THERMODYNAMIC EQUILIBRIA

OF VANADIUM IN AQUEOUS SYSTEMS

AS APPLIED TO THE INTERPRETATION

OF THE COLORADO PLATEAU ORE DEPOSITS

By Howard T. Evans, Jr., and Robert M. Garrels

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

May 13, 1958

AEC-449/8

Mr. Robert D. Nininger
Assistant Director for Exploration
Division of Raw Materials
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Bob:

Transmitted herewith are three copies of TEI-666, "Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits," by Howard T. Evans, Jr., and Robert M. Garrels, December 1957.

We plan to submit this report for publication in Geochimica et Cosmochimica Acta.

Sincerely yours,

John H. Eric

for W. H. Bradley
Chief Geologist

UNITED STATES
DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY
WASHINGTON 25, D. C.

May 13, 1958

AEC-448/8

Dr. Paul W. McDaniel, Acting Director
Division of Research
U. S. Atomic Energy Commission
Washington 25, D. C.

Dear Dr. McDaniel:

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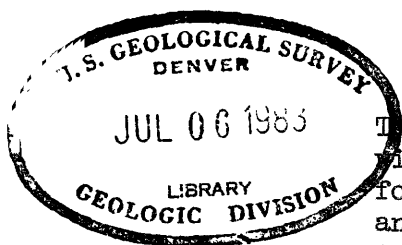
GEOLOGICAL SURVEY

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AS APPLIED TO THE INTERPRETATION

OF THE COLORADO PLATEAU ORE DEPOSITS*

By

Howard T. Evans, Jr., and Robert M. Garrels

December 1957

This preliminary report is distributed without editorial and technical review for conformity with official standards and nomenclature. It is not for public inspection or quotation.

*This report concerns work done on behalf of the Divisions of Research and Raw Materials of the U. S. Atomic Energy Commission.

USGS - TEI-666

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OF THE COLORADO PLATEAU ORE DEPOSITS

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ABSTRACT

All available chemical and thermodynamic information are utilized to construct a diagram showing the stability relationships of the known vanadium compounds in aqueous equilibrium in terms of oxidation potential and pH. The disparity between the observed precipitation conditions and those calculated from the published free energies of the oxides is used to estimate the free energy of hydration of the hydrated forms found in nature. The well-established vanadium mineral species (not including silicates) are assigned regions of stability on the equilibrium diagram on the basis of chemical constitution, crystal structure and observed petrologic associations. It is found that a completely self-consistent alteration sequence appears on the mineral diagram, showing the changes that occur in the vanadium ores under weathering conditions. Montroseite, $VO(OH)$, is evidently the primary mineral source of vanadium. Two distinct branches appear in the alteration sequence: one is confined to acid conditions characteristic of zones of primary vanadium oxide concentration in the sandstone in the presence of pyrite; and the other occurs in more basic conditions where calcite is common. The equilibrium diagram is used to draw tentative conclusions regarding the conditions under which the original montroseite was deposited in the sandstones, presumably through the action of mineralizing solutions.

INTRODUCTION

An outstanding feature of the uranium ores in the Colorado Plateau sandstones is their high vanadium content. Vanadium has a maximum at the eastern bounds of the Plateau and tends to decrease toward the west, whereas the uranium content tends to decrease toward the east. Thus, at Rifle, on the flank of the Park Range in Colorado, uranium is virtually absent from the vanadium ore, while in the White Canyon, Green River and San Rafael areas of Utah, vanadium is usually absent from the uranium ore. In the intermediate regions of western Colorado, known appropriately as the Uravan mineral belt (Fischer and Hilpert, 1952), the ores are mainly vanadium ores with a uranium content corresponding to a V:U ratio ranging from 20:1 to 4:1. It is apparent that vanadium is the predominant extrinsic element in most of these ores and that our knowledge of their deposition, transportation, and properties will depend to a large extent on our understanding of this element. Consequently, in recent years considerable effort has been devoted to the study of the geochemistry of vanadium in sandstones.

Five years ago, the state of knowledge concerning vanadium geochemistry had not materially advanced since a review of the subject was written by F. L. Hess (1933). At that time, the Plateau ores were generally considered to have been syngenetic with the sandstones of Jurassic age, having been deposited largely in the oxidized state. Hess was one of the first to recognize the possibility that the primary ores may have been deposited in a reduced form. As a result of the intensive program of study and

development in the Colorado Plateau area sponsored by the Atomic Energy Commission and the U. S. Geological Survey, a large mass of new data and information has accumulated since 1950. As a consequence, the syngenetic view has been significantly altered. It is now generally held that the ores were deposited in the reduced state from aqueous fluids in the Late Cretaceous or early Tertiary epoch and subsequently subjected to weathering by meteoric waters and exposure to the atmosphere. An extensive summary of these geochemical investigations is in preparation by the U. S. Geological Survey. Meanwhile, the new interpretation of the geologic history of the Colorado Plateau ore deposits has been reviewed and evaluated by McKelvey, Everhart, and Garrels (1955).

One of the major sources of information for the geochemical studies has been the description and characterization of new mineral species and redefinition of old species. The mineralogy of vanadium is exceedingly complex because of its sensitivity to oxidation potential, its strong amphoteric behavior in the higher valence states, and its sensitivity to degree of acidity in the higher valence states in the formation of complex polyions of high molecular weight. Mineralogical studies have been further complicated by the fact that most of the secondary minerals involved were formed at low temperatures (probably less than 40° C) and, therefore, since grain growth is slow and effective nucleation more frequent than at higher temperatures, they occur in a finely divided state, and in intimate mixtures. Nevertheless, great progress has been made, particularly as a result of the work of A. D. Weeks and J. W. Gruner

and their colleagues (Weeks and Thompson, 1954; Gruner, Gardiner and
Smith, 1953). The elucidation of the geochemical behavior of vanadium
has depended finally on the comprehensive definition and compilation of
the mineral species that form in the sandstone horizons.

