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THERMODYNAMIC STUDIES OF THE U^{3+} — U^{4+} HALF REACTION

Oscar A. Cook and E. D. Eastman

September 1944

Issued December 1949

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Introduction

Present interest in uranium and its compounds makes it desirable to have accurate thermodynamic data available. Although the following electromotive force measurements are not easily interpreted perhaps they can serve as a first approximation in the estimation of some free energies.

Experimental

The anhydrous uranium chlorides were always handled in a dry box containing an inert atmosphere of CO_2. Lead amalgams were prepared by electrolysis from lead nitrate solutions. Cells were made up and placed in the ice bath thermostat before introducing the solid anhydrous trichloride. All cells were thermostated in melting ice and nitrogen was bubbled through both compartments in an effort to retard the oxidation of the UCl_3.

Initial attempts to measure a cell of the type Au: UCl_3(sol.), UCl_4(sol.), 10M HCl; 10M HCl, UCl_4(sol.), $PbCl_2$(sol.): Pb(Hg) failed. The polarity of the cell was just the opposite from predictions based on the instability of UCl_3. The cell was definitely irreversible and its EMF increased steadily from 0.4 to 0.8 volts over a period of twenty two hours. Another almost identical cell in which 4.13 HCl and molar UCl_4 were substituted also behaved in the same manner.

An electrolytic experiment was then tried with the gold cathode in M UCl_4, 4M HCl solution. A current of five milliampere immediately started the evolution of hydrogen gas from the gold electrode. From this it became apparent that an electrode having a higher hydrogen overvoltage was preferable as the anode. In the electrolytic apparatus

mercury exhibited completely reversible characteristics with currents up to ten milliampere. In these experiments the blood red U^{3+} could instantly be seen rising from the surface of the mercury without any evolution of hydrogen. From these experiments we can conclude that $U^{3+} \rightleftharpoons U^{4+}$ half reaction is not reversible on gold but is reversible on mercury.

Therefore the next cell was set up as follows: Hg: UCl_3(sol.), M UCl_4, 4.13M HCl; 4.13M HCl, M UCl_4, Hg_2Cl_2 (sol.), Hg. This cell had the predicted polarity and was completely reversible. Experimental EMF's are listed in Table I.

Analysis of the cell three solutions after complete oxidation of $U^{3+} \rightleftharpoons U^{4+}$ gave for the molality of uranium 2.2 in the anode and 1.28 in the cathode compartments.

A fourth cell was set up which was identical in construction with its immediate predecessor. Experimental measurements are given in Table II.

The analysis of the final solution gave for the molality of U^{4+} 2.23 in the anode, and 1.38 in the cathode compartment.

The next cell was set up with a lead chloride lead amalgam reference. Hg: UCl_3 (sol.), M UCl_4, 4.13M HCl; 4.13M HCl, M UCl_4, $PbCl_2$(sol.), Pb(Hg). This cell was completely reversible and gave good EMF. Results are given in Table III.

The analysis of its final solutions gave for the U^{4+} molality 1.89 in the anode and 1.27 in the cathode compartment.

The electromotive force of a reference cell was measured for a direct comparison of the reference electrodes of the previous cells. This cell had nitrogen bubbled through both compartments and was thermostated in the melting ice bath. (Hg)Pb, $PbCl_2$(sol.), M UCl_4, 4.13M HCl; 4.13M HCl, M UCl_4, Hg_2Cl_2(sol.), Hg. This cell had an EMF of 0.52614 ± 2 for the first day and 0.52621 ± 2 for the second day.

Table I

Cell 3

Time Minutes	EMF Volts				
2	0.7700	230	0.7690	1320	0.7406
6	0.7270	240	0.7535	1334	0.7408
8	0.7210	250	0.7639	1362	0.7409
10	0.7190	954	0.7414	1367	0.7409
13	0.7185	970	0.7418	1395	0.7411
17	0.7298	983	0.7418	1416	0.7414
22	0.7173	991	0.7414	1453	0.7421
30	0.7460	1003	0.7413	1478	0.7421
35	0.7270	1017	0.7414		
43	0.7380	1028	0.7415		
50	0.7320	1042	0.7414*		
67	0.7330	1064	0.7419		
126	0.7580	1077	0.7421		
137	0.7560	1090	0.7425		
148	0.7580	1110	0.7421		
157	0.7542	1126	0.7418		
183	0.7540	1143	0.7419		
200	0.7542*	1220	0.7405		
206	0.7512	1240	0.7403		
212	0.7470	1259	0.7405		
219	0.7485	1289	0.7407		

Table of Mean Values

Time Interval Minutes	EMF Volts
4 to 13	0.720 ± 2
120 to 153	0.757 ± 1
153 to 200	0.7541 ±1
950 to 1500	0.74141±49

* Additional spatula full of solid UCl_3 added before next measurement.

