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MCW-175

Subject Category: CHEMISTRY

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UNITED STATES ATOMIC ENERGY COMMISSION

REDUCTION OF URANYL FLUORIDE
WITH HYDROGEN. A. REACTION RATE.
B. REACTION MECHANISM

By
C. W. Kuhlman

March 14, 1949

Mallinckrodt Chemical Works
St. Louis, Missouri

Technical Information Service, Oak Ridge, Tennessee

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1955

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REDUCTION OF URANYL FLUORIDE WITH HYDROGEN

- A. Reaction Rate
- B. Reaction Mechanism

By C. W. Kuhlman

March 14, 1949

Work done by:

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Mallinckrodt Chemical Works
St. Louis, Missouri

REDUCTION OF URANYL FLUORIDE WITH HYDROGEN

A. Reaction rate.

B. Reaction mechanism.

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Summary:

Hydrogen reacts with uranyl fluoride (UO_2F_2) in two ways.

At the reaction temperatures studied reaction (1) predominates, but reaction (2) becomes increasingly important as the temperature is increased. Thus the reaction product is a mixture of UO_2 and UF_4 .

Apparatus:

The apparatus employed in making these measurements has been previously described.^{1,2}

Experimental:

Uranyl fluoride was prepared by passing anhydrous HF over M.C.W. uranium trioxide for two hours at 350°C . in an air free system. This product was completely water soluble and had the analysis

U-77.2

F-12.3

molar ratio $\frac{\text{U}}{\text{F}} = 0.501$

The technique used in measuring the reaction rates has been described.² 3.000g samples of the uranyl fluoride preparation were used giving a layer thickness in the reaction boat of about 5mm. About a 10,000 fold excesses of hydrogen was employed to insure an excess of reactant at the solid surface at all times.

After the reaction had reached completion e.g. no further weight loss was observed, the sample was cooled to room temperature in an atmosphere of H_2 , withdrawn from the apparatus and analyzed.

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Data		T-700°C		T-800°C	
Time		w.	Time	w.	
0 min.		0 mg.	0 min.	0 mg.	
1		53	3		34
2		109	5		57
3		163	10		89
4		195	15		127
5		213	20		158
7		258	25		184
9		305	30		211
10		323	35		234
12		327	40		259
15		328	45		283
17		328	50		309
20		328	55		326
25		328	60		343
			65		344
			85		344

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3

T-500°C

Time	w.	Time	w.
0 min.	0 mg.	115	230
3	8	120	238
5	13	130	255
10	27	140	270
15	43	150	283
20	53	160	298
25	63	170	302
30	74	180	315
35	87	190	325
40	98	200	337
45	105	210	347
50	123	230	349
55	123	230	349
60	128	240	349
65	138	250	349
70	148		
75	158		
80	168		
85	178		
90	188		
95	195		
100	203		
105	212		
110	221		

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T-450°C

Time	w.		
0 min.	0 mg.	330	212
2	3	360	234
4	6	390	251
8	10	420	263
12	12	450	273
20	14	480	288
30	21	510	306
40	26		
50	30		
60	37		
82	52		
90	56		
105	64		
120	74		
135	84		
150	96		
170	107		
190	124		
210	138		
230	149		
250	161		
270	171		
290	184		
310	198		

Results

The primary reaction between hydrogen gas and uranyl fluoride at these temperatures 450°-700°C may be written

A secondary reaction also occurs to a greater or less extent probably depending on the temperature and several other factors.

Reactions 3 & 4 may be considered together as the reaction

Assuming reactions 3 & 5 are the only ones involved, the fraction of the UO_2F_2 reacting by equation 5 may be calculated from the weight loss during the reduction and the analysis of the product.

If x = grams of UO_2 present in product, y = grams of UF_4 present in the product, a = gravimetric factor $\text{UO}_2\text{F}_2 \rightarrow \text{UO}_2$ (by reaction 3), b = factor $\text{UO}_2\text{F}_2 \rightarrow \text{UO}_2$ (by reaction 5), c = factor $\text{UO}_2\text{F}_2 \rightarrow \text{UF}_4$ (reaction 5), f = fraction UO_2F_2 reacting by equation 5, p = fraction UO_2 in final product, g = initial weight of UO_2F_2 .

$$x = gb + g(1-f)a$$

$$y = gfc$$

$$p = \frac{fb + (1-f)a}{fb + (1-f)a + fc} \quad (6)$$

$$\text{but } b = \frac{a}{2}$$

$$a = 0.8767$$

$$c = 0.5096$$

$$p = \frac{0.8767 - 0.4384f}{0.8767 + 0.0712f} \quad (7)$$

If Δw = weight loss during reaction (has positive sign when weight is lost)

$$\Delta w = g - (x+y) \quad (8)$$

or substituting and simplifying

$$\Delta w = g\left(1 - f\frac{a}{2} - a + fa - fc\right) \quad (9)$$

or

$$f = \frac{\Delta w - 0.1233g}{-0.07125g} \quad (10)$$

As a check on the interpretation of this reaction, the final composition of the sample was calculated from the weight change and the calculated composition compared with the measured composition. f was calculated from Δw using equation (10). This value of f was then used in equation (7) to calculate p .

Temp.	Time for Completion	ΔW	Measured*		Calculated Composition of Product	
			Composition of product UO_2	UF_4	UO_2	UF_4
700°C	10 min.	-0.328g	88.3%	11.8%	88.7%	11.3%
600°C	56 min.	-0.344g	93.7%	6.7%	93.1%	6.9%
500°C	220 min.	-0.349g	93.9%	6.5%	94.3%	5.7%

*These samples contained 0.20, 0.23, 0.14% UO_2F_2 (water soluble fraction), respectively.

