SOME THERMODYNAMIC RELATIONS AMONG THE URANIUM OXIDES AND THEIR RELATION TO THE OXIDATION STATES OF THE URANIUM ORES OF THE COLORADO PLATEAUS*

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ABSTRACT

Fields of stability of uranium (VI) and uranium (IV) hydroxides and oxides in water solution at 25° C. and one atmosphere pressure have been calculated as functions of Eh and pH. Equilibrium values of the activity of UO_2^{++} ion and of U^{4+} ion also have been calculated and are shown as contours on the stability fields. Thermodynamic relations among the uranium (VI) hydroxides and hydrated oxides indicate that the free energy differences among the various species are small. The data are interpreted to mean that a variety of such uranium (VI) compounds may form and even coexist. Similar studies of the uranium (IV) hydroxide indicate that it is unstable relative to the oxide and may well be expected to change to the oxide at a finite rate. Uranium (V) compounds probably have a transitory existence because of the instability of the UO_2^+ ion; uranium (III) oxides and hydroxides would not be expected to occur naturally because the uranium (III) ion would decompose water. A comparison of the behavior of the vanadium (III) and (IV) hydroxides with uranium (IV) oxide and uranium (VI) hydroxides indicates that vanadium (III) hydroxide should oxidize to the vanadium (IV) hydroxide at a lower potential than that required for the change from uranium (IV) to uranium (VI). A rather highly speculative diagram showing probable fields of stability of many of the major minerals of the Colorado Plateaus is presented, and the suggestion is made that a consistent picture results if it is assumed that the ores, as viewed today, represent the superimposition of a weathering environment on a mineral assemblage that was formed in a primary reducing environment. It is emphasized that such an interpretation is consistent but not necessarily unique.

INTRODUCTION

Prior to about 1950, the uranium-vanadium ores of the Colorado Plateaus presented few problems in the interpretation of the oxidation-reduction conditions of their environment of formation. The oxidation-reduction "sensitive" elements of the major minerals uniformly exhibited the higher valences consistent with moderate to strongly oxidizing environments. During the last several years this consistency has disappeared; with the discovery of large quantities of "blue-black" or "black" ores, a variety of minerals containing the same elements, but in lower valence states, have become of economic importance.

The genetic relation of the "blue-black" ores to the more oxidized, or "carnotite" ores, is not clear, but one definite possibility is that the primary ores were an assemblage of minerals deposited under reducing conditions, and hence with the "sensitive" elements in their lower

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valence states, and that the more oxidized ores have been, at least in part, derived from them by ordinary weathering processes. If so, the primary oxidizing agent was oxygen carried by ground water, and the temperature and pressure of the reactions were close to 25° C. and 1 atmosphere.

The stability relations of many of the minerals involved under such conditions can be calculated. In a previous paper (Garrels, 1953) relations of some of the vanadium oxides were considered. In this report various uranium oxides, hydroxides, and hydrated oxides, for which thermodynamic data are available, are discussed.

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Thermodynamic Properties of Some Compounds and Ions of the System U-O-H_2O

Data on the thermodynamic properties of compounds and ions in the system U-O-H_2O have been assembled (Table 1) from Latimer (1952)

Table 1. Thermodynamic Properties of Some Compounds and Ions of the System U-O-H_2O at 25° C.
(Heat and free energy of formation in kcal; entropy of substance in cal./deg. Data from Latimer, 1952, except as noted)

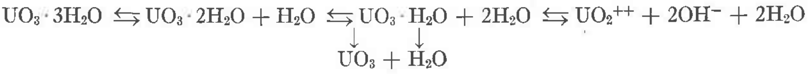
Compound or Ion	ΔH^0	ΔF^0	S^0	State
$UO_3 \cdot 3H_2O$		[−376][1]		Crystalline
$UO_2 \cdot 2H_2O[UO_2(OH)_2 \cdot H_2O]$	−446.2	[−399][1]	[40.4][1]	Crystalline
$UO_3 \cdot H_2O$	−375.4	−343	(33)	Crystalline
UO_3	−291.6[2]	−273.1[2]	23.57	Crystalline
UO_2	−259.2[2]	−246.6[2]	18.6	Crystalline
$U(OH)_4$		(−351.6)[3]		Crystalline
$U(OH)_3$		(−263.2)[3]		Crystalline
UO_2^{2+}	−250.4	−236.4	−17	Aqueous
UO_2^{+}	−247.4	−237.6	12	Aqueous
$U(OH)^{3+}$	−204.1	−193.5	−30	Aqueous
U^{4+}	−146.7	−138.4	−78	Aqueous
U^{3+}	−123.0	−124.4	−30?	Aqueous
H_2O	− 68.317	− 56.690	16.716	Liquid
O_2	0.0	0.0	49.003	Gaseous
H_2	0.0	0.0	31.211	Gaseous
OH^-	− 54.957	− 37.595	− 2.52	Aqueous

[1] Estimated by the author.
[2] Seaborg and Katz (1954, p. 174).
[3] Estimated by Latimer.

and from Seaborg and Katz (1954), with the exception of the bracketed values, which have been calculated by the present author. The method of calculation is described in the appendix.

Relations among the uranium (VI) compounds

If $UO_3\cdot 3H_2O$ is put into water, the following reactions among the known species are possible (coexistence at equilibrium of all the species listed is not implied):



$$\begin{tikzcd}[column sep=small] UO_3\cdot 3H_2O \arrow[r, leftrightarrows] & UO_3\cdot 2H_2O + H_2O \arrow[r, leftrightarrows] & UO_3\cdot H_2O + 2H_2O \arrow[d] \arrow[r, leftrightarrows] & UO_2^{++} + 2OH^- + 2H_2O \\ & & UO_3 + H_2O & \end{tikzcd}$$

The monohydrate is shown ionizing to the uranyl and hydroxide ions because of the likelihood that $UO_3\cdot H_2O$ is better expressed as $UO_2(OH)_2$. The free energy changes of the various hydration reactions $UO_3\cdot 3H_2O \leftrightarrows UO_3\cdot 2H_2O + H_2O \leftrightarrows UO_3\cdot H_2O + 2H_2O$ probably are small. This conclusion is based in part on analogy with the free energies of hydration of other compounds and in part on the fact that ΔF^0 for the formation of $UO_2(OH)_2\cdot H_2O$, calculated from ΔH^0 and an estimated value of ΔS^0, corresponds closely to the value calculated on the assumption that the free energy change of hydration of $UO_2(OH)_2$ is zero. (See appendix.) On the other hand, UO_3 seems definitely unstable relative to $UO_2(OH)_2$:

$$UO_2(OH)_2 \leftrightarrows UO_3 + H_2O$$
$$\Delta F^0 = \Delta F^0{}_{UO_3} + \Delta F^0{}_{H_2O} - \Delta F^0{}_{UO_2(OH)_2}$$
$$\Delta F^0 = -273.1 + (-56.7) - (-343) = +13.2 \text{ kcal.}$$

