of the phase diagram in which Bi-rich, unsaturated alloys exist and for temperatures between 775 and 1100°K.

The solubility of Li in Bi has been calculated at chosen temperatures from eq. 3 and the reference electrode potential. The results are shown in Fig. 4.

Discussion

The excess chemical potential of Li is very large and negative. This behavior may be explained qualitatively in terms of the strong interaction of Li and Bi which is evidenced by the formation of the solid compound Li_3Bi.

Originally, an attempt was made to fit the data to a function of the form $\Delta\mu^E_{Li} = X_{Bi}^2 f(T, X_{Li})$, where $f(T, X_{Li})$ is a function of the temperature and composition. This attempt failed in that the calculated values tended to become more positive than the observed values as the concentration of Li in the alloy increased. Apparently, this behavior occurred in the attempt to reach the zero point of the curve (at a composition of pure Li). In reality, the curve for $\Delta\mu^E_{Li}$ at constant temperature must be discontinuous through the composition range where solid Li_3Bi is present in equilibrium with a liquid solution. The mole fraction of Li in the Li-rich solution in equilibrium with solid Li_3Bi ranges from 0.02 to 0.25. It is expected that the values of $\Delta\mu^E_{Li}$ for these solutions, while still negative, would be much smaller in absolute value.[11] Thus, the

(11) This was confirmed in a cell in which a Li-rich alloy in equilibrium with $Li_3Bi(s)$ was used as an anode *vs.* a reference electrode (a Bi-rich alloy in equilibrium with $Li_3Bi(s)$). The cell potential observed was, within experimental error, the same as that observed for a cell of type 2, indicating that the values for $\Delta\mu^E_{Li}$ in Li-rich solutions saturated with $Li_3Bi(s)$ are near zero.

TABLE I
STANDARD FREE ENERGY OF FORMATION OF $Li_3Bi(s)$

Temp., °K.	$\Delta G_f°$, kcal./mole
800	−50.5
850	−49.7
900	−48.8
950	−47.8
1000	−46.6
1050	−45.3
1100	−44.0

calculated curve of $\Delta\mu^E_{Li}$ as a function of composition should probably be sigmoid in shape. With these difficulties, it was decided to use the simpler, but empirical, function given in eq. 3.

The cell reaction for the reference electrode potential studies may be written

$$Li(l) + {}^1/_3Bi(l) \text{ (saturated with } Li_3Bi) \longrightarrow {}^1/_3Li_3Bi(s) \quad (4)$$
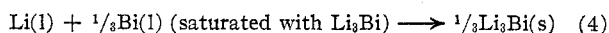
If $Li(l)$ and $Li_3Bi(s)$ are said to exist in their standard states in the cell environment, then for the cell reaction given we may write

$$\Delta G = -FE = {}^1/_3\Delta G_f° - {}^1/_3RT \ln a_{Bi} \quad (5)$$

where a_{Bi} is the activity of Bi in the alloy saturated with $Li_3Bi(s)$ with the reference state the pure liquid metal in the cell environment and $\Delta G_f°$ is the standard free energy of formation of $Li_3Bi(s)$ from the elements. The activity of Bi was calculated by application of the Gibbs–Duhem equation and eq. 3. Values of $\Delta G_f°$ for the formation of 1 mole of Li_3Bi at various temperatures are given in Table I. The estimated error of these values is 0.9 kcal./mole.


Hydrogen Tracer Studies on the Reactions of Uranium Hydride with Aqueous Oxidizing Agents

By JOHN B. HUNT AND HENRY TAUBE

The reaction of UD_3 with concentrated HCl in H_2O forms HD as the principal gaseous product. When the concentration of the acid is reduced to *ca.* 9.5 *M*, reaction is much slower, and H_2 and D_2 are the chief gaseous products. Little D is lost to the solvent by exchange, although D loss does become a feature of the results at still lower acidity. The rates of the reaction are very sensitive to the anion which is present. When a metal ion such as Ce(IV) is the oxidizing agent, the D_2 originally contained in the solid is liberated essentially quantitatively and no other gaseous product is formed. These and related results are interpreted on the assumption that a barrier layer, presumably UO_2, governs the rate and mechanism of the reaction.

The main reactions of the salt-like hydrides LiH^1 and NaH^2 with D_2O can be expressed by equations of the type

$$MH + D_2O = HD + M^+ + OD^- \quad (1)$$
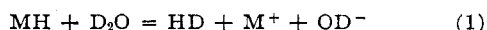
(1) H. Beutler, G. Brauer, and H. O. Junger, *Naturwissenschaften*, **24**, 347 (1936).

Also in the reaction of the complex hydride $LiAlH_4{}^2$ with D_2O, HD is the dominant gaseous product.[3]

(2) I. Wender, R. A. Friedel, and M. Orchin, *J. Am. Chem. Soc.*, **71**, 1140 (1949).

(3) The reaction of $LiAlH_4$ with D_2O has been recommended as a way to prepare pure HD. However, when KBH_4 is the reactant, there is a substantial admixture of H_2 and D_2 in the gases: W. L. Jolly and R. E. Mesmer, *ibid.*, **83**, 4470 (1961).

