous uranous oxychloride resulted from photochemical reduction of an ether solution of uranyl chloride in direct sunlight. The product was described as light green in color. Reduction in alcohol-ether mixtures gave complex mixtures of basic salts; in aqueous solution, only hydrated uranium dioxide formed. Little reliance can be placed on these results; no experimental details were given, and the description of the products evokes doubt as to their correct identification.

Aloy found that evaporation of a uranium tetrachloride solution at low temperatures in vacuum yielded an amorphous precipitate. Redissolution of this precipitate in ethanol and reprecipitation by ether gives a product which, after thorough washing with ether and drying in a desiccator, has the composition UOCl$_2 \cdot 0.5H_2O$. It is described as a bright-green crystalline substance, rather soluble in water; such solutions decompose on heating with separation of hydrated uranium dioxide. These findings are confirmed by observations at the University of California Radiation Laboratory that an aqueous solution of uranium tetrachloride, when dried at 100°C in air or at 120°C in dry hydrogen chloride, gives solids with the composition UO$_{1.1}$Cl$_{1.9} \cdot 1.2H_2O$ and UOCl$_{2.02} \cdot 1.25H_2O$ (UCRL 4) (see also Chap. 14).

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by Rimbach (1904) by crys-
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per cent hydrochloric acid.
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drochloric acid solution of
t forms very unstable crys-
ound. It dissolves in water,
-, di-, and trimethylamine
of the type $[(CH_3)_3N]_2UO_2Cl_4$.

The most direct and generally satisfactory synthesis of uranous oxychloride consists in dissolving UO_2 in excess molten UCl_4 (600°C) (Brown 1,5). The equilibrium

$$UO_2 + UCl_4 \rightleftharpoons 2UOCl_2 \qquad (19)$$

is established under these conditions. After cooling and grinding, the excess UCl_4 can be removed at 450°C in vacuum, conditions under which disproportionation of the uranous oxychloride is negligible.

Uranous oxychloride has also been prepared at the University of California Radiation Laboratory (cf. UCRL 4) by treating UO_2 with UCl_4 vapors. The uranous oxychloride obtained in this way is not as pure as that prepared by liquid-phase reaction.

At Ames two unsuccessful attempts were made to prepare uranium(IV) oxychloride. In one, chlorine was reacted with $U_3O_2S_4$ (in analogy to a reaction successfully used in the preparation of uranous oxybromide), but the product was only a mixture of uranyl chloride with higher uranium chlorides. In the second attempt, superheated water vapor was conducted (in a stream of inert gas) over UCl_4; this, too, failed to produce $UOCl_2$ of satisfactory purity (MP Ames 5).

Uranous oxychloride was described by the Ames group as yellow feather-shaped crystals, but these were called green by workers at Brown University. The yellow crystals are stable in air and dissolve in water to form a green solution. Preliminary x-ray data at Ames (MP Ames 7) on single crystals have been obtained. They appeared to be tetragonal or hexagonal. The spacing along the needle axis is 3.32 A, as derived from layer line spacings. The layer line spacings normal to the needle axis are about 40 A but are indistinct. Some preliminary x-ray work has also been done elsewhere, but no conclusions as to the structure are as yet available (Johns Hopkins 1). A value of 2.4 has been reported for the dielectric constant of solid uranous oxychloride (CEW-TEC 3).

4.1 Heat of Formation of Uranium(IV) Oxychloride. (UCRL 5.) The heat of solution of uranium(IV) oxychloride has been determined as $\Delta H = -16.7 \pm 0.2$ kcal per mole, from which the heat of formation can be calculated.

$$U \text{ (solid)} + Cl_2 \text{ (gas)} + \tfrac{1}{2}O_2 \text{ (gas)} \rightarrow UOCl_2 \text{ (solid)} \qquad (20)$$
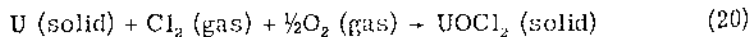
$$\Delta H_{298°K} = -261.7 \text{ kcal per mole}$$

4.2 Equilibrium Pressure of Uranium Tetrachloride above Uranous Oxychloride. (UCRL 6.) As mentioned above, the reaction

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UO_2 (solid)

is reversible. The equ oxychloride has been are summarized in Tab action 21 a value of 5

Table 16.8 — Equilibr

Temp., °C
460
470
480
490
500
510
520
530
540

Table 16.9   Equilibrium C

Temp., °C
300
350
385
400
450

$*K = p_{HCl}$

sure of UCl_4 over uran one hundred times su same temperature.