There is also a large free energy change accompanying the ionization of $UO_2(OH)_2$:

$$UO_2(OH)_2 \leftrightarrows UO_2^{++} + 2OH^-$$
$$\Delta F^0 = \Delta F^0{}_{UO_2^{++}} + 2\Delta F^0{}_{OH^-} - \Delta F^0{}_{UO_2(OH)_2}$$
$$\Delta F^0 = -236.4 + (-75.2) - (-343) = +31.4 \text{ kcal.}$$

From this free energy change the activity product of $UO_2(OH)_2$ can be calculated:

$$UO_2(OH)_2 \leftrightarrows UO_2^{++} + 2OH^-$$
$$a_{UO_2^{++}}a^2{}_{OH^-} = K_{UO_2(OH)_2}$$
$$\Delta F^0 = -RT \ln K$$

At 25 C, ΔF^0 (kcal) $= -1.364 \log K$ (Latimer, 1952, p. 8). Therefore:

$$31.4 = -1.364 \log a_{UO_2^{++}}a^2{}_{OH^-}$$
$$a_{UO_2^{++}}a^2{}_{OH^-} = 10^{-23} \tag{1}$$

From these relations, the free energy changes of the various reactions of uranium (VI) in water can be summarized diagrammatically:

$$\begin{tikzcd}
UO_2(OH)_2\cdot 2H_2O \arrow[r, leftrightarrows, "\Delta F^0 \cong 0"] & UO_2(OH)_2\cdot H_2O+H_2O \arrow[r, leftrightarrows, "\Delta F^0 \cong 0"] & UO_2(OH)_2+2H_2O \arrow[r, leftrightarrows, "\Delta F^0=31.4\ \text{kcal}"] \arrow[d, shift left] & UO_2^{++}+2OH^-+2H_2O \\
 & & UO_3 + H_2O \arrow[u, shift left, "\Delta F^0=13.2\ \text{kcal}\downarrow"] &
\end{tikzcd}$$

Therefore, it would seem that the various hydrated oxides have no very great tendency to transform one into the other and that several might be expected to coexist metastably for considerable periods of time. Anhydrous UO_3 would not be expected, even as a metastable phase. $UO_2(OH)_2$ does not ionize freely and in the absence of complexes would dissolve perceptibly only in moderately acid solutions.

Relations among uranium (V) compounds

Uranium (V) can be formed metastably in water solution (Kraus, Nelson, and Johnson, 1949) as a more or less hydrolized UO_2^+ ion. Its rate of disproportionation into U^{4+} and UO_2^{++} ions, according to the reactions: $2UO_2^+ + 4H^+ \rightarrow U^{4+} + UO_2^{++} + 2H_2O$, is at a minimum between pH values of 2 and 4. The rate is finite, however, even in this range, so that the disproportionation may be a clue to the apparent lack of UO_2^+ compounds in nature.

Relations among the uranium (IV) compounds

In the system under consideration, free energy data are available only for the uranium (IV) compounds $U(OH)_4$ and UO_2. The reactions with water are:

$$UO_2 + 2H_2O \leftrightarrows U(OH)_4 \leftrightarrows U^{+4} + 4OH^-$$

The free energy change of the reaction on the left is:

$$\Delta F^0 = \Delta F^0_{U(OH)_4} - \Delta F^0_{UO_2} - 2\Delta F^0_{H_2O}$$
$$\Delta F^0 = -351.6 - (-246.6) - (-113.4) = +8.4\ \text{kcal.}$$

Therefore, the hydroxide is definitely unstable with respect to the oxide, and, although the free energy relations give no information on rates, the hydroxide would not be expected to form and persist indefinitely but to change to the oxide. The instability of the uranium (IV) hydroxide is in accord with the instability of Am (IV), Th (IV), and Sn (IV) hydroxides. The hydroxide, however, probably forms metastably during any laboratory precipitation, and then changes to the oxide on standing, so that the measured solubility would be that of the hydroxide, rather than that of the oxide. The probable relations between oxide and hydroxide can be shown from a consideration of their activity products.

For the ionization of $U(OH)_4$:

$$U(OH)_4 \leftrightarrows U^{4+} + 4OH^-$$
$$\Delta F^0 = \Delta F^0{}_{U^{4+}} + 4\Delta F^0{}_{OH^-} - \Delta F^0{}_{U(OH)_4}$$
$$\Delta F^0 = -138.4 + (-350.4) - (-351.6) = +62.8 \text{ kcal.}$$

From this value of ΔF^0, the activity product of $U(OH)_4$ is:

$$a_{U^{4+}}a^4{}_{OH^-} = K_{U(OH)_4}$$
$$\Delta F^0 = -RT \ln K$$
$$62.8 = 1.364 \log a_{U^{4+}}a^4{}_{OH^-}$$

$$a_{U^{4+}}a^4{}_{OH^-} = 10^{-46} = K_{U(OH)_4}. \qquad (2)$$

For the direct ionization of UO_2:

$$UO_2 + 2H_2O \leftrightarrows U^{4+} + 4OH^-$$
$$\Delta F^0 = \Delta F^0{}_{U^{4+}} + 4\Delta F^0{}_{OH^-} - \Delta F^0{}_{UO_2} - 2\Delta F^0{}_{H_2O}$$
$$\Delta F^0 = -138.4 + (-150.4) - (-246.6) - 2(-56.7) = +71.2 \text{ kcal.}$$

The activity product of UO_2 is:

$$a_{U^{4+}}a_{OH^-} = K_{UO_2}$$
$$\Delta F^0 = -RT \ln K_{UO_2}$$
$$71.2 = 1.364 \log K_{UO_2}$$
$$K_{UO_2} = a_{U^{4+}}a^4{}_{OH^-} = 10^{-52}$$

When U^{4++} is precipitated from water solution, two paths seem possible:

$$\begin{tikzcd}
U^{4+} + 4OH^- \arrow[r, shift left, "K = 10^{-46}"] & U(OH)_4 \arrow[l, shift left] \arrow[d] \\
& UO_2 + 2H_2O \arrow[ul, leftrightarrow, "K = 10^{-52}"]
\end{tikzcd}$$

If precipitation takes place at true equilibrium, the precipitate should be UO_2, which has the smaller K. But experimentally it is almost impossible to avoid exceeding both K_{UO_2} and $K_{U(OH)_4}$, and the metastable $U(OH)_4$ would be expected to form more rapidly, changing later to UO_2.