Preliminary experiments[4] with the metal-like hydride UH_3 showed that the mechanism of dissolution for it can be quite different from that implied by eq. 1. In 11 M DCl, the reaction of UH_3 is slow and yields a gas in which H_2 and D_2 rather than HD are the dominant species, and the principal reaction taking place under these conditions is described by the equation

$$2UH_3 + 8D^+ = 2U^{4+} + 3H_2 + 4D_2 \qquad (2)$$
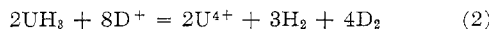
In very concentrated DCl the reaction is rapid, even violent, and under these conditions HD becomes the principal gaseous product.

In this paper, a more detailed investigation of the isotopic course of the reactions of uranium hydride with acids is described, and the study has been extended to include other oxidizing agents as well. For the latter, even the stoichiometry is a matter of considerable interest because all of the reagents used have the capacity to oxidize hydrogen; thus it is of interest to learn to what extent hydrogen is evolved by their action.

Experimental

Reagents and Preparations.—Uranium metal used in the preparation of the hydride or deuteride was first treated with 8 N HNO_3 to remove the oxide coating, then washed with distilled water and dried *in vacuo*. Massive uranium metal was converted to UH_3 in an apparatus like that described by Spedding, *et al.*[5] The hydrogen tracer experiments are more economically done using UD_3 in a solvent of normal isotopic composition, and all of the experiments after the preliminary ones were done in this way. The uranium was of the highest purity and was used in the form of foil. Deuterium was purified by passing it through a liquid air trap and then absorbing it in uranium metal. It was released from the metal by heating the solid to 650° while the weighed sample to be converted to the deuteride was maintained at 250°. The deuterium used for reaction was contained in a closed volume, and, for the later preparations, the amount of deuterium consumed was measured by a gas buret so that the composition of the deuteride could be calculated. The UH_3 or UD_3 prepared by us was undoubtedly in the β modification.[6]

Gaseous DCl was produced by adding PCl_3 to excess D_2O in a closed system. The gas was absorbed in D_2O at 0° to produce DCl solutions. Solutions of D_2SO_4 and D_3PO_4 were prepared by mixing the corresponding anhydrides with D_2O.

Solid $Ce(HSO_4)_4$ was converted to $Ce(DSO_4)_4$ by heating it to dryness several times after the addition of small amounts of D_2O. The solution of $TlCl_3$ in D_2O was prepared by oxidizing a suspension of anhydrous TlCl with Cl_2, then removing the excess Cl_2 with a stream of dry N_2. Anhydrous $FeCl_3$ was prepared by the reaction of Cl_2 with Fe wire.

Oxygen enriched in O^{18} was prepared by thermal decomposition of HgO. The O^{18}-enriched HgO was obtained by the reaction of $HgCl_2$ with O^{18}-enriched alkali.

Isotopic Analyses.—Analyses for the H_2–HD–D_2 content of the gases were made with a Consolidated 21-620A analytical mass spectrometer. A correction for the change in sample pressure during analysis was made by extrapolation to zero time, and for the contribution of H_3^+ to the HD^+ peaks by extrapolation to zero pressure.[7] Isotopic ratios thus determined were precise to 1%. The validity of the measurements of isotopic composition

was tested by mixing measured volumes of H_2 and D_2. A mixture calculated to contain 40.4 mole % H_2 analyzed as 40.5 mole %. To determine whether dilution by H occurred during the preparation and handling of the D-rich solution, samples of hydrogen were prepared by the reaction of the acid solutions with Mg. No appreciable dilution of D_2O was found to have taken place.

The analysis for the O^{18} content of the residue left by the reaction of acid with the hydride was done by the Anbar–Guttmann[8] method.

Chemical Analyses.—Hydrogen and oxygen were measured manometrically. When oxygen was admixed with hydrogen, the amount was determined by noting the decrease in pressure attendant on absorbing oxygen in alkaline pyrogallol or in an acidic solution of chromous perchlorate.

The uranium content of the solutions resulting from the dissolution of the hydride in ceric sulfate solution was determined by reducing uranium to uranium(IV) with a Jones reductor, then titrating[9] uranium(IV) with cerium(IV).

Uranium hydride was analyzed by adding a weighed sample to an excess of ceric sulfate solution. The hydrogen evolved, the cerium(IV) consumed, and the uranium contained in the solutions were determined. Uranium hydride is consumed completely and the stoichiometry of the reaction of the hydride with cerium(IV) conforms closely to the equation

$$2UH_3 + 12Ce^{+4} + 4H_2O =$$
$$2UO_2^{+2} + 12Ce^{+3} + 8H^+ + 3H_2 \quad (3)$$
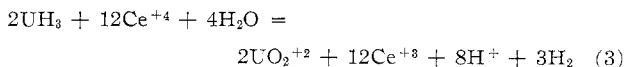
As evidence in support of this conclusion, the data of Table I are offered.