With the geologic and mineralogic background now fairly well filled
in, it has been found possible to relate the geochemical properties of
vanadium with those that can be predicted from thermodynamic studies which
have appeared intermittently over the years in the chemical literature.
In the study described in this paper, these thermodynamic properties have
been used to evolve an equilibrium diagram which shows the stability of
the various vanadium compounds and minerals in the presence of water with
respect to the prevailing oxidation potential and acidity at 25° C. As
a result, the weathering process and alteration sequence of minerals are
clarified. Further, it is also possible to place severe restrictions on
the conditions that obtained during the deposition of the original ores.

The validity of the application of thermodynamic principles in this
way to the geochemical environment under consideration depends on the
rapidity with which equilibrium conditions are achieved. In a weathering
environment, the ultimate equilibrium state obtains when all elements
are in a fully oxidized state and present in the most stable form, a
condition in which there is no tendency for further changes in the
mineral suite. The presence of minerals in a lower valence state
indicates either a gradient in the oxidation potential, or a lack of

equilibrium, or both. Local equilibrium conditions may change rapidly in the buried deposits, and the thermodynamic studies have proved extremely useful to determine what changes are to be expected as the fully oxidized state is approached; that is, what the mineral alteration sequences should be.

The studies described in this paper have been greatly aided by the work and generous cooperation of many other people in this laboratory. Especial mention should be made of the mineralogical studies of A. D. Weeks and her associates, the chemical studies of synthetic vanadates by R. F. Marvin, and the thermodynamic and physical chemical studies of P. B. Barton and A. M. Pommer. This work is part of a program being undertaken by the U. S. Geological Survey on behalf of the Divisions of Raw Materials and Research of the U. S. Atomic Energy Commission.

EQUILIBRIUM DIAGRAM

The value of diagrams showing the stability of phases in aqueous systems in terms of oxidation potential (Eh) and hydrogen ion concentration (pH) has been most effectively demonstrated by M. J. N. Pourbaix (1949) in the field of metal corrosion, and Krumbein and Garrels (1952) in geochemistry. As pointed out by the latter authors, these two variables can be used to characterize almost all geochemical changes in sedimentary environments. A preliminary study of the thermodynamic stability of the vanadium oxides was made by Garrels (1953), and the results subsequently correlated with the uranium oxide system and the Colorado Plateau ores (Garrels, 1955).

It is now possible to expand Garrels' preliminary diagram to include many more vanadium-bearing species. Figure 1 shows the key relations among the various ions in solution and stable solids in the vanadium-water system. Shaded areas are fields of stability of solids and are defined as areas in which the solubility of the solid is less than approximately 0.01 mole per liter of the major vanadium species in equilibrium. Unshaded areas are fields in which the predominant dissolved vanadium species exceeds 0.01 mole per liter, and are labeled with these species. Boundaries between dissolved species are drawn where the molar concentration ratio of the two major ions is unity. The only solids considered are those resulting from interaction of vanadium and water. A diagram very similar to the theoretical one portrayed would be achieved by controlling pH with $HClO_4$ and NaOH, and oxidation potential with H_2O_2. None of these reagents would yield solids involving Na^+ or ClO_4^---they would be essentially inert diluents, and would serve chiefly to maintain electrical neutrality.

The dashed lines on the diagram indicate the range of stability of water and, hence, by inference the general limits of a natural system. Above the upper dashed line water is in equilibrium with more than one atmosphere of oxygen; below the lower dashed line with more than one atmosphere of hydrogen.

An independent study of the vanadium-water system has recently been reported by Deltombe, Zoubov, and Pourbaix (1956). Detailed information is available in their paper on the concentration distribution of individual ions, as well as a variety of diagrams somewhat similar to

our figure 1. Their paper has provided us with valuable checks on our work, even though we have felt it necessary to place a different interpretation on the chemistry of vanadium in some instances, particularly in the quinquevalent vanadium fields.

Figure 1 is drawn on the basis of thermodynamic data for anhydrous oxides. Actually, these oxides are normally precipitated from aqueous solutions in hydrated forms which have slightly but significantly different free energy contents. It is not surprising to find discrepancies between various precipitation pH values experimentally determined (that is, the pH determined at which the solubility of vanadium falls below about 0.01 mole per liter) and those predicted by figure 1. These discrepancies are utilized in a later section to estimate the energies of hydration of V_2O_3, V_2O_4, and V_2O_5. On the basis of these estimates, the equilibrium diagram has been modified and redrawn in figure 2. Presumably, since all of the mineral vanadium oxides (except the metastable paramontroseite) are hydrated, the diagram of figure 2 will have significant bearing on the natural system.

Perhaps, the most satisfactory scheme in developing the interrelations of the diagram is to discuss them sequentially in terms of the various valences of vanadium—to work from the top of the diagram to the bottom, considering first the behavior of vanadium (V), then that of (IV), (III), and (II). Free energy data basic to the discussion are given in table 1.

Table 1.--Free energies of vanadium compounds and ions.