In summary:

$$\begin{tikzcd}
UO_2 + 2H_2O \arrow[r, leftrightarrows, "\Delta F^0 = 8.4 \text{ kcal.}"] \arrow[rr, bend right, dash, "\Delta F^0 = 71.2 \text{ kcal}"'] & U(OH)_4 \arrow[r, leftrightarrows, "\Delta F^0 = 62.8 \text{ kcal.}"] & U^{4+} + 4OH^-
\end{tikzcd}$$

Uranium (IV) would be expected to come out of solution as the hydroxide, and then change to the oxide, but the true equilibrium is between UO_2 and the ions.

Relations among the uranium (III) compounds

It seems unlikely that uranium (III) compounds would be found under natural conditions at low temperature (Latimer, 1952, p. 301), for the

U^{3+} ion is highly unstable with respect to the liberation of hydrogen from water and would be expected to react immediately to a higher valence.

Relations between the uranium (VI) and the uranium (IV) systems

In water solution, the uranium (VI) and uranium (IV) compounds can be considered to be connected through the UO_2^{++} and the U^{4+} ions. Under oxidizing conditions there is a tendency to transform U^{4+} to UO_2^{++} and, as a result, to shift the equilibria toward the formation of uranium (VI) compounds. Under reducing conditions the reverse is true. The relation can be expressed as an equation:

$$U^{4+} + 2H_2O \leftrightarrows UO_2^{++} + 4H^+ + 2e.$$

The free energy change can be calculated as before:

$$\begin{aligned} \Delta F^0 &= \Delta F^0_{UO_2^{++}} + 4\Delta F^0_{H^+} - \Delta F^0_{U^{4+}} - 2\Delta F^0_{H_2O} \\ \Delta F^0 &= -236.4 \quad +(0) \quad - (-138.4) - (-113.4) = +15.4 \text{ kcal.} \end{aligned}$$

In other words, at unit activity of all constituents, UO_2^{++} tends to reduce to U^{4+}.

Because the uranium (VI) system presumably goes into solution through the ionization of $UO_2(OH)_2$, and the uranium (IV) system through UO_2, the three controlling reactions are:

$$\begin{aligned} UO_2(OH)_2 &\leftrightarrows UO_2^{++} + 2OH^- \\ UO_2 + 2H_2O &\leftrightarrows U^{4+} + 4OH^- \\ U^{4+} + 2H_2O &\leftrightarrows UO_2^{++} + 4H^+ + 2e \end{aligned}$$

The equilibrium relations are:

$$a_{UO_2^{++}} a^2_{OH^-} = 10^{-23} \qquad (1)$$

$$a_{U^{4+}} a^4_{OH^-} = 10^{-52} \qquad (2)$$

$$Eh = -E^0 + 0.03 \log \frac{a_{UO_2^{++}} a^4_{H^+}}{a_{U^{4+}}} \qquad (3)$$

Equation 3 is the standard oxidation equation relating oxidation potential of the system (*Eh*) to the standard electrode potential (E^0) and the ionic ratios. Pourbaix (1949) gives a fuller discussion of this relation.

If $UO_2(OH)_2$ and UO_2 are in equilibrium, equations 1 and 2 hold. Then, dividing 1 by 2 and transforming:

$$\frac{a_{UO_2^{++}}}{a_{U^{4+}}} = 10^{29} a^2_{OH^-} \qquad (4)$$

and:

$$\log \frac{a_{UO_2^{++}}}{a_{U^{4+}}} = 29 + 2 \log a_{OH^-} \qquad (5)$$

The a_{OH^-} can be related to the pH. Because

$$a_{H^+}a_{OH^-} = Kw = 10^{-14} \text{ at } 25°\text{C}.$$

then:

$$a_{OH^-} = \frac{Kw}{a_{H^+}}$$

and:

$$\text{og } a_{OH^-} = \log Kw - \log a_{H^+}.$$

By definition, $pH = -\log a_{H^+}$, so:

$$\log a_{OH^-} = pH - 14.$$

Substituting this relation in equation 5:

$$\log \frac{a_{UO_2^{++}}}{a_{U^{4+}}} = 29 + 2(pH - 14)$$

or:

$$\log \frac{a_{UO_2^{++}}}{a_{U^{4+}}} = 2\ pH + 1. \tag{6}$$

Equation 3 can be rewritten to contain pH:

$$Eh = E^0 + 0.03 \log \frac{a_{UO_2^{++}}}{a_{U^{4+}}} - 0.12\ pH$$

Substituting the value from equation 6 for $\log a_{UO_2^{++}}/a_{U^{4+}}$

$$Eh = -E^0 + 0.03(2\ pH + 1) - 0.12\ pH$$

and:

$$Eh = -E^0 + 0.03 - 0.06\ pH.$$

Therefore, Eh is a linear function of pH at conditions of equilibrium for UO_2 and $UO_2(OH)_2$.

Substituting the numerical value of E^0, which is -0.334 volt at 25° C. (Latimer, 1952, p. 301), the simple equation is obtained:

$$Eh = 0.364 - 0.06\ pH. \tag{7}$$

Figure 1 shows the boundary between the stability fields of the two compounds, calculated from equation 7. Above the boundary $UO_2(OH)_2$ is the stable solid phase; below, UO_2. Because of the small free energy differences between the various uranium (VI) hydrates, it is not unlikely that any one or a combination of them may form and persist. On the other hand, the uranium (IV) oxide is definitely stable with respect to the hydroxide, which, if formed, would be expected to change at a finite rate to UO_2. The boundary shown for the stability of water apparently precludes the possibility of occurrence of uranium (III) compounds; the stability field of $U(OH)_3$ is more than 0.5 volt below this