TABLE I
DISSOLUTION OF URANIUM HYDRIDE IN CERIC SULFATE SOLUTION
Ce(IV), 0.219 M; H_2SO_4, 1.0 M

H/U for hydride	2.94
Ce(IV) consumed, equiv./g.-atom of U	6.05
H_2 evolved, mole/g.-atom of U	1.48

Procedure.—In the early stages of the research, the uranium hydride which was prepared was stored in a sealed ampoule, and samples as needed were weighed and transferred in the nitrogen atmosphere of a drybox. The hydride is very reactive, and in spite of precautions taken in the transfer, different samples showed variations in composition, presumably owing to reaction during transfer. In view of this difficulty, the hydride for the later experiments was prepared separately for each run in a side arm of the vessel in which the dissolution reaction was carried out. To initiate reaction the reagent solution was admitted, under atmospheric pressure, into the evacuated vessel containing the hydride. In a typical experiment 0.4 g. of uranium was converted to the hydride and then mixed with at least 15 ml. of the solution of the oxidizing agent. A Teflon-coated stirring bar was included in the reaction vessel. The vessel was fitted with a ground-glass joint to facilitate connection to a vacuum train or the pressure measuring device. Reactions were carried out at ambient temperature.

Results

It is necessary for the presentation and discussion of the results to distinguish between hydrogen, as comprised by all species of atomic number one, and the different isotopic forms of the element. When no differentiation with respect to mass is called for, the terms "hydrogen" or "hydride" will be used, and formulas will be used to identify the isotopic species.

When hydrogen ion is the only oxidizing agent,

(4) U. Agarwala, J. B. Hunt, and H. Taube, *J. Chem. Phys.*, **32**, 1567 (1960).

(5) F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns, and A. Daane, *Nucleonics*, **4**, No. 1, 4 (1949).

(6) B. M. Abraham and H. E. Flotow, *J. Am. Chem. Soc.*, **77**, 1446 (1955).

(7) I. Friedman, *Geochim. Cosmochim. Acta*, **4**, 89 (1953).

(8) M. Anbar and S. Guttmann, *J. Appl. Rad. Isotopes*, **5**, 233 (1959).

(9) I. M. Kolthoff and B. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957.

U(IV) is expected as the equilibrium product in the oxidation, although U(III) may be formed as a transient species and subsequently oxidized to U(IV) by hydrogen ion. Indeed, the red-violet color of U(III) was observed in the early stages of the oxidation by *ca.* 15 *M* HCl,[4] but only the green color of U(IV) was observed at lower acidities, and analyses of the solutions at the end of several experiments with 9.5 *M* HCl showed all of the uranium to be present as U(IV). The reaction with hydrogen ion is then expected to conform to the stoichiometry expressed by the equation

$$2UH_3 + 8H^+ = 2U^{4+} + 7H_2 \qquad (4)$$
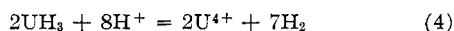
The deviations from this equation have two causes: (a) not all the hydride has reacted and (b) the hydridation of the uranium is incomplete. For the experiments in which the composition of the hydride is unknown, for want of a better basis, the per cent of theoretical hydrogen evolution is calculated with reference to eq. 4. In the experiments for which the composition of the hydride was determined (as UH_n, for example), 100% evolution of hydrogen is taken as conforming to the equation

$$2UH_n + 8H^+ = 2U^{4+} + (4 + n)H_2 \qquad (5)$$
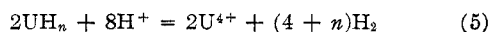
The experiments with oxidizing agents such as Ce^{+4}, Ag^+, etc., are discussed with reference to the equation

$$4H_2O + 2UH_n = nH_2 + 2UO_2^{2+} + 8H^+ + 12e^- \qquad (6)$$
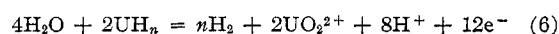
as representing the theoretical stoichiometry for the hydride half-reaction.

The time of reaction recorded in the tables is the total time elapsed from the time of mixing. At the time recorded all the gas was removed so that the succeeding sample, if any, represents the gas liberated in the next time interval.

(A) **The Dissolution of Uranium Hydride in Aqueous Acids.** (1) **Hydrochloric Acid.**—In Table II we record some experimental results which serve to confirm the general nature of the results which were reported earlier.[4] The reaction in 16 *M* DCl is rapid and HD is the predominant form of the gas evolved. At lower acid (*cf.* expt. 8), the reaction becomes much slower, and H_2 and D_2 are the dominant forms in the gas phase.

TABLE II
THE ISOTOPIC COURSE OF THE REACTION OF
UH₃ IN CONCENTRATED DCl SOLUTION

Expt. no.	Time of reaction, min.	Av. (DCl), *M*	H₂/HD	D₂/HD	D/H
3		16	0.11	0.19	1.13
4	1.7 × 10²	16	0.18	0.40	1.32
2	8.9 × 10²	14.5	1.02	1.40	1.25
8	5.2 × 10²	9.0	4.9	14.5	...

The reaction of the hydride with hydrochloric acid solution was in no case complete, even when, as for expt. 3 and 4, the reaction was violent in the initial stages. In all cases at least a small amount of black residue remained when the last gas sample was taken.

The results of a number of experiments using hydrochloric acid at 10 *M* or lower concentration are summarized in Table III.