4.3 Equilibrium of (UCRL 7.) Although t by hydrogen have not b be the most likely pr been referred to the r

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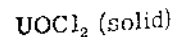
RANIUM

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excess molten UCl$_4$ (600°C)

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7) Oxychloride. (UCRL 5.)
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→ UOCl$_2$ (solid)   (20)

r mole

Tetrachloride above Ura-
ned above, the reaction

$$UO_2 \text{ (solid)} + UCl_4 \text{ (gas)} \rightleftharpoons 2UOCl_2 \text{ (solid)} \tag{21}$$

is reversible. The equilibrium pressure of UCl$_4$ above uranium(IV) oxychloride has been measured between 460 and 540°C; the results are summarized in Table 16.8. These values yield for the ΔH of reaction 21 a value of 55.1 kcal. The equilibrium decomposition pres-

Table 16.8 — Equilibrium Pressure of Uranium Tetrachloride above Pure Uranous Oxychloride

| Temp., °C	$\frac{1}{T} \times 10^3$	Pressure of UCl$_4$, mm Hg
460	1.364	7.1×10^{-4}
470	1.346	1.18×10^{-3}
480	1.328	1.95×10^{-3}
490	1.311	3.13×10^{-3}
500	1.294	5.0×10^{-3}
510	1.277	8.1×10^{-3}
520	1.261	1.28×10^{-2}
530	1.245	1.97×10^{-2}
540	1.230	3.03×10^{-2}

Table 16.9 — Equilibrium Constants for Hydrogen Reduction of Uranous Oxychloride*

Temp., °C	Temp., °K	$\frac{1}{T} \times 10^3$	K
300	573	1.745	<0.004
350	623	1.605	0.0061
385	658	1.520	0.0095
400	673	1.486	0.011
450	723	1.383	0.020

*$K = p_{HCl}/p_{H_2}^{1/2}$ (p in atmospheres).

sure of UCl$_4$ over uranium(IV) oxychloride at 500°C is approximately one hundred times smaller than the vapor pressure of UCl$_4$ at the same temperature.

4.3 Equilibrium of Hydrogen Reduction of Uranous Oxychloride. (UCRL 7.) Although the products of reduction of uranous oxychloride by hydrogen have not been identified with certainty, UOCl appears to be the most likely product. Consequently, all the calculations have been referred to the reaction

$$UOCl_2 \text{ (solid)} + \tfrac{1}{2}H_2 \text{ (gas)} \rightleftharpoons UOCl \text{ (solid)} + HCl \text{ (gas)} \tag{22}$$
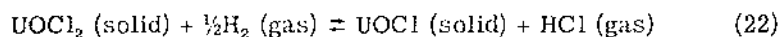
The experimental values of the equilibrium constant are given in Table 16.9. From these data the value $\Delta H_{673°K} = 10.6$ kcal per mole (± 10 to 15 per cent) is obtained; $\Delta F_{673°K}^{°}$ is then 6.03 kcal per mole, and $\Delta S_{673°K}^{°} = 6.79$ e.u.

4.4 Thermodynamic Constants. (UCRL 8.) MacWood has given the following values for the thermodynamic constants of uranium oxychloride:

$$\Delta H_{298°K} = -261.7 \text{ kcal per mole}$$

$$\Delta F_{298°K} = -246.3 \pm 1.5 \text{ kcal per mole}$$

$$S_{298°K} = 38.1 \text{ e.u.}$$

For details of the calculations and the assumptions involved, the reader is referred to MacWood's paper.

4.5 Chemical Properties. Few of the chemical properties of uranous oxychloride have been studied. Uranous oxychloride reacts with carbon tetrachloride at 170°C to form uranium tetrachloride. Liquid hydrogen fluoride at room temperature gives uranium tetrafluoride and not uranous oxyfluoride.

5. URANYL BROMIDE, UO_2Br_2

Uranyl bromide appears to be distinctly less stable than the fluoride and chloride. The preparation of anhydrous uranyl bromide was first described by Hermann (1861) and later by von Unruh (1909). Bromine vapors were passed over a mixture of uranium dioxide and charcoal at elevated temperatures, producing a mixture of uranium tetrabromide and uranyl bromide. Von Unruh separated the uranyl bromide by dissolving the reaction product in a mixture of alcohol and ether. Uranyl bromide etherate, $UO_2Br_2 \cdot 2(C_2H_5)_2O$, can be obtained as hygroscopic, red, fluorescent needles from this solution. Most of the ether is lost in vacuum. Richards and Merigold (1902) treated U_3O_8 with bromine or with hydrogen bromide but observed no reaction. A number of workers have prepared anhydrous uranyl bromide by dehydration of uranyl bromide hydrate. This work is discussed in Sec. 5.2.

5.1 Preparation of Anhydrous Uranyl Bromide. (MP Ames 8.) The Ames group prepared anhydrous uranyl bromide by reaction of oxygen with uranium tetrabromide.

$$UBr_4 + O_2 \rightarrow UO_2Br_2 + Br_2 \tag{23}$$

equilibrium constant are given in
value $\Delta H_{673°K}$ = 10.6 kcal per mole
$\Delta F°_{673°K}$ is then 6.03 kcal per mole,

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kcal per mole

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ed. Uranous oxychloride reacts with
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ROMIDE, UO$_2$Br$_2$

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nruh separated the uranyl bromide
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Merigold (1902) treated U$_3$O$_8$ with
but observed no reaction. A num-
ydrous uranyl bromide by dehydra-
is work is discussed in Sec. 5.2.