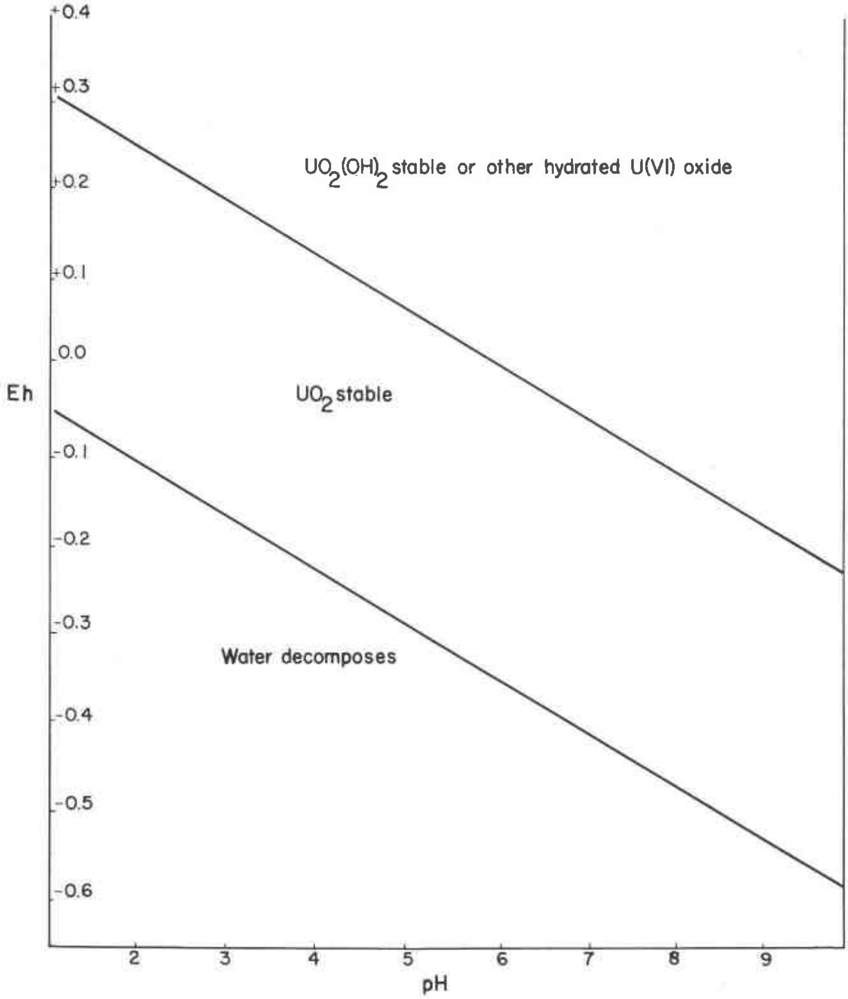


FIG. 1. Fields of stability of UO_2 and of hydrated U^{+6} oxides.

boundary, which practically assures that $U(OH)_3$ would decompose water at a finite rate.

Figure 2 shows the same stability fields with contours of the activity of UO_2^{++} ion superimposed.[1] The activity is significant ($>10^{-6}$) only in mildly oxidizing acid solutions.

In Fig. 3 contours of the activity of U^{4+} ion are shown. Activity ex-

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[1] For details of the construction of such contoured diagrams, see Krumbein and Garrels (1952) or Pourbaix (1949).

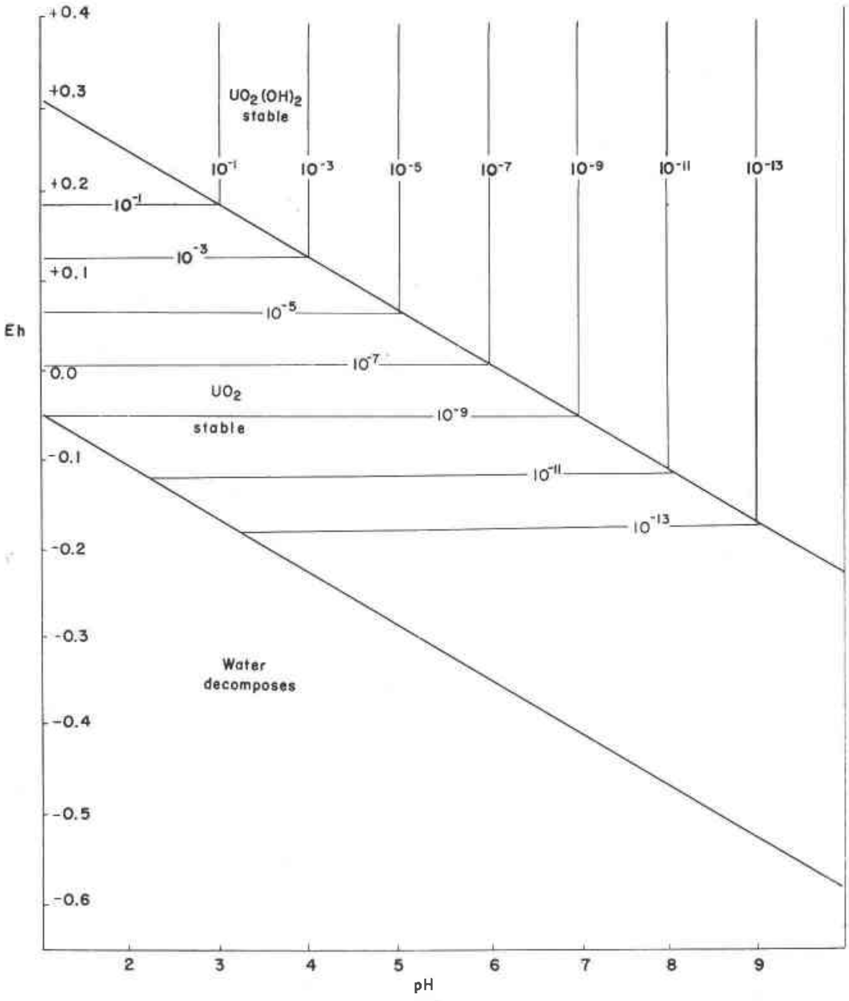


FIG. 2. UO_2^{++} ion activity in equilibrium with $UO_2(OH)_2$ and UO_2.

ceeds 10^{-6} only at *p*H values of 2.5 or less.

Figure 4 shows contours of the sum of $a_{U^{4+}}$ and $a_{UO_2^{++}}$ and re-emphasizes the low activity of either ion in very weakly acid or alkaline solutions.

Figure 5, a plot of the ratio of UO_2^{++} activity to U^{4+} activity, shows that the contribution of U^{4+} ion is relatively insignificant except under acid reducing conditions. In other words, UO_2^{++} ion activity far exceeds that of U^{4+} under most conditions, even in the field of stability of UO_2.