An attempt was made in two of the experiments at chemical analysis of the black residue. The analysis was done by adding the residue to ceric sulfate solution, determining the consumption of cerium(IV) in this step, and then determining the uranium content of the solution. In calculating the average oxidation state of the uranium, it was assumed that hydride hydrogen was liberated with no loss by ceric oxidation, as established by the data of Table I. The average oxidation state of uranium in the residue from one of the experiments was calculated as 2.36 and as 2.20 for the other. The total hydrogen evolved was not measured; its isotopic composition was found to correspond to 98.2% H_2, even though the reaction medium was completely deuterated. The chloride content of the residues was found to correspond to less than 1 chloride for each 35 uranium atoms.

The residue from expt. 18 was collected, washed in nitrogen-saturated dilute HCl, transferred to a glass plate, and dried *in vacuo*. After drying, it was placed in the beam of an X-ray diffractometer. In Table IV, the peaks observed between 25 and 77° for 2θ are shown and are compared with those reported for UO₂.

(2) **Sulfuric Acid.**—UH₃ was found to react vigorously in 9.4 *M* D₂SO₄ and the hydride was completely consumed in 16 hr. at room temperature. Some reduction at least of SO_4^{2-} took place, as evidenced by the odor of H₂S which became apparent when the reaction vessel was opened. The isotopic composition (H₂: HD: D₂) of the hydrogen formed was found to be 0.81: 1.00: 3.23.

A sample of UD₃ prepared *in situ* was brought into contact with 2.0 *M* H₂SO₄. The reaction began vigorously, but it virtually ceased within a few minutes, and after 16 hr. only 0.80% of the total hydrogen expected was evolved (H₂: HD: D₂ = 2.96: 1.00: 1.88).

(3) **Phosphoric Acid.**—The reaction of UH₃ with 85% D₃PO₄ began vigorously and appeared to be complete after 26 days. The hydrogen evolved constituted 89.2% of that expected assuming that the hydride was UH₃ (H₂: HD: D₂ = 0.63: 1.00: 2.4).

(4) **Hydrofluoric Acid.**—The reaction of UD₃ with 1.4 *M* HF is vigorous, and the bulk of the UH₃ was found to be consumed in a few minutes. The reaction was allowed to proceed for 14 hr., and although a copious precipitate, presumably UF₄, was present, it appeared to contain no black residue. The ratio H₂: HD: D₂ was measured as 1.73: 1.00: 1.25 giving H/D = 1.27. The results at 4 *M* HF were not substantially different and in this experiment H₂: HD: D₂ = 1.60: 1.00: 0.97 with H/D = 1.43.

(B) **The Reaction of Uranium Hydride in Solutions of Various Oxidizing Agents.**—A differentiation of the results obtained when hydrogen ion is the only oxidizing agent and those obtained when other oxidizing agents are present seems appropriate for two reasons. All of the oxidizing agents which were used except

Table III

Stoichiometry and Isotopic Course of the Reaction of UD_3 in Aqueous HCl

Expt. no.	H/U	Av.[a] (HCl), M	Sample no.	Time, hr.[b]	Hydrogen evolved, % theo.[c]	H_2/HD	D_2/HD	H/D
9	...	9.8	1	4.6×10^3	85	12.0	8.8	1.35
10	...	9.8	1	0.25	10	17.8	9.1	1.91
			2	0.50	5.7	16.2	11.8	1.36
			3	20	40.5	11.8	7.0	1.64
			4	44	0.7	7.0	5.0	1.36
19	2.91	9.5	1	288	83.4	11.2	7.8	1.41
12	...	9.4	1	5	71.3	15.1	11.0	1.36
			2	25	11.3	11.5	7.2	1.56
			3	49	0.2	6.5	2.9	2.1
13	2.96	9.5	1	0.05	4.3	6.9	3.6	1.80
			2	48	90.7	9.6	6.6	1.42
15	2.94	4.7	1	192	15.4	3.72	2.02	1.67
			2	1.2×10^3	46.5	5.49	2.28	2.16
16[d]	...	4.7	1	68	88.2	9.88	7.10	1.37
17[e]	2.62	2.2	1	0.17	17.5	19.2	7.7	2.4
			2	14	30.4	18.1	7.7	2.4
			3	168	43.7	11.7	4.2	2.5
18	2.92	9.6	1	50	93.9	...	...	...

[a] The change during an experiment in no case exceeded 4%. [b] The time in each case represents that elapsed from the time of mixing. [c] 100% theory corresponds to eq. 4 (or 5 when initial D/U is known). [d] 5.2 M LiCl. [e] 7.6 M LiCl.

hydrogen ion are capable of oxidizing hydrogen and it is a matter of interest to learn whether hydrogen can be liberated when the hydride reacts in such solutions; in addition, the majority of the oxidizing agents (UO_2^{2+} and H^+ are the only exceptions) under the conditions used have the capability of oxidizing uranium to the +6 state. In fact, striking differences in behavior are noted when on the one hand hydrogen ion is the only oxidizing agent, and when on the other stronger oxidizing agents are used. The results obtained with a number of oxidizing agents are summarized in Table V.