Phase	State [1]	Valence	Latimer (1952)	Deltombe and others (1956)	This paper
V	cr	0	0	0	0
V^{+2}	aq	2	-54.7	-54.2	-54.2
V^{+3}	aq	3	-60.6	-60.1	-60.1
VO^{+2}	aq	4	-109	-109.0	-109.0
VO_2^+	aq	5	-143 [2]	-142.6	-142.6
V_2O_2	cr	2	-189	-189.0	-189.0
V_2O_3	cr	3	-271	-271.0	-271.0
V_2O_4	cr	4	-318	-318.0	-318.0
V_2O_5 (aged)	s	5	-344	-344.0	-344.0
V_2O_5 (fresh)	s	5	..	-342.0	-342.0
$V(OH)_3$	s	3			-218.0 [3]
$V(OH)^{+2}$	aq	3		-112.8	-112.8
$VO(OH)_2$	s	4			-213.6 [4]
NH_4VO_3	cr	5	-221.8		-221.8
$V_4O_9^{-2}$	aq	4		-665.3 [5]	-665.3
$H_2V_{10}O_{28}^{-4}$	aq	5	-1867 [6]		-1875.2 [7]
$HV_{10}O_{28}^{-5}$	aq	5			-1875.3 [7]
$V_{10}O_{28}^{-6}$	aq	5	-1863 [6]	-1856 [8]	-1862.4 [7]

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[1] Symbols: cr, crystalline; s, solid; aq, aqueous solution.

[2] Latimer (1952) gives for $V(OH)_4^+$, $\Delta F^O = -256$ kcal $\underline{M}$; $V(OH)_4^+ = VO_2^+ + 2H_2O$.

[3] From $Eh^O = 0.10$ volt observed for reaction $V(OH)_3(s) \longrightarrow VO(OH)_2(s) + H^+ + e^-$ (A. M. Pommer, personal communication).

[4] From precipitation pH of 4.1 observed by Ducret (1951), and free energy of VO^{+2}.

[5] Deltombe and others (1956) give for $HV_2O_5^-$, $\Delta F^O = -361$ kcal/$\underline{M}$; $2HV_2O_5^- = V_4O_9^{-2} + H_2O$.

[6] Latimer (1952) gives for $HV_6O_{17}^{-3}$, $\Delta F^O = -1132$ kcal/M, and for $H_2V_6O_{17}^{-2}$, $\Delta F^O = -1135$ kcal/$\underline{M}$; $5HV_6O_{17}^{-3} = 3V_{10}O_{28}^{-6} + 3H^+ + H_2O$, and $5H_2V_6O_{17}^{-2} = 3H_2V_{10}O_{28}^{-4} + 2H^+ + H_2O$.

[7] Calculated from solubility of V_2O_5 (fresh) (Ducret, 1951) and dissociation constants of Rossotti and Rossotti (1956).

[8] Deltombe and others (1956) give for $H_3V_2O_7^-$, $\Delta F^O = -451$ kcal/$\underline{M}$; $5H_3V_2O_7^- = V_{10}O_{28}^{-6} + H^+ + 7H_2O$.

Quinquevalent vanadium

In water solutions in equilibrium with air at room temperatures, only solids and dissolved species containing quinquevalent vanadium are quantitatively important. Vanadium forms a pervanadyl cation VO_2^+ only at low pH; the isoelectric point is between pH 1 and 2, above which the vanadium is converted to complex anions. At this point, the solubility of vanadium falls to a minimum, as is evidenced by the stability field of the solid hydrated V_2O_5. At higher pH values a variety of anions occurs; in general, they range from deeply colored highly polymerized species at lower pH values to colorless, less condensed ions at high pH values.

The most direct information concerning the fields of stability of vanadates in solutions is provided by the diffusion rate studies of Jander and Jahr (1933). According to their technique, vanadium in a solution at a specified pH is allowed to diffuse upward into a vanadium-free solution of equal ionic strength and pH for a period of days, after which time the solution is separated and analyzed by layers. Several sharp breaks were found in their diffusion-rate-pH curve, which is redrawn from their data in figure 3b. They also attempted to approximate values of the molecular weights of the diffusing ions by assuming that the molecular weight is proportional to the inverse square of the diffusion rate, but this assumption is subject to gross errors. The most careful titration experiments have been made by Ducret (1951), and his final titration curve (pH versus added $HClO_4$) is shown redrawn in figure 3a.
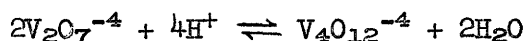
It is very similar to a curve determined by Jander and Jahr (1933).
Ducret also attempted to determine the formula of the reacting
vanadate ions by careful interpretation of the shapes of the curves.
Such an interpretation is very uncertain, and his conclusion that
the largest vanadate ion produced is $H_3V_2O_7^-$ (corresponding to the
orange polyvanadate) is not supported by any other evidence that has
been accumulated for this system.

Crystallographic data on the vanadate system are meager. A
series of very soluble crystalline orthovanadates have been described
which are isomorphous with the corresponding phosphates and arsenates
(Baker, 1885), thus indicating the existence of the VO_4^{-3} ion in
solution. A series of compounds have been shown by crystallographic
study to be salts of the ion $V_{10}O_{28}^{-6}$, which corresponds to the orange
polyvanadate ion (Evans, Mrose, and Marvin, 1955), but its structure
is still unknown. Crystal structures of two metavanadates (NH_4VO_3,
Syneček and Hanic, 1954; $KVO_3 \circ H_2O$, Christ, Clark, and Evans, 1954)
reveal chain structures, which do not indicate directly the nature of
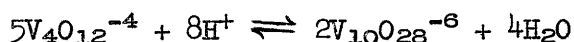the species in solution.