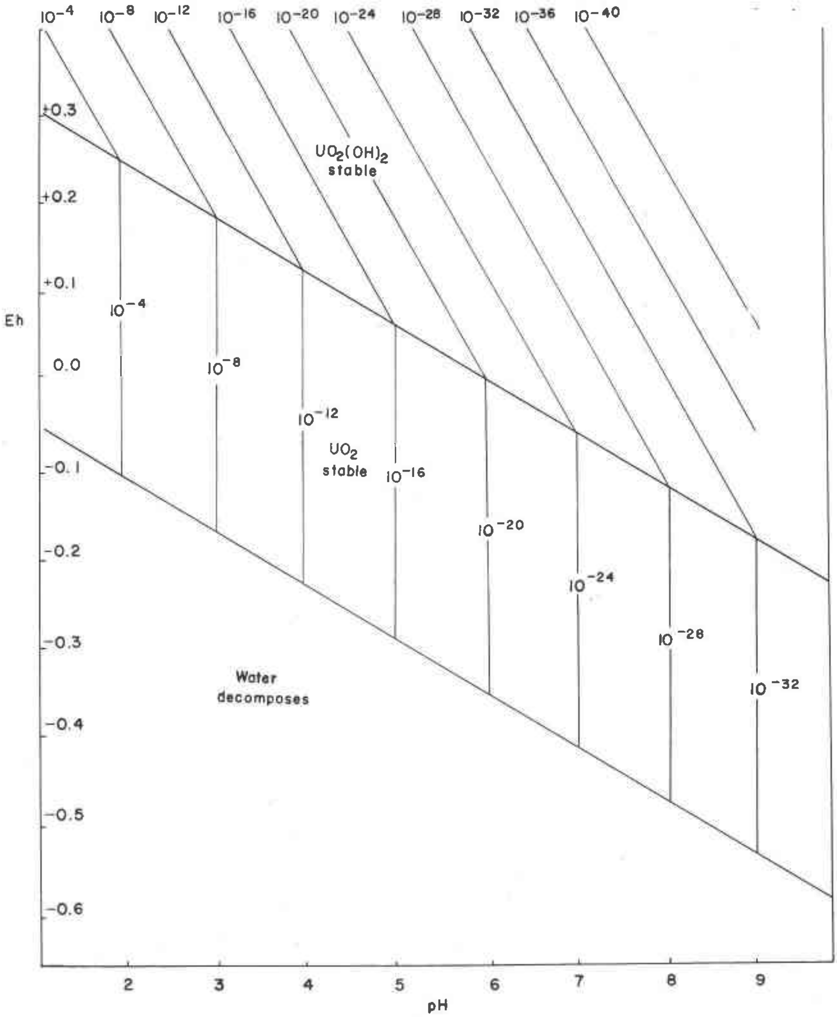


FIG. 3. U^{4+} ion activity in equilibrium with $UO_2(OH)_2$ and UO_2.

Relation of vanadium and uranium oxide stability fields

A study of the fields of stability of the vanadium oxides already has been made (Garrels, 1953). In Fig. 6 the fields of the uranium and vanadium oxides are shown together. Contours have been drawn to show conditions under which the total activity of various vanadium ions $[\Sigma a_{V^{++}}+a_{V^{3+}}+a_{VO^{++}}+a_{V(OH)_4^+}]$ is appreciable (10^{-2}) and negligible (10^{-6}). Similar treatment has been accorded $\Sigma a_{UO_2^{++}}+a_{U^{4+}}$.

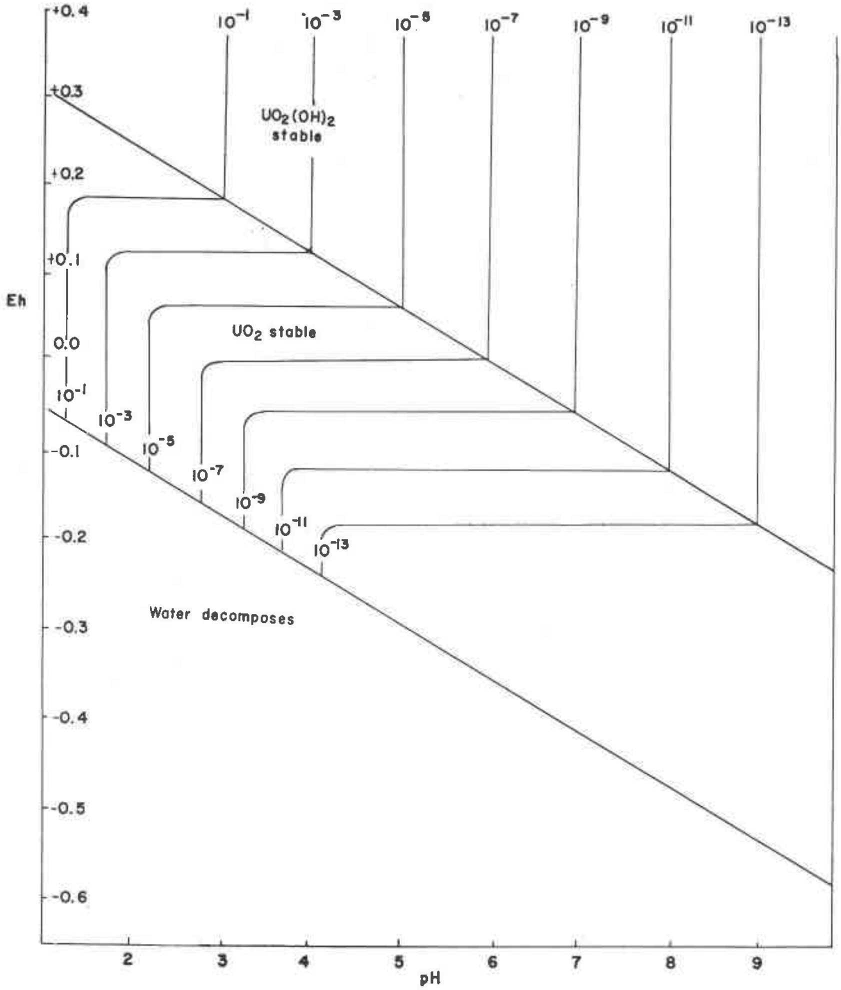


FIG. 4. Sum of activities of UO_2^{++} and U^{4+} ions in equilibrium with $UO_2(OH)_2$ and UO_2.

DISCUSSION AND INTERPRETATION

It is possible to draw a theoretical and partly hypothetical diagram showing overall *Eh-p*H stability relationships for an aqueous system containing the chief minerals of the various deposits on the Colorado Plateaus. (See Fig. 7.)

Fields 1 to 5 on this diagram have reasonable validity in that they actually have been calculated from thermodynamic data for the chemical compounds. Fields 6 and 7 are very highly speculative. To delimit