Table IV

Powder Diffraction Pattern for Residue

Cu Kα source: $25° < 2\theta < 77°$

Observed 28.3 32.7 47.0 55.7 58.5 68.6 75.9
Reported[a] 28.26 32.74 46.97 55.75 58.4 68.59 75.80
for UO_2

[a] H. J. Garrett and R. E. Brocklehurst, Wright Air Development Center Technical Report 57-381, 1958, p. 10.

No residue was left in the experiments using $FeCl_3$ or Ce(IV) as oxidizing agents, and the visual evidence suffices for the conclusion that the dissolution was complete in these experiments. The reaction with $FeCl_3$ in concentrated acid was very rapid and was substantially complete in 5 min. The reactions in alkaline H_2O_2 and with Ce(IV) in H_2SO_4 are also very rapid, and the long reaction time was chosen only to ensure that reaction was really complete and to gain some assurance that rapid equilibration of hydrogen with the product solution does not take place. With $TlCl_3$ as oxidizing agent, $TlCl$ is formed, and we judge from the white color of the final solid that oxidation was complete also in this case. Likewise, we judge from the yellow color of the uranyl peroxide residue that oxidation with H_2O_2 was complete. When $Fe(CN)_6^{3-}$ is the oxidizing agent, reaction is vigorous, and a brown

sludge, presumably uranyl ferro- or ferricyanide, is produced. In spite of the vigor displayed by the reaction in the early stages, the process was apparently not complete in the reaction mixture left for 12 hr.; however, since recovery of D was essentially complete for the mixture left to react for 95 hr., the reaction must have been complete in this case. The reaction of UH_3 with aqueous $AgNO_3$ proceeds rapidly.[10] Since recovery of H_2 was approximately 96% of that assumed for a hydride of composition UH_3, it is likely that the hydride was completely consumed in this case. The main product of each of the reactions summarized in Table VI appeared to be U(VI).

Several experiments were done with O_2 present in the acidic solutions, but the observations will be described in some detail only for the experiment which was the most complete. UD_3 (but with the initial composition not defined) was used in a medium 4.8 M in HCl and with O_2 at 0.4 atm. pressure. After 5 days the hydrogen evolved corresponded to 74% of the theoretical as defined by eq. 6 assuming $n = 3$; the ratio $D_2:HD:H_2$ in the gas was measured as 12.0: 1.00:0.94. It is entirely likely that hydride was left in the copious black residue which remained, yet the average oxidation number of the U in solution exceeded 4 and was found to be 4.32. The black residue was separated, washed with aqueous HCl, and dried. Its oxygen isotopic composition was found to correspond closely to that of the medium which was of normal isotopic composition; the O_2 gas was 8.07-fold enriched in O^{18}.

UO_2SO_4 at 0.99 M in 1.4 N H_2SO_4 was also used as the oxidizing mixture acting on UD_3. In 40 hr., reaction was only 4.6% complete; $D_2:HD:H_2$ in the gas was measured as 4.70:1.00:2.00.

(10) A. S. Newton, J. C. Warf, F. H. Spedding, O. Johnson, I. B. Johns, R. W. Nottorf, J. A. Ayres, R. W. Fisher, and A. Kant, *Nucleonics* 4, No. 2, 17 (1949).

TABLE V

STOICHIOMETRY AND ISOTOPIC COURSE OF THE REACTION OF URANIUM HYDRIDE WITH VARIOUS OXIDIZING AGENTS

Reactants	D or H/U	Time, hr.	Hydrogen,[a] % theor.	H₂/HD	D₂/HD
UH₃; 0.9 M FeCl₃ in D₂O	. . .	72	89	32.3	0.03
UD₃; 1.2 M FeCl₃, 15 M HCl in H₂O	2.96	20	118	3.45	4.64
UH₃; 1.5 M TlCl₃ in D₂O	. . .	16	84.2	31.1	0.13
UD₃; 1.0 M Fe(CN)₆³⁻, 0.7 M HCl in H₂O	2.93	12	89.5	2.0	68.3
UD₃; 1.1 M Fe(CN)₆³⁻, 1.0 M HCl in H₂O	2.42	95	93.9	2.0	49.0
UH₃; 1.0 M AgNO₃ in D₂O	. . .	0.5	97	40.6	0.04
UD₃; 1.0 M H₂O₂, 1.1 N H₂SO₄	. . .	16	96.0	0.66	33.1
UD₃; 1.0 M H₂O₂	. . .	14	69.5	0.5	26.4
UD₃; 1.0 M H₂O₂, NH₄Cl–NH₃ at pH 8.9	2.94	12	94.1	0.24	105
UD₃; 0.22 M Ce(IV), 2 N H₂SO₄	. . .	15	. . .	0.39	29.9
UD₃; 0.22 M Ce(IV), 2 N H₂SO₄	2.94	16	101	0.78	54.7

[a] 100% theory taken as conforming to eq. 6.