Iranyl Bromide. (MP Ames 8.) The
ranyl bromide by reaction of oxy-

$$O_2Br_2 + Br_2 \qquad\qquad (23)$$

The temperature regulation is important. Below 140°C the reaction is extremely slow; at 200°C considerable amounts of U$_3$O$_8$ are produced. The best range is 150 to 160°C; preparations analyzing 96 per cent uranyl bromide can be readily obtained at this temperature. X-ray photographs showed no UO$_2$, U$_3$O$_8$, UO$_3$, or UBr$_4$ to be present in the product.

Uranium tribromide, UBr$_3$, when treated with oxygen at room temperature burns vigorously. This is therefore not a good preparative method. It had been observed (MP Ames 9) that uranium dioxide does not react with bromine even at 720°C. Anhydrous hydrogen bromide reacts at 100°C with dry ammonium diuranate, (NH$_4$)$_2$U$_2$O$_7$, to give, among other products, a water-soluble substance thought to be a double salt of ammonium bromide and uranyl bromide.

5.2 Preparation of Hydrated Uranyl Bromide. Richards and Merigold (1902) prepared aqueous solutions of uranyl bromide by the old method of Berthemot (1830), wherein uranium dioxide suspended in water is heated with bromine. After excess bromine has been removed by evaporation, a solution of uranyl bromide remains which can then be concentrated to a syrup. The yield of crystals from the syrup is small, and their solubility in water and in alcohol is so great that it is almost impossible to wash them free of mother liquor.

Sendtner (1879) obtained crystals of the hydrate by dissolving hydrated uranium dioxide in aqueous hydrobromic acid. The yellow solution was concentrated to a syrup and then dried in a desiccator. The hygroscopic unstable crystals so obtained had the composition UO$_2$Br$_2$·7H$_2$O. Repeated evaporation of uranyl acetate, first with hydrobromic acid and then with water, also yields an aqueous solution of uranyl bromide (von Unruh, 1909). Large yellow-green crystals form in a desiccator from this solution. These crystals are soluble in amyl alcohol; water of crystallization forms a separate layer, and the alcoholic solution can be decanted. The solution can be dehydrated even more completely by azeotropic distillation. Von Unruh suggested the use of ether for dehydration, but Richards and Merigold (1902) had stated that uranyl bromide reacts with ether. It is doubtful whether alcohol-free uranyl bromide can be obtained at all from alcoholic solutions.

5.3 Properties of Uranyl Bromide. Uranyl bromide is a bright-red, very hygroscopic solid that turns yellow in the presence of water vapor. It dissolves very readily in water to a yellow solution. Ethanol solutions of uranyl bromide are rather stable; in the presence of moisture and light some reduction to uranium(IV) occurs (MP Berke-

ley 2). Uranyl bromide, as has already been noted, is also soluble in ether and amyl alcohol.

Uranyl bromide hydrate, $UO_2Br_2 \cdot 7H_2O$, decomposes in moist air with evolution of hydrogen bromide and formation of hydrated uranium oxide. The compound is very soluble in water and exhibits reactions characteristic of UO_2^{++} ions. Aqueous solutions undergo extensive hydrolysis on boiling (de Coninck, 1902).

Uranyl bromide is thermally unstable as decomposition with slow liberation of bromine occurs even at room temperature; bromine is more rapidly evolved in a helium atmosphere at 250°C. However, even at 350°C, 48 hr is necessary for the complete decomposition. Since reverse reaction does not take place even at 720°C, the decomposition is irreversible, and its rate depends only on temperature and not on the partial pressure of bromine (MP Ames 10). Ignition of $UO_2Br_2 \cdot 7H_2O$ in the absence of air leads eventually to the formation of uranium dioxide, accompanied by evolution of bromine and hydrogen bromide. The uranium dioxide is red and appears to present one more of the many different varieties of this oxide (see Chap. 11).

Uranyl bromide, like the fluoride and chloride, readily forms double salts. The ammoniates $UO_2Br_2 \cdot 2NH_3$, $UO_2Br_2 \cdot 3NH_3$, and $UO_2Br_2 \cdot 4NH_3$ can be prepared by treatment of ethereal or ethanolic solutions of uranyl bromide with ammonia (von Unruh, 1909). $UO_2Br_2 \cdot 4NH_3$, a deeply colored orange-red compound made by treating the diammoniate with liquid ammonia, decomposes rapidly at room temperature.