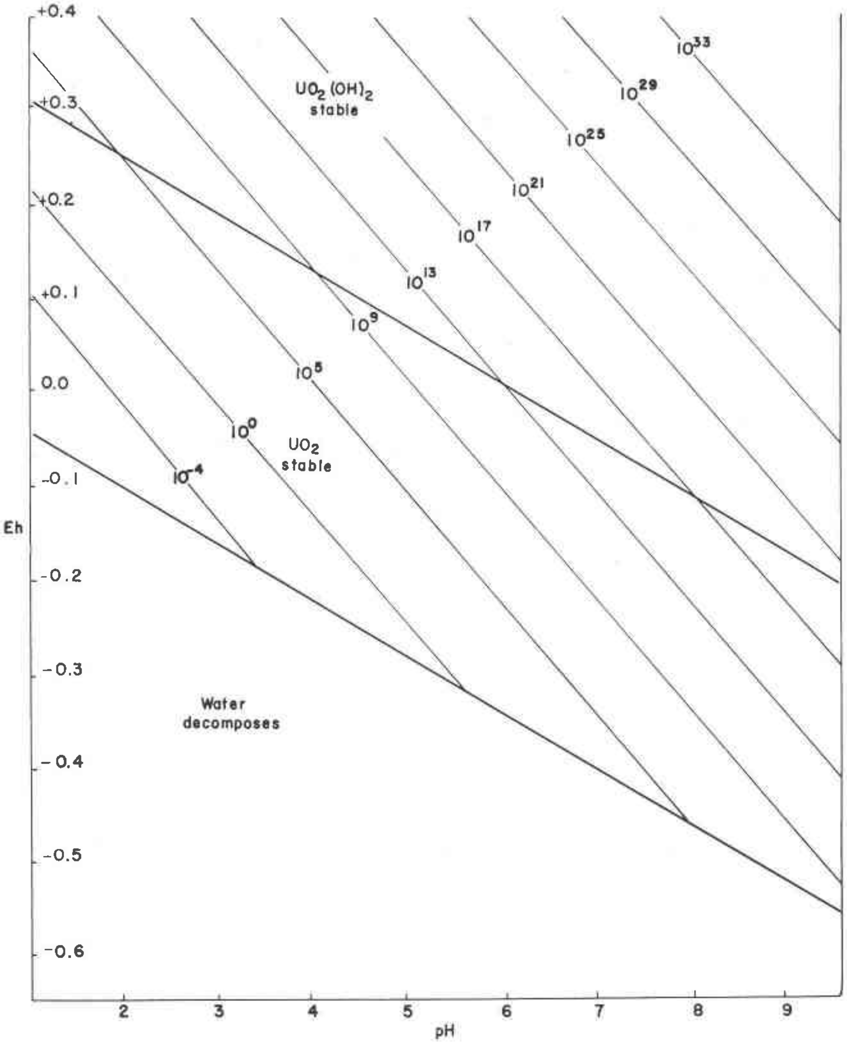


FIG. 5. Ratio of UO_2^{++} and U^{4+} ions in equilibrium with $UO_2(OH)_2$ and UO_2.

the stability fields of the various sulfides it has been necessary to make an assumption as to composition of the solutions. The assumption is that total sulfur ($SO_4^{=}+H_2S+HS^{-}+S^{=}$) is 0.1 mol per liter; this seems not unreasonable in that it is of the order of magnitude of total sulfur in mine water, which should be somewhat comparable to those of a naturally oxidizing ore deposit. Furthermore, a decrease of total sulfur to 0.001 molar would not change the pattern significantly.

The various fields delimited by the boundaries represent the best in-

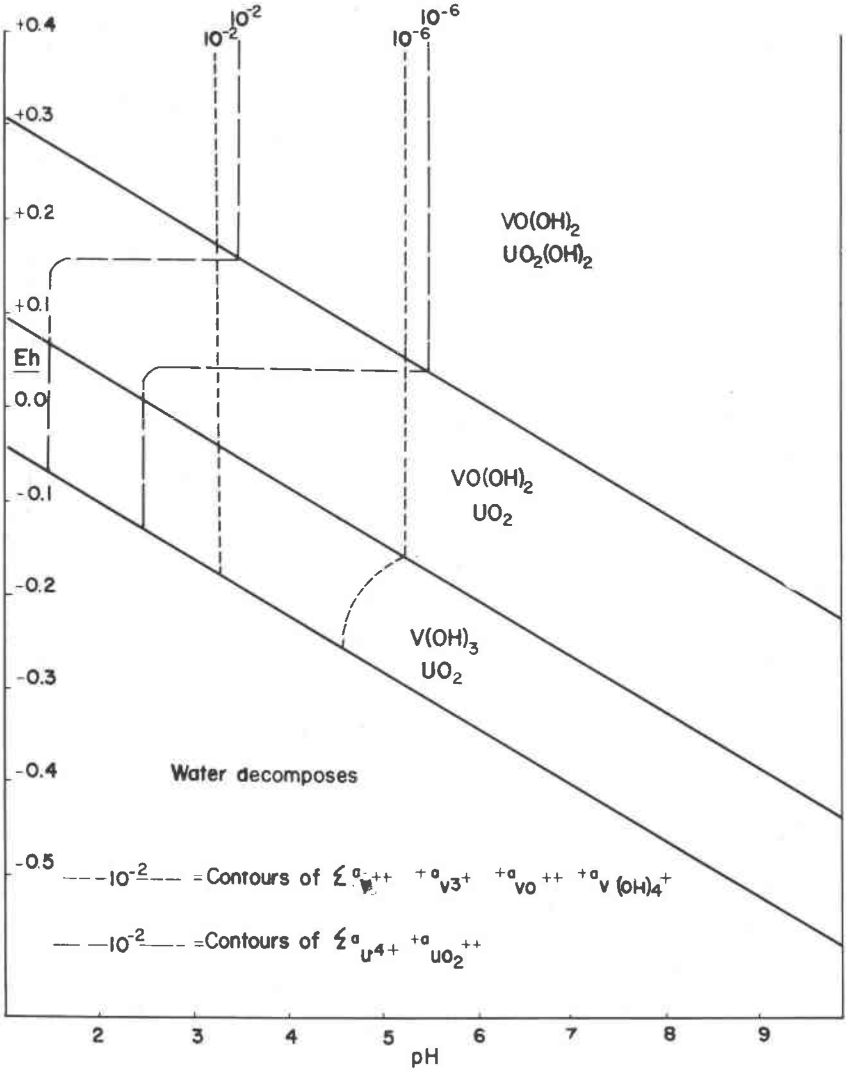
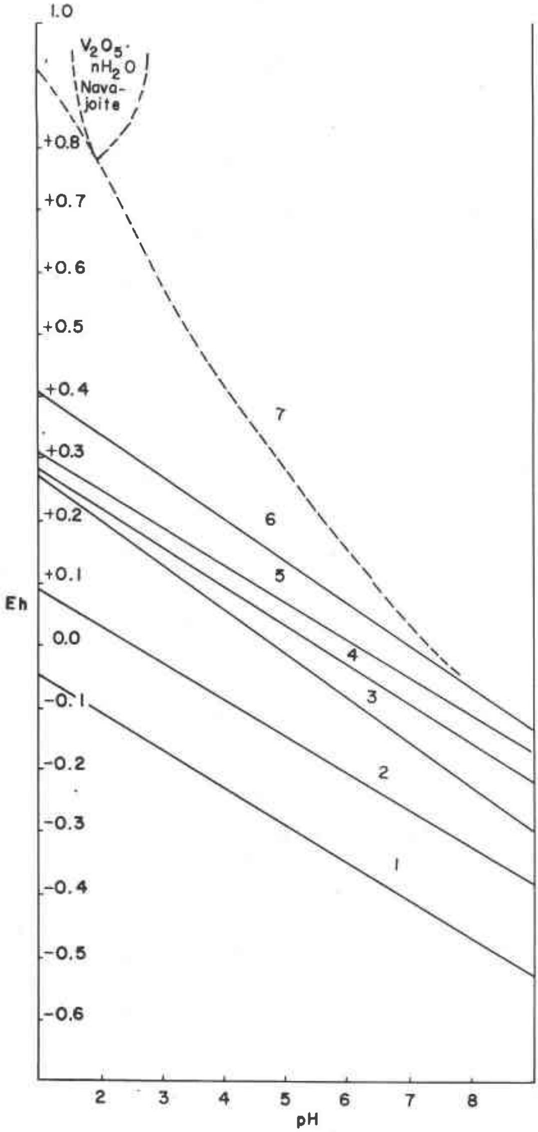


FIG. 6. Composite diagram showing fields of stability of some uranium and vanadium oxides and hydroxides.

terpretation possible at the present time as to stable mineral assemblages. Perhaps, to illustrate the kinds of changes expected as a result of oxidation of the most reduced assemblage, the best device is a discussion of the progressive changes expected as the oxidation potential is increased, carrying this original assemblage upward through the various fields.