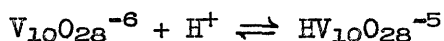The best expression of the condensation reactions involved that can be written at present is as follows:

$$2VO_4^{-3} + 2H^+ \rightleftharpoons V_2O_7^{-4} + H_2O$$
$$[VO_4^{-3}] = [V_2O_7^{-4}] \text{ at pH} \quad 12.6$$

$$2V_2O_7^{-4} + 4H^+ \rightleftharpoons V_4O_{12}^{-4} + 2H_2O$$
$$[V_2O_7^{-4}] = [V_4O_{12}^{-4}] \text{ at pH} \quad 9.6$$

$$5V_4O_{12}^{-4} + 8H^+ \rightleftharpoons 2V_{10}O_{28}^{-6} + 4H_2O$$
$$[V_4O_{12}^{-4}] = [V_{10}O_{28}^{-6}] \text{ at pH} \quad 6.7$$

$$V_{10}O_{28}^{-6} + H^+ \rightleftharpoons HV_{10}O_{28}^{-5}$$
$$K = 10^{5.8}$$

$$HV_{10}O_{28}^{-5} + H^+ \rightleftharpoons H_2V_{10}O_{28}^{-4}$$
$$K = 10^{3.6}$$

$$H_2V_{10}O_{28}^{-4} + 4H^+ \rightleftharpoons 5V_2O_5 \cdot nH_2O(s) + (3-\underline{n})\ H_2O$$
$$[H_2V_{10}O_{28}^{-4}] = 0.01\underline{M} \text{ at pH} \quad 2.2$$
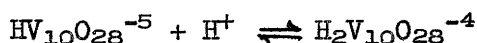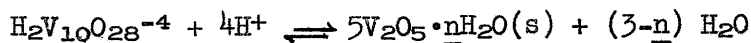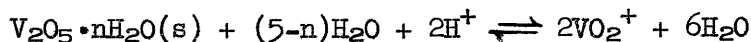
$$V_2O_5 \cdot \underline{n}H_2O(s) + (5-\underline{n})H_2O + 2H^+ \rightleftharpoons 2VO_2^+ + 6H_2O$$
$$[VO_2^+] = 0.01\underline{M} \text{ at pH} \quad 0.8$$

The pH data for the condensation and precipitation reactions are taken from Jander and Jahr (1933). In all of their experiments, the ionic strength was held constant, corresponding to $1\underline{M}$ KNO$_3$ or NaNO$_3$ and the concentration of V was 0.112 mole per liter. The equilibrium constants for the acidification of the polyvanadate ion are given by Rossotti and Rossotti (1956).

The boundaries in figure 1 are drawn approximately where the two reacting ions are in equal molar concentration. They may shift slightly with variation of concentration of ions indicated, or changes in ionic strength of the solutions.

The pH boundaries of $V_2O_5 \cdot nH_2O$ as drawn are based upon "aged" material, rather than upon freshly precipitated oxide. Aged material is more stable than that newly precipitated, as indicated by the difference of 2 kilocalories in the standard free energies of formation (table 1). Rapid neutralization of an acid solution 0.01M in VO_2^+, in fact, permits passage from VO_2^+ to the orange polyvanadates without precipitation of the hydrated pentoxide, whereas the same titration, if done slowly, results in formation of the yellow-brown oxide. The increase in stability with time may be correlated with a decrease in hydration as well as with a change in crystalline state.

The striking behavior of the vanadates, that of forming higher and higher molecular weight complexes with increasing acidity, strongly suggests that, unlike the phosphates and arsenates, the acidified ions are inherently unstable and immediately split out water through condensation reactions. Only the acidified polyvanadate ions $HV_{10}O_{28}^{-5}$ and $H_2V_{10}O_{28}^{-4}$ persist as predominant species in solution, but even these may actually be metastable. Below pH 5.5, polyvanadate solutions on heating or long standing precipitate insoluble products such as $K_2V_6O_{16}$ and $CaV_6O_{16} \cdot 9H_2O$ (hewettite) (R. F. Marvin, unpublished data). The tendency of vanadates to form high molecular weight complexes in acid solutions is very similar to that of the molybdates and tungstates. These form isopoly ions in solutions of

pH 3 to 6 such as $Mo_7O_{24}^{-6}$, $Mo_8O_{26}^{-4}$, and $H_{10}W_{12}O_{46}^{-20}$. The structure of these complexes are known, but no relation has been found between the structure of the polyvanadate ion and the polymolybdate and polytungstate compounds. Laboratory investigations of compounds of this type are hampered by the sluggishness with which the condensation and decomposition reactions occur in solution. Sometimes, many hours are required for a freshly prepared solution of a polyion to reach a stable condition.

Quadrivalent vanadium

Ducret (1951) gives acid-base titration curves for quadrivalent vanadium. At low pH the ion in the blue solution is vanadyl, VO^{+2}, which behaves like a simple metallic cation. It hydrolyzes to form $VO(OH)^+$ according to the reaction (Rossotti and Rossotti, 1955):

$$VO^{+2} + H_2O \longrightarrow VO(OH)^+ + H^+ \qquad (8)$$
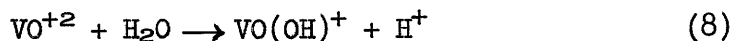
Further hydrolysis results in precipitation of the hydroxide:

$$VO(OH)^+ + H_2O \longrightarrow VO(OH)_2(s) + H^+ \qquad (9)$$
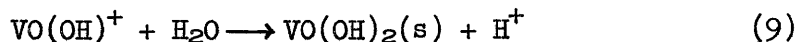
At a $VO(OH)^+$ content of 0.01$\underline{M}$, the precipitation pH is observed by Ducret to be 4.2. On the other hand, the precipitation pH calculated from the free energy of formation of the anhydrous oxide is 3.5 (figure 1; table 1). This difference in precipitation pH may be ascribed to the hydration free energy of V_2O_4:

$$V_2O_4(s) + 2H_2O \longrightarrow 2VO(OH)_2 \qquad \Delta F = 4.1 \text{ kcal}$$
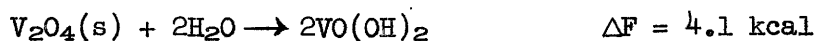
Garrels (1953) estimated that the free energy of hydration would be 2 kilocalories or less; the new data show a greater difference. It is not known whether the rate of conversion of hydroxide to anhydrous oxide is finite; the hydroxide is always produced experimentally, and the stable anhydrous oxide has not been found in nature.