Compounds of the type $M_2UO_2Br_4 \cdot 2H_2O$ have also been prepared (Sendtner, 1879). Ammonium or potassium diuranates dissolved in hydrobromic acid and evaporated to crystallization on a water bath form $(NH_4)_2UO_2Br_4 \cdot 2H_2O$ or $K_2UO_2Br_4 \cdot 2H_2O$; these compounds are large rhombic yellow crystals and are very soluble in water. These salts form only if a large excess of acid is used. If the pure salt is dissolved in water, it cannot be regenerated. Ignition of the potassium complex leads to a mixture of uranium oxide and potassium salts. The uranyl bromide double salts are more unstable than the corresponding chlorine compounds. The pyridine compound, $(C_5H_6N)_2UO_2Br_4$, has been prepared by addition of pyridine to a boiling solution of uranium trioxide in excess alcoholic hydrobromic acid. On cooling, yellow crystals of the complex are formed (Loebel, 1907).

Uranyl bromide forms a series of addition compounds with various basic organic compounds. An etherate, $UO_2Br_2 \cdot 2(C_2H_5)_2O$, has been described by von Unruh (1909). It is a yellow-green, fluorescent, crystalline substance, very hygroscopic, which decomposes rapidly in air with evolution of bromine. Răscanu (1930-1931b,c,e; 1932-1933)

has examined .
organic nitro[..]
lar uranyl chlo[..]
uranyl bromide
compound. The

The xanthyliu
also been prep[..]

Table 16.1[..]

Organic base

p-Nitroso dimethyl
aniline

p-Nitroso diethyl
aniline
Methyl acetanilide

Acet-p-phenetidine

Antipyrine

Bromantipyrine

6. URANIUM[..]

The preparatio[..]
(MP Ames 9) that
limation of uraniu
nous oxybromide
reactions has been

$3UO_2 +$

$U_3O_2S_4$

has examined a series of addition compounds of uranyl bromide with organic nitrogen bases. These are prepared exactly as the very similar uranyl chloride derivatives (cf. Sec. 3.3). The solubilities of the uranyl bromide complexes differ from those of the uranyl chloride compound. They are given in Table 16.10.
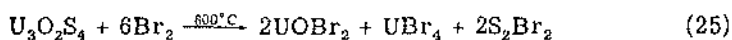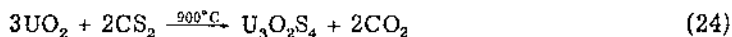
The xanthylium compound, $UO_2Br_2 \cdot 2C_{13}H_9OBr$ (yellow crystals), has also been prepared (Fosse and Lesage, 1906).

Table 16.10 — Complex Compounds of Uranyl Bromide with Organic Bases

Organic base	Complex	Description	Solubility
p-Nitroso dimethyl aniline	$UO_2Br_2 \cdot 2(CH_3)_2NC_6H_4NO$	Stable in air; brick-red powder	Sl. sol. in water; insol. in alcohol, ether, acetone, and chloroform
p-Nitroso diethyl aniline	$UO_2Br_2 \cdot 2(C_2H_5)_2NC_6H_4NO$	Dark brick-red powder	Same as above
Methyl acetanilide	$UO_2Br_2 \cdot 2C_6H_5N(CH_3)(C_2H_3O)$	Stable in air; shiny yellow crystals	Sol. in water and alcohol; insol. in ether
Acet-p-phenetidine	$UO_2Br_2 \cdot 4C_{10}H_{11}O_2N$	Orange-yellow; stable in air	Insol. in water; dif. sol. in alcohol, acetone, and chloroform; insol. in ether and amyl alcohol; completely sol. in amyl alcohol on heating
Antipyrine	$UO_2Br_2 \cdot 2C_{11}H_{12}N_2O$	Stable in air	Sol. in water; sl. sol. in alcohol; insol. in ether and chloroform
Bromantipyrine	$UO_2Br_2 \cdot 2C_{11}H_{11}BrN_2O$	Yellow needles	Sol. in warm H$_2$O or alcohol; sl. sol. in boiling acetone; insol. in ether or CHCl$_3$; sol. in HCl

6. URANIUM(IV) OXYBROMIDE, UOBr$_2$ (URANOUS OXYBROMIDE)

The preparation of this compound was prompted by the observation (MP Ames 9) that a yellow residue was frequently observed on sublimation of uranium tetrabromide. Its analysis indicated it to be uranous oxybromide. A method of preparation based on the following reactions has been developed at Ames (MP Ames 11):

$$3UO_2 + 2CS_2 \xrightarrow{900°C} U_3O_2S_4 + 2CO_2 \tag{24}$$

$$U_3O_2S_4 + 6Br_2 \xrightarrow{600°C} 2UOBr_2 + UBr_4 + 2S_2Br_2 \tag{25}$$

Bromine vapor, carried in a stream of nitrogen, is passed over $U_3O_2S_4$ at 600°C until distillation of UBr_4 and S_2Br_2 ceases. The nonvolatile uranous oxybromide is a greenish-yellow to yellow powder. Analysis shows it to correspond very closely to the composition $UOBr_2$, and x-ray studies show it to be a pure phase and not a mechanical mixture of uranium dioxide and uranium tetrabromide.