Discussion

The experiments of Table II confirm the conclusion that when concentrated (16 M) HCl is the oxidizing medium, the dominant form of hydrogen is made up with one atom derived from the medium and the other from the hydride. They also lead to the conclusion that the H of the UH₃ is largely transferred to the gas phase in the deuterated reaction medium so that little exchange of hydride with hydrogen of water takes place.[11] This follows because for the reaction

$$UH_3 + 3D^+ = U^{3+} + 3(H) + 3(D) \qquad (7)$$
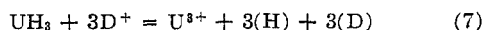
the expected ratio D/H when no exchange occurs is 1.00. In expt. 3, the value of D/H observed is only slightly in excess of this, and a small excess is to be expected because some U^{+4} was almost certainly formed. In expt. 2 and 4, the reaction of U^{3+} to U^{4+} was certainly complete, and for this experiment the ratio of D/H is close to the theoretical value of 1.33 expected for complete oxidation with no exchange. Since the dissolution of the solid was not complete in any case, slight deviations from ideal stoichiometry are ascribable to this cause, but the amount of unreacted material could not have exceeded 10% in expt. 2 or 4.

Experiments 9, 10, 12, 13, and 19 agree on the conclusion that when the reaction medium acting on UH₃ is ~9.5 M DCl, the principal forms of hydrogen become H₂ and D₂ rather than HD. In these experiments, too, the hydride deuterium is conserved; *i.e.*, there is little exchange with the solvent. Thus, if it is assumed for expt. 19 that the hydride which has not reacted has the same composition as the starting material, the ratio of H/D computed for no D exchange is 4/2.91 = 1.38 compared to 1.41 observed. For expt. 13, in which consumption of UD₃ was most complete, theory and experiment compare as 1.36 and 1.44.

(11) In all experiments the hydrogen of water was at least 500 times as abundant as the hydrogen of the hydride.

For expt. 9, theory calls for H/D > 1.33 (where this is the value if the hydride has the theoretical composition UD₃.₀₀) and the experimental value is 1.35.

The variations in the ratios H/D with extent of reaction show no uniform behavior, and the rates of reaction also are not closely reproducible.

At lower concentrations of HCl (see expt. 15 with HCl at 4.7 M) the reaction rate becomes much less. HD becomes a much more important component of the gaseous mixture, and the H/D ratio shows that there is extensive exchange of D in UD₃ with the environment.

Anions exert a profound effect on the results when hydrogen ion is the oxidizing agent. Thus, comparison of expt. 16 (4.7 M HCl, 5.2 M LiCl) with 15 shows that LiCl restores the behavior of the system to that characteristic of 9.5 M HCl as the reaction medium. Even in relatively dilute HF, the reaction of uranium hydride is quite rapid. H₂, HD, and D₂ are all present in approximately equal amounts. However, very little exchange of hydride hydrogen with the solvent takes place. This particular result contrasts with the corresponding one obtained with 85% H₃PO₄ as the reaction medium.

Of the oxidizing agents that are capable of oxidizing U all the way to the +6 state, Ce(IV) exemplifies an ideal type of behavior: all the hydride hydrogen appears as gaseous product, and very little besides this. Deviations from this ideal behavior will be referred to in the discussion of the results.

The results obtained in this study can be understood by postulating a barrier layer. In fact, the results at 9.5 M HCl which show that hydride hydrogen and solvent hydrogen are kept effectively apart seem to be proof that a barrier layer exists under these conditions. These latter results cannot be explained in terms of decomposition of the hydride to hydrogen and uranium metal followed by reaction of the metal with the sol-

vent; the decomposition pressure of the hydride at 25° is only 1.4×10^{-6} mm.[5] The reduction of hydrogen ion and the release of hydride hydrogen must then occur simultaneously, and it seems necessary that these processes be separated by some physical barrier, since the hydride surface has been shown to be an effective catalyst for hydrogen–deuterium equilibration.[12]

The inertia of UH_3 toward reaction with water and most nonoxidizing acids[13] has been ascribed previously to the presence of a protective oxide film.[10] In view of the identification of crystalline UO_2 in the residue from the reaction of hydrochloric acid with UH_3, it seems reasonable to assume, as did Waber[14] in discussing the corrosion of uranium, that the hydride is at least partially covered with a protective film of UO_2 when in contact with water. The volume change when UH_3 changes to UO_2 is only about 11%, and the strain resulting from the transformation should not be large. Further, any UO_2 which is formed by the reaction of UH_3 with an acidic solution must be formed at the hydride surface and not by deposition from the solution. The thermodynamic properties of UO_2 are such that though it is stable with respect to UH_3 and H_2O, it is unstable with respect to U^{4+} and H_2O in strong acid. The latter conclusion follows from the values of $\Delta G°$ for $UO_2(s)$[15] and U^{4+} and H_2O[16] which have been recorded. These give as equilibrium quotient for the reaction

$$UO_2 + 4H^+ = U^{4+} + H_2O \qquad (8)$$
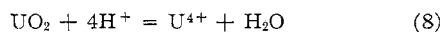
the value of 6×10^3. Thus UO_2 would not be expected as an equilibrium product in $1\ M\ H^+$. The rates of dissolution of UO_2 by most dilute acids are slow, but bulk UO_2 is oxidized rapidly to UO_2^{2+} by the metal ion oxidizing agents used in this study.[17]