As pH is further increased, the hydroxide dissolves to form an anion, and the solution turns brown-red:

$$4VO(OH)_2(s) \longrightarrow V_4O_9^{-2} + 3H_2O + 2H^+ \tag{10}$$
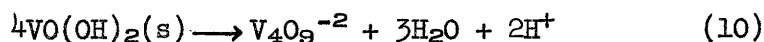
The free energy of the vanadite ion (written tentatively as $V_4O_9^{-2}$) is derived from that of $VO(OH)_2$ and the precipitation point of pH 8.0 observed by Ducret.

Trivalent vanadium

Trivalent vanadium dissolves in acid to form V^{+3} in blue-green solution. It hydrolyzes to $V(OH)^{+2}$ before the gray-black hydroxide precipitates from 0.01$\underline{M}$ solution at pH 4; according to free-energy relations, the anhydrous oxide should precipitate at equilibrium at pH 3. No extensive experiments have been made to see if a solution held in the pH 3-4 interval will eventually precipitate the anhydrous oxide. The free energy of hydration, based on the precipitation pH of the hydroxide and the published free energy of the anhydrous oxide is:

$$V_2O_3(s) + 3H_2O \longrightarrow 2V(OH)_3(s) \qquad \Delta F = 5.1 \text{ kcal}$$
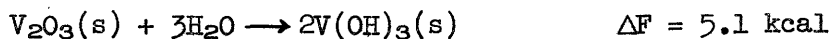
Thus, V_2O_3 is more stable than $V(OH)_3$, and is analogous in this respect to Fe_2O_3 and Mn_2O_3. The apparent difficulty in obtaining artificially

the anhydrous oxide, or perhaps a compound such as $V_2O(OH)_4$ or $VO(OH)$, is not surprising in view of the fairly small free energy change on hydration. The free energy of montroseite, $VO(OH)$, is unknown, but its prevalence in the Colorado Plateau sandstones, and the absence of V_2O_3, suggest that it is the most stable hydrated phase at the temperature of formation. At present, we can only assume that the energy of formation of montroseite from V_2O_3 is quite small, without predicting whether at the lower temperatures it is positive or negative. An estimated stability field for $VO(OH)$ is indicated by the dotted lines in figure 2, and is used in interpreting the mineral system in figure 4, described in later sections.

The hydroxide shows no amphoteric behavior in the pH range up to 14. Trivalent vanadium ions and compounds are notably unstable with respect to the atmosphere; even the natural oxide montroseite alters at an appreciable rate in the laboratory.

Bivalent vanadium

Bivalent vanadium will decompose water at 25° C under all pH conditions; and, therefore, as Garrels (1955) has pointed out, it is not likely to occur in nature.

Boundaries between species of different valence

The preceding paragraphs have discussed pH boundaries for vanadium within its several valence states; it remains to be shown how the sloping boundaries between these valence domains are obtained.

Boundaries between ions

In the case where the solubility of the ionic species of vanadium in different valence states exceeds 0.01$\underline{M}$, so that only dissolved species are represented, the boundary is calculated from equations exemplified by the V^{+2} - V^{+3} relation:

$$V^{+2} \longrightarrow V^{+3} + e^-$$

$$\Delta F^O = \underline{n}E^O F$$

where E^O is the standard electrode potential, F is the Faraday, and $\underline{n}$ the number of electrons involved. Thus E^O is obtained from ΔF^O, and Eh is obtained from:

$$Eh = E^O + \frac{0.059}{\underline{n}} \log \frac{(V^{+3})}{(V^{+2})} \qquad (25^O \text{ c})$$

The further condition is imposed that (V^{+3}) and (V^{+2}) (activities) are equal. As can be determined from the equation, or from figure 1, the boundary between these two species is simply E^O, and extends parallel to the pH axis.

The slope of the V^{+3} - VO^{+2} boundary results from the necessity of including water and hydrogen ion in the half-cell reaction:

$$V^{+3} + H_2O \longrightarrow VO^{+2} + 2H^+ + e^-$$
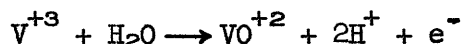
The Eh equation becomes:

$$Eh = E^O + 0.059 \log \frac{(VO^{+2})}{(V^{+3})} - 2 \times 0.059 \ pH$$

The pH term causes a downward slope of the boundary from left to right, with an intercept of E^O at pH 0.

Boundaries between solids

Where two solids containing vanadium in different valence states are juxtaposed, the boundary is determined by equations such as that relating V_2O_3 and V_2O_4:

$$V_2O_3(s) + H_2O \longrightarrow V_2O_4(s) + 2H^+ + 2e^-$$

$$Eh = E^O + \frac{0.059}{2} \log (H^+)^2$$

or,

$$Eh = E^O - 0.059 \text{ pH}$$

Boundaries between a solid and an ion

Several cases occur involving a solid containing vanadium in one valence and solution containing dissolved vanadium in a species of higher or lower valence. For example, V_2O_3 dissolves to form $V_4O_9^{-2}$ as the oxidation potential is increased in alkaline solution. The equation is:

$$2V_2O_3(s) + 3H_2O \longrightarrow V_4O_9^{-2} + 6H^+ + 4e^-$$
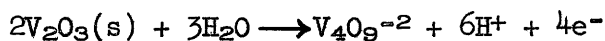
$$Eh = E^O + \frac{0.059}{4} \log [V_4O_9^{-2}] - \frac{6}{4}\times0.059 \text{ pH}$$

The specific position of the line thus is fixed by knowledge of E^O, pH, and the stipulation that $[V_4O_9^{-2}]$ is 0.01$\underline{M}$.