Field 7: Copper, iron, aluminum, and calcium vanadates; and potassium and calcium uranyl vanadates; lead sulfate and carbonate; zinc carbonate and silicate; ferric oxides; copper oxides, hydroxy carbonates, silicates; and native copper.

Field 6: Mixed vanadium (IV) and (V) oxides; potassium and calcium uranyl vanadates; lead sulfate and carbonate; zinc carbonate and silicate; ferric oxides; copper oxides, hydroxy carbonates, silicates; and native copper.

Field 5: Vanadium (IV) oxides; uranium (VI) hydrated oxides; lead sulfate and carbonates; zinc carbonates and silicates; ferric oxides; copper sulfides.

Field 4: Vanadium (IV) oxides; uranium (IV) oxide; lead sulfate and carbonate; zinc carbonate and silicates; ferric oxides; copper sulfide.

Field 3: Vanadium (IV) oxides; uranium (IV) oxide; lead sulfide; zinc carbonates and silicates; iron sulfide; copper sulfide.

Field 2: Vanadium (IV) oxides; uranium (IV) oxide; lead sulfide; zinc sulfide; iron sulfide; copper sulfide.

Field 1: Vanadium (III) oxide; uranium (IV) oxide; lead sulfide; zinc sulfide; iron sulfide; copper sulfide.

FIG. 7. Summary of information on stability relations of some major minerals of the Colorado Plateaus.

Field 1 is characterized by vanadium (III) oxides or hydroxides; uranium (IV) oxide; and zinc, lead, copper, and iron sulfides. Mineralogically this might represent a mineral association of montroseite, uraninite, galena, sphalerite, covellite, and pyrite. The first of these to oxidize would be montroseite, and a field (field 2) presumably exists in which a vanadium (IV) oxide is stable in association with uraninite and the metal sulfides. Further increase in the oxidation of the environment through fields 3, 4, and 5 up into field 6, presumably would result in the oxidation in sequence of sphalerite, galena, pyrite, uraninite, and copper sulfide. In essence, then, the upper boundary of field 5 would seem to represent the most oxidizing conditions under which sulfide ion could resist oxidation up to sulfate. Zinc sulfide dissociates in water solution more easily than lead sulfide, which in turn dissociates more easily than copper sulfide; this explains the sequential oxidation of the sulfides, with sphalerite tending to decompose at lower *Eh* values. The exact position of pyrite is not known, although studies of the relative *rate* of oxidation (Koch and Grasselly, 1951) suggest that its ease of oxidation, at least, is comparable to that of other sulfides.

Above field 5 the relations are highly hypothetical, and no good data are known for the actual calculation of the stabilities of any of the uranium-vanadium compounds. Relations among some of the oxidized copper and lead compounds are known, and the fields of stability have been delimited (Garrels, 1954), but it seems unnecessary to attempt to show detailed relationships among them because their uranium-vanadium counterparts have not been worked out. The dashed line separating fields 6 and 7, however, represents a rough boundary interpreted from the work of Ducret (1951, p. 729–737) on the vanadium (IV)–(V) oxidation potential. Field 7 is the area in which vanadium exists as a complex series of vanadate ions, and where the ratio of these ions, carrying vanadium (V), to ions with quadrivalent vanadium (VO^{++}), is large (greater than 10). Field 6 on the other hand is an area in which the ratio of vanadium (IV) to vanadium (V) is significant and an area in which Ducret (1951, p. 729–737) found a whole series of vanadium IV–V oxides of variable composition. Therefore, it seems reasonable to assign to field 6 the complex mixture of natural vanadium (IV) and (V) oxides called corvusite and to field 7 the various metal-uranyl vanadates and metal vanadates such as carnotite, tyuyamunite, hewettite, pascoite, rossite, and others. One special point should be made in passing; at a *p*H of approximately 2, vanadium changes from an anionic role to a cationic one, from vanadate to the vanadyl (VO_2^+) ion (Ducret, 1951, p. 714). In this general *p*H range, during the transition, hydrated V_2O_5 precipitates; therefore, it seems likely that navajoite, the naturally occurring V_2O_5 hydrate (Weeks, Thompson, and Sherwood, 1954), is an excellent indicator of rather strongly acid oxidizing solutions.

On the basis, then, of the estimation of stability fields as shown in field 7, a "narrative" interpretation of the oxidation of a primary montroseite, uraninite, pyrite, sphalerite, galena, covellite ore can be attempted. Under ordinary ground-water conditions the environment is reducing and alkaline (Garrels, 1953, pp. 1263–1264). On the other hand, atmospheric oxygen brought into the system is a strong oxidizing agent, and even traces of oxygen tend to raise the oxidation potential to plus values of several tenths of a volt. The effect is to superimpose a strongly oxidizing environment, represented perhaps by fields 6 and 7, on the original reduced-mineral assemblage. The tendency is to pull all the compounds up to highly oxidized species. If equilibrium were attained instantaneously, the original association would jump to the associations of fields 6 and 7. The oxygen, however, is probably supplied slowly during weathering, and the rate of reaction with the various species would be expected to differ markedly. If considered entirely from the oxidation potential standpoint, that is, if the rates are entirely functions of the difference in potential between the environment and the upper limit of mineral stability, then it would be expected that the vanadium oxides would weather to vanadium (IV) compounds before the sulfides were significantly attacked and that uraninite should oxidize to uranium (VI) compounds when the sulfides change to sulfate, oxides, and carbonates. Actual experiment is necessary, however, to assess the relative effect of the potential versus the rate characteristics of the individual species.

When the sulfides become unstable, sulfide ion is converted to sulfate, and the freed metal ions become involved in a variety of reactions depending upon the relative stabilities of the various solids that can form with the chief anionic constituents of the oxidized solutions. Lead tends to form slightly soluble sulfates and carbonates; zinc to form moderately soluble carbonates and silicates; copper to form a variety of oxides, carbonates, and hydroxy-carbonates, as well as native copper and copper silicate. The iron from pyrite tends to hydrolyze into hematite or various hydrated ferric oxides.