Uranium(IV) oxybromide is not particularly hygroscopic, but it dissolves readily in water to give a green solution. The solution is stable

Table 16.11 — Equilibrium Constants for Hydrogen Reduction of Uranous Oxybromide*
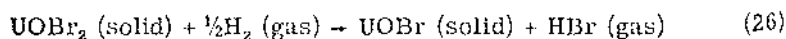
Temp., °C	Temp., °K	$\frac{1}{T} \times 10^3$	K
300	573	1.745	<0.004
350	623	1.605	0.0061
375	648	1.543	0.0078
400	673	1.486	0.0108
425	698	1.433	0.0139
440	713	1.403	0.0162

*$K = p_{HBr}/p_{H_2}^{1/2}$ (p in atmospheres).

for several hours, after which a black precipitate, presumably hydrated uranium dioxide, begins to precipitate. This precipitate is similar to that obtained when aqueous solutions of uranium tetrabromide are treated with a base. It has been suggested by the Ames workers (MP Ames 12) that stable UO^{++} ions exist in solutions of uranous oxybromide; this interpretation is supported by the fact that electrometric titration shows that four equivalents of hydroxide are required for precipitation per mole of uranium tetrabromide and only two per mole of $UOBr_2$. This point is discussed at greater length in the second portion of this volume.

Uranium(IV) oxybromide appears to be stable and nonvolatile at 600°C in an inert atmosphere; at 800°C, however, disproportionation to uranium dioxide and uranium tetrabromide occurs. U_3O_8 forms on ignition in air.

6.1 Hydrogen Reduction Equilibrium of Uranous Oxybromide. (UCRL 9.) The equilibrium of uranous oxybromide reduction by hydrogen has been studied between 300 and 400°C. Reduction proceeds with the formation of hydrogen bromide; the analysis of the data is made on the assumption that UOBr is the other product.

$$UOBr_2 \text{ (solid)} + \tfrac{1}{2}H_2 \text{ (gas)} \rightarrow UOBr \text{ (solid)} + HBr \text{ (gas)} \tag{26}$$
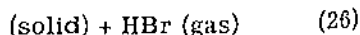
The experimental equilibrium constants are given in Table 16.11.

nitrogen, is passed over $U_3O_2S_4$
$_2Br_2$ ceases. The nonvolatile
ow to yellow powder. Analysis
the composition $UOBr_2$, and
e and not a mechanical mixture
omide.

ularly hygroscopic, but it dis-
olution. The solution is stable

n Reduction of Uranous Oxybromide *

$\frac{1}{T} \times 10^3$	K
1.745	<0.004
1.605	0.0061
1.543	0.0078
1.486	0.0108
1.433	0.0139
1.403	0.0162

precipitate, presumably hy-
cipitate. This precipitate is
olutions of uranium tetrabro-
been suggested by the Ames
$^{++}$ ions exist in solutions of
is supported by the fact that
equivalents of hydroxide are
ranium tetrabromide and only
iscussed at greater length in

be stable and nonvolatile at
however, disproportionation
mide occurs. U_3O_8 forms on

m of Uranous Oxybromide.
oxybromide reduction by hy-
400°C. Reduction proceeds
; the analysis of the data is
other product.

(solid) + HBr (gas)   (26)

re given in Table 16.11.

From the data given in Table 16.11, the following values are calculated for reaction 26:

$$\Delta H_{673°K} = 10.1 \text{ kcal per mole}$$

$$\Delta F_{673°K} = 6.06 \text{ kcal per mole}$$

$$\Delta S_{673°K} = 6.01 \text{ e.u.}$$

6.2 Thermodynamic Constants. (UCRL 8.) The following thermodynamic constants have been given by MacWood for uranous oxybromide:

$$\Delta H_{298°K} = -246.9 \pm 0.7 \text{ kcal per mole}$$

$$\Delta F_{298°K} = -231.3 \pm 2.0 \text{ kcal per mole}$$

$$S_{298°K} = 42.9 \text{ e.u. (estimated)}$$

The above heat of formation is based on a calorimetric determination of the heat of solution of uranous oxybromide, which gave $\Delta H = -16.3 \pm 0.2$ kcal per mole (UCRL 5).

7. URANYL IODIDE, UO_2I_2

It is doubtful whether pure uranyl iodide has ever been prepared in the solid state. From what little is known about this substance, it appears likely that it is considerably less stable than uranyl bromide, which already has a distinct tendency to lose its halogen. Various workers have attempted to prepare uranyl iodide by reaction of iodine vapors, hydrogen iodide vapors, or hydrogen iodide with a mixture of uranyl dioxide and carbon but without success (von Unruh, 1909).

Aqueous solutions of uranyl iodide may be readily prepared, however. Von Unruh (1909) prepared such solutions by treating uranyl acetate with hydriodic acid. Concentration of such a solution by heating results in extensive decomposition. Drying in vacuum yields yellow-green fluorescent needles which decompose rapidly in air with liberation of iodine. The substance was not analyzed. Previous attempts by Sendtner (1879) to concentrate solutions of $UO_3 \cdot H_2O$ in hydriodic acid resulted in every case in the evolution of large amounts of iodine (Sendtner, 1879); and a product heavily contaminated with free iodine was obtained. It appears unlikely that aqueous solutions of uranyl iodide can be dehydrated without extensive decomposition.