Considerable uncertainty attends the boundaries drawn between V_2O_4 and the vanadates. As shown on figure 1, mixed oxides containing both quadrivalent and quinquevalent vanadium occur in this position. The possibility presents itself that these mixed oxides may be regarded as "vanadyl vanadates," but the few structures of these compounds that have

been published indicate that they have no saltlike character (for example,
NaV_6O_{15}, Wadsley, 1955). No thermodynamic data are available for them,
but there is no evidence to indicate that their appearance will appreciably
shift the precipitation boundary as it is shown.

Effect of temperature

The effect of temperature on the field boundaries shown in figure 1
cannot be calculated with assurance in the absence of data on heat
capacities of the species involved. However, the temperature coefficient
at 25° C can be found and used to determine the trend and probable change
of boundaries over a limited temperature change. Changes in boundaries can
be calculated in terms of $\dfrac{\partial E^O}{\partial T}$ or $\dfrac{\partial \Delta F^O}{\partial T}$:

$$\frac{\partial E^O}{\partial T} = -\frac{1}{Fn}\Delta S^O;$$

$$\frac{\partial \Delta F^O}{\partial T} = -\Delta S^O.$$

In general, a temperature change of a few tens of degrees would
appear to have little effect on the general fields of stability. For
example, for the reaction:

$$V_2O_3 + H_2O \longrightarrow V_2O_4 + 2H^+ + 2e^-; \qquad \Delta S^O = -15.65 \text{ cal/}\underline{M}\text{/degree}$$
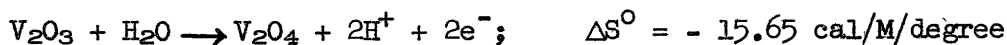
$$\frac{\partial E^O}{\partial T} = \frac{15.65}{2 \times 23,060} = 0.00034 \text{ volts per degree.}$$

Thus for a 30° rise in temperature, assuming ΔS^O constant, E^O would be
raised only 0.01 volts, giving rise to a corresponding change in the phase
boundary. Such changes are fairly typical of the oxidation reactions.

For the precipitation-pH boundaries, changes are of the order of -0.01 to -0.02 pH units per degree, using estimated entropies for the ions involved. In other words, the precipitation boundaries of the oxides move to lower pH values with rising temperature, and with approximately the same coefficient as for the change of pH of pure water alone. Unfortunately, neither ΔH nor ΔS values can be obtained at present to determine the direction of migration of the boundary between V_2O_4 and $V_4O_9^{-2}$.

REGIONS OF THERMODYNAMIC STABILITY FOR
THE VANADIUM MINERALS

The first oxide of vanadium which was recognized as a distinct mineral species was montroseite, $VO(OH)$ or $V_2O_3 \cdot H_2O$ (Weeks, Cisney, and Sherwood, 1953). Its discovery showed that the vanadium minerals of the Colorado Plateau span the whole range of oxidation states of vanadium consistent with an aqueous environment. Since montroseite was described, many new mineral species have been discovered and characterized representing vanadium in all valence states from (III) to (V). When each species is examined with respect to its probable thermodynamic properties, it is found that it can be assigned to a particular field of the equilibrium diagram with little ambiguity. In the following paragraphs, a number of vanadium minerals are reviewed from the point of view of their stability properties. Figure 4 shows the basic equilibrium diagram of figure 2, with these minerals indicated on it, each in its appropriate range of stability.

Montroseite, $V_2O_3 \cdot H_2O$ or $VO(OH)$ (Weeks, Cisney, and Sherwood, 1953).
As shown in figure 2, there is an extended portion of the hydrated V_2O_3
stability field above the water decomposition boundary between pH 4 and
pH 10. As has been noted earlier, this region probably expands slightly
upward and to the left at higher temperatures. Montroseite is formed in
this region.

Paramontroseite, V_2O_4 (Evans and Mrose, 1955). This mineral is
derived by solid state oxidation from montroseite; it is probably metastable
and has no place on the aqueous equilibrium diagram. Nevertheless, it is
important in the weathering process, because it provides a path for the
breakdown of the chemically resistant montroseite. It probably always
forms an intermediate first step in the weathering of montroseite.

Doloresite, $3V_2O_4 \cdot 4H_2O$ or $V_3O_4(OH)_4$ (Stern, Stieff, Evans, and Sherwood,
1957). This species is common in partially oxidized ores replacing
montroseite. Its mode of occurrence indicates that it results from solid
state alteration of montroseite (or paramontroseite) under conditions in
which vanadium is not dissolved.

Duttonite, $V_2O_4 \cdot 2H_2O$ or $VO(OH)_2$ (Thompson, Roach, and Meyrowitz,
1957). This species is a hydrated quadrivalent phase, occurring as
crystalline crusts lining cavities. It evidently forms from solution in
ground waters carrying vanadium not yet oxidized beyond the quadrivalent
state.

Simplotite, $CaO \cdot 2V_2O_4 \cdot 5H_2O$ (Thompson, Roach, and Meyrowitz, 1958).
Though its formula may be written $CaV_4O_9 \cdot 5H_2O$, simplotite is green in
color and does not represent fixation of the soluble brown-red vanadite ion.

Its structure appears to be a complex sheet related to that of autunite, and as yet has no synthetic analog. It is commonly associated with duttonite but appears to indicate a relatively alkaline environment.