At 450° C sample had lost 307 g in 520 minutes but the reaction had not reached completion.

The value of f in the above equations is determined by the ratio of diffusion of the HF formed in the primary reaction away from the reaction mixture as opposed to the rate of the fluorination reaction with UO_2 .^{1,3} The fluorination reaction rate varies exponentially with the absolute temperature (1) while the rate of diffusion of a gas through a porous bed is proportional to $T^{1/2}$. Thus at higher temperatures the fluorination of the dioxide formed by the reduction reaction becomes more important and the product contains a larger fraction of uranium tetrafluoride.

In this reaction hydrogen fluoride does not act as an inhibitor of the reduction reaction as in the case in the reduction of uranium trioxide.⁴ In this latter reaction it was postulated that the inhibition was due to a preferential adsorption of HF on the surfaces of the uranium trioxide or some other to the reaction intermediate exclusion of the hydrogen. In the reaction studied in this paper the hydrogen fluoride is formed principally in the interior of the particle and diffuses outward, partially reacting with UO_2 molecules on the way. Upon reaching the surface the HF must be disorbed. Since the supply of hydrogen to the interior of the particle is not halted by the presence of this HF on the surface (reduction continues to completion), it is evident that different surface properties are observed here than in the case of reduction of UO_3 . The most plausible explanation seems to be the assumption of differing behaviors of surfaces of UO_2 and UO_2F_2 with respect to the tenacity with which HF and H_2 molecules are held.

Report:

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- 2) Report M.C.W. 142—Reduction of Uranium Trioxide to Uranium Dioxide with Hydrogen—Reaction rates at various temperatures.
- 3) Report M.C.W. 138—Fluorination of Uranium Dioxide with Hydrogen Fluoride— Water Mixtures.
- 4) Report M.C.W. 147—A Note on the Inhibitory Effect of Hydrogen Fluoride on the Hydrogen reduction of Uranium Trioxide.

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- Reaction rate.
- Reaction mechanism.

by G. W. Kuhlman

March 14, 1949

Mallinckrodt Chemical Works
St. Louis, Mo.

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Hugh Kinner
Authorizing Official

Date 5/5/05

Work Done by:

Mr. C. J. Buckheim
Mr. C. P. Ritchie
Mr. C. D. Harrington
Mr. G. W. Kuhlman

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Hydrogen reacts with uranyl fluoride (UO_2F_2) in two ways.

At the reaction temperatures studied reaction (1) predominates, but reaction (2) becomes increasingly important as the temperature is increased. Thus the reaction product is a mixture of UO_2 and UF_6 .

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The apparatus employed in making these measurements has been previously described. 1,2.

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Uranyl fluoride was prepared by passing anhydrous HF over M.C.W. uranium trioxide for two hours at 350°C . in an air free system. This product was completely water soluble and had the analysis

U - 77.2

F - 12.8

molar ratio $\frac{\text{U}}{\text{F}}$ - 0.501

The technique used in measuring the reaction rates has been described.³ 3.000g samples of the uranyl fluoride preparation were used giving a layer thickness in the reaction boat of about 3mm. About a 10,000 fold excesses of hydrogen was employed to insure an excess of reactant at the solid surface at all times.

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X 273-2

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RGL-178

Time

T = 740°C.

Time

T.

0 min.

0 g.

1

55

2

105

3

155

4

190

5

215

6

250

9

275

10

300

11

327

12

355

13

375

20

375

25

375

T = 800°C.

Time

T.

0 min.

0 g.

3

34

5

57

10

85

15

127

20

155

25

184

30

211

35

234

40

259

45

285

50

309

55

335

60

345

65

344

70

344

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432-173

$\lambda = 400^\circ\text{C}$

Time	%	Time	%
0 min.	0 mg.	115	230
1	0	120	230
5	15	135	230
10	27	140	270
15	43	145	293
20	58	150	298
25	68	155	302
30	76	160	315
35	87	165	316
40	88	170	337
45	90	175	347
50	92	180	348
55	93	185	348
60	93	190	348
65	94	195	349
70	95		
75	96		
80	97		
85	97		
90	98		
95	98		
100	99		
105	99		
110	100		

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Results

The primary reaction between hydrogen gas and uranium fluoride at these temperatures 400°-700° C may be written

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If x = grams of UO_2 present in product, y = grams of UH_4 present in the product, a = gravimetric factor $UO_2F_2 \longrightarrow UO_2$ (by reaction 3), b = factor $UO_2F_2 \longrightarrow UO_2$ (by reaction 5), c = factor $UO_2F_2 \longrightarrow UH_4$ (reaction 5), f = fraction UO_2F_2 reacting by equation 5, p = fraction UO_2 in final product, g = initial weight of UO_2F_2 .

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As a check on the interpretation of this reaction, the final composition of the sample was calculated from the weight change and the calculated composition compared with the measured composition. f was calculated from Δw using equation (10). This value of f was then used in equation (7) to calculate p .

Temp.	Time for Completion	ΔW	Measured ^a Composition of product		Calculated Composition of Product	
			UO ₂	UF ₄	UO ₂	UF ₄
700°C	10 min.	-0.328g	88.5%	11.5%	88.7%	11.3%
600°C	56 min.	-0.344g	93.7%	6.7%	93.1%	6.9%
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* These samples contained 0.20, 0.23, 0.14% UO₂F₂ (water soluble fraction)

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- 4) Report M.C.W. 147 - A Note on the Inhibitory Effect of Hydrogen Fluoride on the Hydrogen reduction of Uranium Trioxide.

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ΔW on 3.000g. Sample (mg)

Hydrogen Reduction of UO_2F_2

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