Solutions of uranyl iodide in water or organic solvents can be readily prepared by double decomposition reactions. The reactants are so chosen that one of the products is uranyl iodide and the other a salt insoluble in the solvent used. Aloy (1901b) dissolved partially

dehydrated uranyl nitrate hexahydrate in ether and added a slight excess of barium iodide. On removing the insoluble barium nitrate and concentrating the red solution in vacuum, an unstable, red, very deliquescent, crystalline material was obtained. A methanolic solution of uranyl nitrate treated with sodium iodide yields a solution of uranyl iodide. Von Unruh prepared nonaqueous solutions of uranyl iodide by dissolving in ether the solid material obtained by evaporation of an aqueous solution and then using calcium chloride and sodium metal to remove water and free iodine. Crystals contaminated with iodine and presumed to be $UO_2I_2 \cdot 2(C_2H_5)_2O$ can be obtained from the ethereal solution by evaporation in vacuum or in a stream of dry air. Double decomposition has also been used for preparing aqueous solutions. Thus a solution of uranyl sulfate may be treated with the equivalent amount of barium or calcium iodide (Truttwin, 1925).

It has been reported that uranyl iodide is soluble in methyl acetate, ethyl acetate, acetone, and pyridine (Naumann, 1904, 1909), as well as in water, ether, and methyl, ethyl, or amyl alcohols.

Uranyl iodide forms a series of addition compounds with ammonia (von Unruh, 1909). Uranyl iodide in ether or amyl alcohol solution gives, with gaseous ammonia, $UO_2I_2 \cdot 2NH_3$; more prolonged treatment with ammonia gives $UO_2I_2 \cdot 3NH_3$ as a golden-yellow amorphous solid. Treatment of the diammoniate with liquid ammonia at 0°C gives the very unstable $UO_2I_2 \cdot 4NH_3$, which decomposes rapidly above 5°C.

Aqueous or ethanolic solutions of uranyl iodide have been alleged to possess the property of dissolving normally insoluble heavy metal iodides, such as bismuth iodide, BiI_3, or mercuric iodide, HgI_2. It has been claimed that compounds such as UO_2BiI_5 can be isolated from these solutions (Truttwin, 1925).

REFERENCES

1824 J. A. Arfvedson, Pogg. Ann., 1: 269.
1824 J. J. Berzelius, Pogg. Ann., 1: 34.
1825 L. R. Lecanu, J. pharm. chim., 11: 285.
1830 J. B. Berthemot, Ann. chim. et phys., (2) 44: 387.
1842a E. Péligot, Ann., 43: 278.
1842b E. Péligot, Ann. chim. et phys., (3) 5: 36.
1856 G. Williams, J. prakt. Chem., 69: 358.
1861 R. Hermann, dissertation, University of Göttingen, p. 31.
1866a H. C. Bolton, Z. Chem., (2) 2: 353.
1866b H. C. Bolton, Z. Chem., (2) 2: 356.
1879 H. Baker, J. Chem. Soc., 35: 760.
1879 R. Sendtner, Ann., 195: 325.
1881 A. R. Leeds, J. Am. Chem. Soc., 3: 145.
1881 C. G. Williams, Chem. News, 44: 308.
1883 A. Smithells, J. Chem. Soc., 43: 130.

1884 A. Ditte, Ann
1885 F. F. Regel
1888 H. Hampe, C
1892 K. Seubert a
1895 H. L. Well
1896 J. Aloy, Com
1897 A. Miolati a
1900 S. Lordkipan
1901a J. Aloy, Bull
1901b J. Aloy, Ann.
1901 F. Mylius an
1902 W. O. de Cor
1902 B. Kalischer
1902 T. W. Richar
    31: 244.
1903 W. O. de Cor
1904 H. Bürger, d
1904 W. O. de Cor
1904 F. Giolitti, G
1904 A. Naumann.
1904 E. Rimbach,
1905 F. Giolitti an
1905 M. Trautz, Z
1906 R. Fosse and
1906 H. Grossman
1906 A. Rosenheir
1907 H. Loebel, di
1909a W. O. de Con
1909b W. O. de Con
1909c W. O. de Con
1909 A. Naumann.
1909 W. Peters, B
1909 A. von Unruh
1910 A. Bolland, N
1912 W. Peters, Z
1915 H. Simonis a
1916 H. Simonis a
1917 A. Benrath, i
1919 E. L. Nichol
1922 J. Aloy and
1925 H. Truttwin.
    Fortschritte
1930 T. Asahina a
1930 F. Olsson, Z
1930-
1931a R. Răscanu,
1931b R. Răscanu,
1931c R. Răscanu,
1931d R. Răscanu,
1931e R. Răscanu,
1931-
1932a R. Răscanu,
1932b R. Răscanu,
1932c R. Răscanu,
1932-

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NCES

5.