The vanadium, after it reaches the quadrivalent stage, probably oxidizes through a complex series of vanadium (IV) and (V) oxides (corvusite). As more and more of the vanadium reaches the quinquevalent state it tends to go into vanadates. Any uranium (VI) possibly present briefly in the pre-vanadate stage as uranium (VI) oxides tends to be converted into potassium or calcium uranyl vanadates. Vanadium in excess of the amount necessary to form these uranyl compounds would tend to precipitate as simple metal vanadates.

SUMMARY AND CONCLUSION

The present information on the fields of stability of the minerals of the Colorado Plateaus-type deposits is quite consistent with an interpretation that the original ores were species containing "sensitive" elements in their lower valence states, and that the great complexity of the mineralogy, as now observed, can be attributed to the superimposition of oxidation, of various degrees of completeness, through the primary agency of atmospheric oxygen. It should also be clearly emphasized that the present picture may also be interpreted on the basis of the influence of a variety of original environments acting at the time of deposition, or by various combinations of these two major conceptual schemes. A determination of the actual processes can be made by extensive study of the paragenesis of the minerals and of the geologic occurrence of the ores. According to the "weathering hypothesis," oxidation should have taken place only in those places accessible to atmospheric oxygen. It should not be difficult to assess the validity of this hypothesis if field studies are made with the question in mind.

REFERENCES

DUCRET, L. P. (1951), Contribution à l'étude des ions des valences quatre et cinq du vanadium: *Annales de Chimie*, **6**, 705–776.

GARRELS, ROBERT M. (1953), Some thermodynamic relations among the vanadium oxides and their relation to the oxidation states of the uranium ores of the Colorado Plateaus: *Am. Mineral.*, **38**, 1251–1265.

——— (1954), Mineral species as functions of *p*H and oxidation-reduction potentials with special reference to the zone of oxidation and secondary enrichment of sulfide ore deposits: *Geochimica et Cosmochimica Acta*, **5**, 153–168.

KOCH, S., AND GRASSELLY, G. (1951), Processes occurring at the decomposition of sulphide ores: *Univ. Szeged, Sec. Sci. Nat., Pars Min. Petr. Acta*, **5**, 15–37.

KRAUS, K. A., NELSON, F., AND JOHNSON, G. L. (1949), Chemistry of aqueous uranium (V) solutions. I. Preparation and properties, analogy between uranium (V), neptunium (V), and plutonium (V): *Am. Chem. Soc. Jour.*, **71**, 2510–2517.

KRUMBEIN, W. C., AND GARRELS, R. M. (1952), Origin and classification of chemical sediments in terms of *p*H and oxidation-reduction potentials: *Jour. Geology*, **60**, 1–33.

LATIMER, W. M. (1952), The oxidation states of the elements and their potentials in aqueous solutions, 2d ed., New York, Prentice-Hall, Inc.

POURBAIX, M. J. N. (1949), Thermodynamics of dilute aqueous solutions, London, Edward Arnold and Co.

SEABORG, G. T., AND KATZ, J. J. (1954), The actinide elements, pt. 1, New York, McGraw-Hill Book Co., Inc.

WEEKS, A. D., THOMPSON, M. E., AND SHERWOOD, A. M. (1953), Navajoite, a new vanadium oxide from Arizona: *U. S. Geol. Survey Trace Elements Inv. Rept.* **393**.

APPENDIX

Calculation of free energy of formation for uranium compounds

Two methods have been used to calculate the values in brackets in Table 1. The first is by estimation of entropy values if ΔH^0 is known, and then using the relation $\Delta F^0 = \Delta H^0 - T\Delta S^0$; the second by using the assumption that the hydration reaction is essentially an equilibrium process, so that the free energies of formation of the products is equal to the sum of the free energies of formation of the reactants.

For $UO_3 \cdot 2H_2O$ both methods can be used. ΔH^0 is known; S^0 can be estimated by the methods outlined by Latimer (1952, pp. 359–369).

Because uranium (VI) in water solution gives the stable UO_2^{++} ion, it seems likely that $UO_3 \cdot 2H_2O$ is better expressed as $UO_2(OH)_2 \cdot H_2O$. According to Latimer's values for the entropies of elements in compounds, uranium is 16, oxygen is 3, OH^- is 4.5, H_2O is 9.4.

U	16
2O	6
$2OH^-$	9
H_2O	9.4
	40.4 = S^0 $UO_2(OH)_2 \cdot H_2O$

ΔS^0 can then be obtained from the reaction:

$$U + 5/2O_2 + 2H_2O = UO_2(OH)_2 \cdot H_2O.$$

Using the entropies of the elements (Table 1):

$$\Delta S^0 = S^0_{UO_2(OH)_2 \cdot H_2O} - S^0_U - 5/2S^0_{O_2} - 2S^0_{H_2}$$
$$\Delta S^0 = 40.4 \quad - 16.0 - 122.5 \quad - 62.4 = -160.5$$

Then:

$$\Delta F^0 = \Delta H^0 - T\Delta S^0$$

At 25° C., ΔH^0 for the formation of $UO_2(OH)_2 \cdot H_2O$ is -446.2 kcal (Table 1). Then:

$$\Delta F^0 = -446{,}200 - (298 \times -160.5) = 398{,}400 \text{ cal} = 398.4 \text{ kcal.}$$

For the second method, the assumption is made:

$$UO_2(OH)_2 + H_2O = UO_2(OH)_2 \cdot H_2O \qquad \Delta F^0 = 0$$
$$\Delta F^0_{UO_2(OH)_2} + \Delta F^0_{H_2O} = \Delta F^0_{UO_2(OH)_2 \cdot H_2O}$$

From Table 1:

$$-343 + (-56.7) = -399.7 \text{ kcal} = \Delta F^0_{UO_2(OH)_2 \cdot H_2O}$$

Therefore the values by the two methods check within 1.3 kcal, or less than 0.4 per cent difference.

For $UO_2 \cdot 3H_2O$ no value of ΔH^0 is available, and the bracketed value in Table 1 is based on the second method:

$$UO_2(OH)_2 + 2H_2O \rightarrow UO_2(OH)_2 \cdot 2H_2O \qquad \Delta F^0 = 0$$
$$\Delta F^0_{UO_2(OH)_2} + \Delta F^0_{2H_2O} = \Delta F^0_{UO_2(OH)2 \cdot 2H_2O}$$

Substituting ΔF^0 values from Table 1:

$$-343 + (-33.4) = -376.4 \text{ kcal} = \Delta F^0_{UO2(OH)_2 \cdot 2H_2O}$$