The influence which anions exert on the rate when H^+ is the oxidizing agent may find an explanation in terms of differing rates of dissolution of oxide when different anions are present. It seems possible that the affinity which U^{4+} has for Cl^- is exploited in bringing about more rapid dissolution of UO_2 when Cl^- is present. Similarly, F^- and PO_4^{3-} may keep the oxide layer very thin or remove it altogether, in these cases exploiting the stabilities of the fluoride and phosphates of U^{4+}. The dramatic decline in rate which is observed as the reaction in dilute HCl progresses finds the reasonable explanation that since no ready means of dissolving the oxide is at hand, it continues to build up. The more rapid rates observed when oxidizing agents known to dissolve UO_2 are present are ascribable to the fact that the barrier layer will be thinner in these cases.

The tracer results are also explained by the postulated barrier film. When very concentrated HCl is

the oxidizing agent, the barrier layer is thin and perhaps nonexistent for much of the reaction time, so that reaction takes place largely by direct union of hydride with hydrogen ion. At lower acid, say 9.5 M HCl, the barrier layer is thicker, and the hydride surface becomes covered with the oxide except in small areas where uranium enters the solution and hydride hydrogen escapes. These small areas would be called anodic sites in electrochemical terms.[18] The flow of electrons from the anodic sites through the hydride and the oxide layer to hydrogen ions at the external surface of the hydride is made possible by the high electrical conductivity of the hydride[5] and the fact that UO_2 is a semiconductor.[19] Thus the reduction of hydrogen ion occurs over most of the surface, whereas the expulsion of hydride–hydrogen occurs in isolated areas, and little mixing of hydrogen isotopes occurs.

While it is necessary to invoke the dissolution of the barrier film as a factor in understanding the results, it seems necessary in addition to assume that attack by H_2O (to form UO_2) and by H^+ are competing processes. Reaction of the hydride with H_2O forms UO_2; when the oxide film is kept from developing, direct reaction of protons from the solvent with hydride hydrogen becomes possible. The experiment with $FeCl_3$ in concentrated HCl shows that the direct action is not limited to hydrogen ion. In this experiment, conducted with UD_3, the total amount of D recovered in the gas is considerably less than that brought in with UD_3, and it is entirely reasonable to assume that in this case the hydride hydrogen is not protected from oxidation by the $FeCl_3$ and some is oxidized to D^+. The equation expressing the stoichiometry of the reaction of $UD_{2.96}$ with $FeCl_3$ in concentrated HCl is

$$5.46Fe(III) + UD_{2.96} + 1.52H^+ =$$
$$1.98[D] + 1.52[H] + U(VI) + 5.46Fe(II) + 0.98D^+ \quad (9)$$
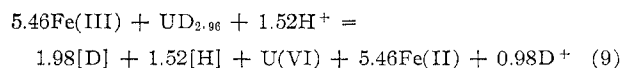
The conservation of the hydride hydrogen in the other experiments with oxidizing agents at lower concentrations of acid thus argues for the presence of a barrier layer in each of these cases.

The effect which is the most difficult to understand is the exchange of hydride hydrogen with solvent hydrogen which is observed under some conditions. The extent of this exchange was quite large in the experiment with 4.7 M HCl. It appeared also in the experiment with H_3PO_4 as oxidizing agent, to a small extent (probably) when $Fe(CN)_6^{3-}$ was the oxidizing agent, and to a considerable extent in the experiment with O_2 as oxidizing agent. The experiments with concentrated HCl as the oxidizing agent show that direct contact of solvent hydrogen with hydride hydrogen by no means is sufficient to ensure the exchange. In these experiments, hydride hydrogen was transferred almost quantitatively to the gas phase. It is possible

(12) J. Biegeleisen and A. Kant, *J. Am. Chem. Soc.*, **76**, 5957 (1954).

(13) The term as used here refers to the anion of the acid.

(14) J. T. Waber, U. S. Atomic Energy Commission, TID-7587, 1959, pp. 307–387.

(15) E. G. Huber, C. E. Holley, and E. H. Meierkord, *J. Am. Chem. Soc.*, **74**, 3406 (1952).

(16) W. M. Latimer, "Oxidation Potentials," Prentice-Hall Inc., Englewood Cliffs, N. J., 2nd Ed., pp. 302, 39.

(17) Unpublished observations by the authors.

(18) T. P. Hoar, "Modern Aspects of Electrochemistry, No. 2," J. O'M. Bockris, Ed., Academic Press, Inc., New York, N. Y., 1959, Chapter 4.

(19) Electron conduction is accomplished by positive hole migration with an activation energy of *ca.* 8 kcal./mole: P. K. Willardson, J. W. Moody, and H. C. Goering, *J. Inorg. Nucl. Chem.*, **6**, 19 (1958).

that under some conditions, *e.g.*, 4.7 *M* HCl, the nature of the oxide film is altered by the incorporation of anions and hydride ions to give compounds such as U(O)XH, which Katzin[20] has suggested is the residue from the dissolution of uranium metal in dilute HCl. Such a barrier layer might be permeable to hydrogen, providing a means for the exchange.