(2) 44: 387.

36.

of Göttingen, p. 31.

5.

1884	A. Ditte, Ann. chim. et phys., (6) 1: 341.
1885	F. F. Regelsberger, Ann., 227: 119.
1888	H. Hampe, Chem. Ztg., 12: 106.
1892	K. Seubert and A. Schmidt, Ann., 267: 239.
1895	H. L. Wells and B. B. Boltwood, Z. anorg. Chem., 10: 183.
1896	J. Aloy, Compt. rend., 122: 1541.
1897	A. Miolati and U. Alvisi, Atti accad. nazl. Lincei, (5) 6: II, 380.
1900	S. Lordkipanidze, J. Russ. Phys. Chem. Soc., 32: 286.
1901a	J. Aloy, Bull. soc. chim. Paris, (3) 25: 154.
1901b	J. Aloy, Ann. chim. et phys., (7) 24: 417.
1901	F. Mylius and R. Dietz, Ber., 34: 2774.
1902	W. O. de Coninck, Bull. classe sci. Acad. roy. Belg., 1025.
1902	B. Kalischer, dissertation, University of Berlin, p. 49.
1902	T. W. Richards and B. S. Merigold, Chem. News, 85: 187; Z. anorg. Chem., 31: 244.
1903	W. O. de Coninck, Bull. classe sci. Acad. roy. Belg., 709.
1904	H. Bürger, dissertation, University of Bonn, p. 49.
1904	W. O. de Coninck, Ann. chim. et phys., (8) 3: 500.
1904	F. Giolitti, Gazz. chim. ital., 34: II, 166.
1904	A. Naumann, Ber., 37: 3601, 4328, 4609.
1904	E. Rimbach, Ber., 37: 461.
1905	F. Giolitti and G. Agamennone, Atti accad. nazl. Lincei, (5) 14: I, 114, 165.
1905	M. Trautz, Z. physik. Chem., 53: 48.
1906	R. Fosse and L. Lesage, Compt. rend., 142: 1544.
1906	H. Grossmann and B. Schuck, Z. anorg. Chem., 50: 26.
1906	A. Rosenheim and F. Jacobsohn, Z. anorg. Chem., 50: 306.
1907	H. Loebel, dissertation, University of Berlin, p. 42.
1909a	W. O. de Coninck, Compt. rend., 148: 1769.
1909b	W. O. de Coninck, Bull. classe sci. Acad. roy. Belg., p. 836.
1909c	W. O. de Coninck, Bull. classe sci. Acad. roy. Belg., p. 173.
1909	A. Naumann, Ber., 42: 3790.
1909	W. Peters, Ber., 42: 4833.
1909	A. von Unruh, dissertation, University of Rostock, p. 37.
1910	A. Bolland, Monatsh., 31: 387, 403.
1912	W. Peters, Z. anorg. Chem., 78: 159.
1915	H. Simonis and A. Elias, Ber., 48: 1513.
1916	H. Simonis and A. Elias, Ber., 49: 777.
1917	A. Benrath, Z. wiss. Phot., 16: 258.
1919	E. L. Nichols and H. L. Howes, Carnegie Inst. Wash. Pub., 298: 218.
1922	J. Aloy and E. Rodier, Bull. soc. chim. France, (4) 31: 247.
1925	H. Truttwin, German Patent D.R.P. No. 420,391, from A. Brauer and J. D'Ans, Fortschritte in der anorganisch-chemischen Industrie, III: 1327 (1924–1927).
1930	T. Asahina and T. Dôno, Z. physiol. Chem., 186: 134.
1930	F. Olsson, Z. anorg. u. allgem. Chem., 187: 112.
1930–	
1931a	R. Răscanu, Ann. sci. univ. Jassy, 16: 461.
1931b	R. Răscanu, Ann. sci. univ. Jassy, 16: 480, 481, 484, 486, 489.
1931c	R. Răscanu, Ann. sci. univ. Jassy, 16: 54.
1931d	R. Răscanu, Ann. sci. univ. Jassy, 16: 465, 466, 467, 470, 473.
1931e	R. Răscanu, Ann. sci. univ. Jassy, 16: 54, 496.
1931–	
1932a	R. Răscanu, Ann. sci. univ. Jassy, 17: 133.
1932b	R. Răscanu, Ann. sci. univ. Jassy, 17: 143.
1932c	R. Răscanu, Ann. sci. univ. Jassy, 17: 75.
1932–	

1933   R. Răscanu, Ann. sci. univ. Jassy, 18: 94.

1936   P. Spacu, Z. anorg. u. allgem. Chem., 230: 181.

1938   A. Chrétien and G. Oechsel, Compt. rend., 206: 254–256.

1947   P. F. Wacker and R. K. Cheney, J. Research Natl. Bur. Standards, 39: 317.

1948   W. H. Zachariasen, Acta Crystallographica, 1: 277.

1949   G. H. Dieke and A. B. F. Duncan, "Spectroscopic Properties of Uranium Compounds," National Nuclear Energy Series, Division III, Volume 2, McGraw-Hill Book Company, Inc., New York, 1949.