Corvusite, $CaO \cdot xV_2O_4 \cdot yV_2O_5 \cdot nH_2O$. This mineral has distinct physical properties but has not been defined chemically within the above general formula. The valence apparently can vary without appreciable alteration of the structure so that it may be either inherently nonstoichiometric or an intimate mixture of two or more closely related phases. The ratio $x:y$ is usually about 1:5 or 1:6. It is associated with acid environments and evidently hovers near the top of the V_2O_4 field.

Melanovanadite, $2CaO \cdot 2V_2O_4 \cdot 3V_2O_5 \cdot nH_2O$. Although this species also has not been clearly defined chemically, it is entirely distinct from corvusite. It is found in alkaline environments and appears to be associated with the metavanadate field, while corvusite is associated with the polyvanadate field.

Navajoite, $V_2O_5 \cdot 3H_2O$ (Weeks, Thompson, and Sherwood, 1955). Navajoite has not been synthesized, but it apparently corresponds to the hydrated V_2O_5 field. It has a crystal structure closely related to that of corvusite and hewettite.

Hewettite, $CaO \cdot 3V_2O_5 \cdot 9H_2O$. Hewettite is an insoluble product of the more acid side of the polyvanadate field, forming below pH 5.5. Its structure consists of a sheet arrangement closely similar to that of navajoite and corvusite.

Pascoite, $3CaO \cdot 5V_2O_5 \cdot 16H_2O$. This mineral has formerly been incorrectly described as $2CaO \cdot 3V_2O_5 \cdot 11H_2O$, (Palache, Berman, and Frondel, 1951, p. 1055) but actually is a soluble salt of the orange polyvanadate complex, $Ca_3V_{10}O_{28} \cdot 16H_2O$, (Evans, Mrose, and Marvin, 1955).

Hummerite, $K_2Mg_2V_{10}O_{28} \cdot 16H_2O$, (Weeks, Cisney, and Sherwood, 1953), also is a soluble polyvanadate.

Rossite, $Ca(VO_3)_2 \cdot 4H_2O$. Rossite is a metavanadate, and is easily synthesized from neutral solutions.

Metarossite, $Ca(VO_3)_2 \cdot 2H_2O$, is the dehydration product of rossite.

Carnotite, $K_2(UO_2)_2V_2O_8 \cdot \underline{n}H_2O$. The least soluble vanadium complex (except possibly montroseite and the silicates) is carnotite and its analogs. It decomposes below pH 2.2 but is stable at the expense of all other quinquevalent vanadium minerals at higher pH values. The crystal structure does not contain orthovanadate groups as proposed by Sundberg and Sillén (1949), but has been found by recent work (Barton and Appleman, 1957; Appleman and Evans, 1958) to have structural and chemical properties of a metavanadate. The structure contains $V_2O_8^{-6}$ groups with vanadium in 5-fold coordination (as in $KVO_3 \cdot H_2O$).

Tyuyamunite, $Ca(UO_2)_2V_2O_8 \cdot \underline{n}H_2O$, is the calcium chemical analog of carnotite.

Rauvite, $\underline{x}UO_3 \cdot \underline{y}V_2O_5 \cdot \underline{z}H_2O$. In acid solutions deficient in metal cations, rauvite is formed as an insoluble colloidal product of variable composition with $\underline{y}$ usually somewhat greater than $\underline{x}$. It is believed to have a structural relationship to the sheet structure complex of carnotite, and may be a precursor to the formation of carnotite in very acid environments.

VANADIUM MINERAL PARAGENESIS UNDER WEATHERING

A typical partially oxidized ore body in the central Colorado
Plateau region consists of bluish-black vanadium oxide disseminated
through the sandstone in bands. Locally, sometimes in conjunction
with woody debris, the vanadium oxide ore is concentrated into pods,
or blue-black "eyes." In the center of these pods, in fresh openings,
jet-black montroseite is often still preserved. Outward from these
cores the vanadium mineral assemblage changes continuously to a more
and more oxidized state. This change in state of oxidation is
accompanied by characteristic color changes. Generally speaking, the
trivalent and trivalent-quadrivalent minerals are black, the
quadrivalent-quinquevalent minerals are dark blue, green, or brown,
and the fully oxidized minerals are lighter brown, yellow, or red-orange.
Sometimes these three zones are separated by sharp boundaries. Pyrite
is usually present, creating locally rather strongly acid conditions
under weathering. Good examples of these relations can be seen at the
Bitter Creek mine and the J. J. mine, Montrose County, Colorado, and
the Monument No. 2 mine, Monument Valley district, Arizona.

More rarely, the environment of oxidation is slightly alkaline,
in regions where pyrite is absent and calcite is abundant. The most
notable example of this situation is the Peanut mine, Bull Canyon,
Montrose County, Colorado. In this case, a wholly different series of
minerals is found in the oxidation sequence.

Petrologic and paragenetic studies almost always indicate that the primary vanadium minerals are silicates and the oxide montroseite. It is very likely that all of the other vanadium minerals in the sandstones, including carnotite, were derived from montroseite. Vanadium bound in silicates apparently is not released by weathering; and, therefore, these minerals, although important commercially, are incidental to the present discussion.