Two points in connection with the observations made with O_2 as oxidizing agent seem worthy of special mention. The oxygen in the oxide layer was found to have been derived from the solvent rather than the O_2. Although the result is consistent with the hypothesis we have advanced, it does not provide additional support. Exchange of massive UO_2 with solvent is known not to be rapid, but exchange at the surface as UO_2 develops slowly may be rapid enough to ensure the isotopic identity of the UO_2 and solvent oxygen. It appears fairly definite that the reaction of UH_3 in 4.8 *M* HCl with oxygen present is more rapid than when HCl alone is used.

(20) L. I. Katzin, L. Kaplan, and T. Steitz, *Inorg. Chem.*, **1**, 963 (1962).

In the experiment, the average oxidation state of U in solution was found to be 4.3. The enhanced reaction rate may result from the fact that the oxide layer contains oxygen in excess of the stoichiometry UO_2. The conductivity of UO_{2+x} increases with increasing oxygen content.[19]

It is interesting to compare the reactions of MgH_2, UH_3, and palladium hydride with solutions of Ce(IV). When MgH_2 is the reactant, Ce(IV) is not at all involved in the net change.

$$MgH_2 + 2H^+ = Mg^{2+} + 2H_2 \tag{10}$$
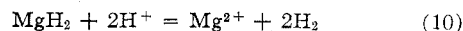
When UH_3 is used, the metal is oxidized, but not the contained hydrogen.

$$2UH_3 + 12Ce^{4+} + 4H_2O = 2UO_2^{2+} + 12Ce^{3+} + 3H_2 + 8H^+ \tag{11}$$
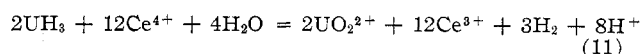
When palladium hydride reacts, the contained hydrogen, but not the metal, is oxidized.
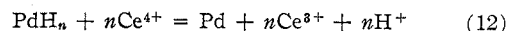
$$PdH_n + nCe^{4+} = Pd + nCe^{3+} + nH^+ \tag{12}$$

The Absorption of Anionic Species by Strong-Acid Cation Exchangers: Identity of the Iron(III) Ion Taken up from Concentrated Aqueous Halide Solutions[1]

By G. E. BOYD, S. LINDENBAUM, and Q. V. LARSON

Spectrophotometric examinations and chemical analyses were conducted on a cross-linked polystyrene sulfonate (0.5% DVB Dowex-50) and on a liquid cation exchanger prepared by dissolving dinonylnaphthalenesulfonic acid in toluene in an attempt to find an explanation for the anomalous increase in the absorption of Fe(III) from concentrated aqueous HBr and LiBr solutions by strong-acid cation exchangers. The characteristic ligand field bands of the tetrahedral anion, $FeBr_4^-$, were observed in both exchangers when they had been brought to equilibrium with solutions more concentrated than 5 *N* in Br^- ion. Measurements of the Li^+ (or H^+) ion content of the liquid exchanger showed that the amount in excess of the exchange capacity was sufficient to give $LiFeBr_4$ (or $HFeBr_4$). It was concluded that the absorption of Fe(III) from concentrated HBr and LiBr involved the $FeBr_4^-$ complex ion, and that the ion pairs, $H^+FeBr_4^-$ and $Li^+FeBr_4^-$, were "salted" into the organic cation-exchange phase. Thus, in special circumstances, ion exchangers may extract salts by essentially a solvent extraction mechanism involving ion association complexes.

The anomalous increase in the absorption of Fe(III) from concentrated electrolyte solutions by sulfonic acid type cation exchangers apparently was first observed in 1950 by Djurfeldt and Samuelson,[2] who found that if too high a concentration of hydrochloric acid were used it became practically impossible to elute Fe(III) quantitatively from the exchanger. Measurements of the equilibrium absorption of iron further showed that for acid concentrations greater than 5.5 *N* the affinity of the exchanger for Fe(III) increased rapidly. Minima have since been observed in the concentration depend-

ence of the uptake of many of the rare earths and several actinides[3] and of calcium, strontium, and sodium[4] from hydrochloric acid solutions by Dowex-50. The absorption of Au(III) and Ga(III) from HCl and LiCl solutions[5] has been found to exhibit a similar concentration dependence, and detailed investigations with In(III)[6] ion have revealed minima with LiI, NaI, KI, MgI_2, LiBr, NaBr, and $MgBr_2$ solutions. Cationic species presumably were not involved in the work with Fe(III), Au(III), Ga(III), and In(III), as all of them

(1) Presented before the Division of Inorganic Chemistry, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 5–10, 1964.

(2) R. Djurfeldt and O. Samuelson, *Acta Chem. Scand.*, **4**, 165 (1950).

(3) R. M. Diamond, K. Street, Jr., and G. T. Seaborg, *J. Am. Chem. Soc.*, **76**, 1461 (1954).

(4) R. M. Diamond, *ibid.*, **77**, 2978 (1955).

(5) K. A. Kraus, D. C. Michelson, and F. Nelson, *ibid.*, **81**, 3204 (1959).

(6) H. Irving and G. T. Woods, *J. Chem. Soc.*, 939 (1963).