Project Literature

British 1: H. S. Peiser and T. C. Alcock, Report BR-589, Mar. 19, 1945.

British 2: Report BR-442, date received, July 6, 1944.

British 3: Report [B]LRG-21, June, 1943.

British 4: Report [B]LRG-22, July, 1943.

Brown 1: C. A. Kraus, Report CC-1717, July 29, 1944.

Brown 2: C. A. Kraus, Report A-256, Aug. 14, 1942.

Brown 3: C. A. Kraus, Report A-360, Oct. 26, 1942, p. 9.

Brown 4: C. A. Kraus, Report N-1769, July 1, 1943.

Brown 5: C. A. Kraus, Report CC-342, Nov. 15, 1942.

CEW-TEC 1: J. W. Gates, L. J. Andrews, and R. B. Pitt, Report CD-4001, Jan. 30, 1945.

CEW-TEC 2: J. W. Gates, G. H. Clewett, L. J. Andrews, and H. A. Young, Report CD-457, Aug. 4, 1944.

CEW-TEC 3: C. Sterett, I. Halpern, J. Van Wazer, and H. A. Young, Report CD-GS-28, Mar. 16, 1945.

Du Pont 1: C. E. Holbrook, Report N-25, Apr. 17, 1943.

Du Pont 2: I. W. Dobratz, R. C. Downing, C. W. Maynard, S. B. Smith, and L. Spiegler, Report N-33, May 13, 1943.

Johns Hopkins 1: W. B. Burford III, Report [A]M-2121, February, 1945.

MP Ames 1: W. D. Cline, Report CC-1983, Dec. 9, 1944, p. 8.

MP Ames 2: F. Vaslow and A. S. Newton, Report CK-1496, June 17, 1944, p. 10.

MP Ames 3: N. C. Baenziger and A. D. Tevebaugh, Report CC-1504, Aug. 10, 1944.

MP Ames 4: O. Johnson, Report CC-1500, June 17, 1944.

MP Ames 5: O. Johnson, Report CC-1781, Oct. 18, 1944.

MP Ames 6: N. C. Baenziger and R. E. Rundle, Reports CC-1504, Aug. 10, 1944, and CC-1778, Aug. 18, 1944.

MP Ames 7: N. C. Baenziger, Report CC-1778, Aug. 18, 1944.

MP Ames 8: J. Powell and R. W. Nottorf, Report CC-1500, June 17, 1944; J. Powell, Report CC-1504, Aug. 10, 1944.

MP Ames 9: J. Powell and R. W. Nottorf, Report CC-1496, May 11, 1944.

MP Ames 10: R. W. Nottorf, Report CC-1778, Aug. 18, 1944.

MP Ames 11: J. Powell, Report CC-1778, Aug. 18, 1944.

MP Ames 12: J. Powell and A. S. Newton, Report CC-1778, Aug. 18, 1944.

MP Ames 13: F. H. Spedding and H. A. Wilhelm, Report CC-1517, Mar. 10, 1944.

MP Berkeley 1: C. S. Garner and J. W. Kent, Report CN-343, Nov. 15, 1942.

MP Berkeley 2: B. J. Fontana, Report CK-810, July 20, 1943.

MP Chicago 1: H. S. Brown, O. F. Hill, 1942.

MP Chicago 2: S. Fried and N. R. Davi

MP Chicago 3: W. H. Zachariasen, Re 1944; and CC-2768, Mar. 12, 1945

MP Chicago 4: W. H. Zachariasen, R

MP Chicago 5: R. Livingston, personal

Montreal 1: J. Hebert and A. G. Mans

Natl. Bur. Standards 1: P. F. Wacker 1947.

Purdue 1: E. T. McBee, Report [A]M

Purdue 2: E. T. McBee, Report [A]M

SAM Carbide and Carbon 1: R. Kunin,

SAM Columbia 1: C. F. Hiskey, Repor

SAM Columbia 2: M. S. Katz, Report

SAM Columbia 3: G. R. Dean, R. Bea

SAM Columbia 4: S. Freed, Report

SAM Columbia 5: J. Spevack and A. V

UCRL 1: S. Kilner and M. J. Polis

UCRL 2: S. H. Babcock, Report RL

UCRL 3: S. Rosenfeld, Report RL 4.6.70, Mar. 13, 1943.

UCRL 4: P. H. Davidson and M. E.

UCRL 5: C. H. Barkelew, Report RL

UCRL 6: P. H. Davidson and I. Stree

UCRL 7: N. W. Gregory, Report RL

UCRL 8: G. E. MacWood, Report RL

UCRL 9: N. W. Gregory, Report RL