Table II

Cell 4

Time Minutes	EMF Volts				
2	0.7760	207	0.7552	964	0.7639
7	0.7520	220	0.7558	984	0.7621
9	0.731	232	0.7571	1008	0.7592
13	0.7165	241	0.7576	1023	0.7580
15	0.7110	253	0.7573	1080	0.7517
20	0.7165	263	0.7568	1109	0.7473
23	0.7145	273	0.7564	1130	0.7436
25	0.7140	283	0.7563	1151	0.7391
27	0.7125	294	0.7558	1168	0.7340
31	0.7130	302	0.7553		
37	0.7139	807	0.7686		
50	0.7140	822	0.7685		
62	0.7130	834	0.7683		
74	0.7165	847	0.7676		
85	0.7120	861	0.7667		
107	0.7130	879	0.7663		
132	0.7180	891	0.7660		
149	0.7177	908	0.7658		
177	0.7549	929	0.7646		
197	0.7565	943	0.7647		

Table of Mean Values

Time Interval Minutes	EMF Volts
15 to 107	0.7137 ± 12
177 to 302	0.7564 ± 6

Table III

Cell 5

Time Minutes	EMF Volts				
3	0.2534	100	0.2057	403	0.2245
7	0.2500	108	0.1996	412	0.2243
10	0.2290	118	0.2012	1064	0.2280
13	0.2180	129	0.2067	1084	0.2281
16	0.2080	145	0.2096	1103	0.2272
19	0.1985	152	0.2300	1122	0.2249
22	0.1895	166	0.2318	1150	0.2210
26	0.1915	173	0.2314	1166	0.2190
31	0.1838	237	0.2295	1188	0.2214
35	0.1841	250	0.2324	1207	0.2199
42	0.1845	260	0.2290	1227	0.2146
47	0.1846	274	0.2280	1253	0.2101
53	0.1842	284	0.2275		
56	0.1846	294	0.2270		
61	0.1828	304	0.2270		
65	0.1840	320	0.2267		
69	0.1834	332	0.2260		
75	0.1814	342	0.2256		
83	0.1887	352	0.2254		
88	0.1922	366	0.2249		
95	0.2002	381	0.2247		

Table of Mean Values

Time Interval Minutes	EMF Volts
30 to 70	0.1840 ± 5
152 to 260	0.2307 ±12
270 to 1120	0.2263 ±12

Attempts were made with cells saturated with UCl_4. These cells failed completely. Their polarity was incorrect and they behaved irreversibly.

Discussion

It becomes immediately apparent that ones interpretation of these cells is made very uncertain because of the inability to write a cell reaction. The lack of adequate solubility data prohibits hazarding any more than good guesses as to the meaning of these measurements.

C. Thurman in CC-938 reports approximate values of UCl_3 solubility to be between 3 and 4.8 molal in water at 0°C. and that in 6M HCl solution was not complete at the end of one hour final concentration of UCl_3 was 1.2M. The amount of UCl_3 in these cells was enough to make the solution 2.5 to 3 molal.

Crude experiments on UCl_3 solubility in 4.13M HCl indicated that the solutions uranium content jumped to 1.3 molal in the first ten minutes and increased only slowly thereafter. This is in agreement with Thurman and it is probably safe to assume the solution saturated with UCl_3.

Nothing is known regarding the solubility of UCl_4 in these solutions. So for convenience in making a calculation it was assumed that these solutions were saturated with UCl_4. One can then write the following cell reactions.

(1) $\frac{1}{2}PbCl_2(s) + UCl_3(s) = Pb_{amalg.} + UCl_4(s)$ $E = 0.226$

(2) $\frac{1}{2}Hg_2Cl_2(s) + Pb_{amalg.} = \frac{1}{2}PbCl_2(s) + Hg$ $E = 0.526$

Adding reactions (1) and (2) gives:

(3) $\frac{1}{2}Hg_2Cl_2(s) + UCl_3(s) = Hg + UCl_4(s)$ $E = 0.752$

This sum compares favorably with the experimental values of 0.756 and 0.741 for this reaction. Therefore the free energy change for reaction (3) is $\Delta F = -0.75 \times 23075 = -17300$ cal. or $F_{UCl_4} - F_{UCl_3} - \frac{1}{2} F_{Hg_2Cl_2} = -17300$. For the difference in free energy of tetra and tri chlorides $F_{UCl_4} - F_{UCl_3} = -17300 - 25100 = -42400$ cal.

The work described in this report was performed under the auspices of the Atomic Energy Commission.