The first stage in the oxidation of montroseite under any conditions is the formation of paramontroseite. The conversion is brought about by a solid state reaction in the presence of oxygen either in the air or in groundwater as explained by Evans and Mrose (1955). Reaction is very rapid, and fresh montroseite specimens alter quickly in the open air. Evans and Mrose have concluded that paramontroseite itself is metastable, owing its existence purely to the crystal structural control of the original montroseite. In the presence of water, paramontroseite is quickly decomposed and new hydrated oxides of quadrivalent and quinquevalent vanadium are formed. This process gives rise to an interesting sequence in which one anhydrous variety of V_2O_4 (paramontroseite) is apparently less stable than various hydrated hydroxides (for example, duttonite, $V_2O_4 \cdot 2H_2O$), which in turn are thermodynamically less stable than the normal anhydrous oxide having a distorted rutile structure. No trace of the stable anhydrous oxide has yet been found in nature; therefore, the rate of conversion of the hydrated oxides is apparently neglible, even in terms of earth processes.

If further oxidation is retarded (especially if the ore is kept submerged below the water table where the supply of oxygen is limited), two other quadrivalent minerals may form in place of the paramontroseite--doloresite or duttonite. Doloresite is observed as a paramorphic replacement of the paramontroseite, with remnants of the latter usually remaining (Stern, Stieff, Evans, and Sherwood, 1957). Duttonite forms as drusy crystals in fissures in the sandstone and, therefore, apparently represents quadrivalent vanadium transported a short distance at least from the site of the paramontroseite source. Duttonite and paramontroseite are the starting points of two branches in the vanadium oxidation sequence, one acid and the other alkaline.

The sequence of vanadium minerals is easily followed in the acid suite. Adjacent to the doloresite-paramontroseite crystalline aggregates are usually found fibrous brown or bluish-black seams of corvusite. Commonly, the intermediate quadrivalent-quinquevalent vanadium oxides form earthy bluish or greenish masses of indeterminate constitution ("blue-black ore"). These oxides are dissolved through leaching of the concentrated ores by acid waters, and the vanadium is washed into the adjacent sandstone. The oxide "eyes" are thus often coated with bright orange crusts of pascoite. Occasionally, dark green "pascoite" is found, isostructural with the ordinary orange variety, indicating that the polyvanadate complexes may form with quadrivalent vanadium at least partly replacing quinquevalent vanadium. The leaching solutions are evidently sufficiently acid to carry appreciable amounts of vanadyl ion

(VO^{+2}), but this ion is quickly oxidized by air if the pH is raised, as when it passes into the surrounding rock and reacts with calcite. Pascoite is metastable with respect to hewettite below about pH 5.5 and probably has only a transitory existence.

In the alkaline environment typified by the Peanut mine, duttonite and simplotite are found. Since duttonite has been found abundantly only at the Peanut mine where the ores are largely submerged below the water table, it is likely that it will form only when the quadrivalent vanadium is protected from active oxidation by the atmosphere. When further oxidation does occur, melanovanadite is likely to result. In the presence of high calcium concentrations, simplotite is formed, and at the end of the oxidation sequence, rossite.

The two branches in the oxidation sequence, acid and alkaline, may be evident in fairly close proximity, especially in the vicinity of sulfide-bearing oxide ore pods. As soon as the original montroseite is oxidized to paramontroseite, the resulting quadrivalent vanadium becomes appreciably soluble. At the original site, the oxidized minerals follow the pattern of the acid branch described above, but at the same time much of the vanadium will be transported into the surrounding sandstone where neutral or slightly alkaline conditions prevail as a result of the calcite cement. In these adjacent regions, therefore, melanovanadite, simplotite, and in the fully oxidized state, rossite, all characteristic of the alkaline branch, are frequently found. In the quinquevalent state vanadium does not form silicates,and,,being soluble, is washed away rapidly, except in the presence of uranium.

As Garrels (1955) has shown, by the time the oxidation of quadrivalent vanadium begins, the uranium, which was originally present as uraninite and coffinite (Stieff, Stern, and Sherwood, 1956), is completely oxidized to the sexivalent state. No synthetic or natural compounds of uranium and trivalent or quadrivalent vanadium have ever been found, and apparently the properties of the two elements in reducing conditions are independent of each other as far as solubilities and mineral formation are concerned. When vanadium reaches the quinquevalent state in the presence of uranyl ion (UO_2^{+2}), the insoluble carnotite or slightly soluble tyuyamunite becomes the stable phase at pH values above 2.2 (R. F. Marvin, personal communication). Their stability range is indicated by the shaded boundary in figure 4, and all other vanadium minerals in this range become metastable with respect to the uranium complex. The ready formation of carnotite from acid solutions has been a puzzle in view of the crystal structure determination of Sundberg and Sillén (1949), which indicated that the vanadium is bound in it as orthovanadate groups (VO_4^{-3}), because in such solutions the orthovanadate concentration is exceedingly small (less than 10^{-12} moles per liter at pH 6). New studies (Appleman and Evans, 1958) have shown that the proposed structure is incorrect, and that vanadium is in fivefold coordination in the carnotite structure in $V_2O_8^{-6}$ groups. Also, it is found (Barton and Appleman, 1957) that carnotite behaves chemically like a metavanadate, so that its association with neutral or slightly acid environments is fully explained.

When the environment is strongly acid, rauvite may be formed. The role of this unusual mineral in the paragenetic sequence is uncertain, but it may have an intermediate position between the formation of the polyvanadate complex and carnotite under very acid conditions. The structure of rauvite cannot be directly determined since it is character-istically noncrystalline, at least in three dimensions; but it is felt that it probably consists of a random stacking of a sheet type of structure, which is related in some way to the sheet structure of carnotite.

In concluding this survey of the weathering paragenesis of vanadium minerals, it may be said that no field or microscopic observations of petrology and mineral associations have been made that contradict the weathering scheme derived herein from the thermodynamic properties of vanadium.

IMPLICATIONS OF THE EQUILIBRIUM DIAGRAM
ON THE PROBLEM OF ORE DEPOSITION

While the paragenesis of the vanadium and uranium minerals under weathering conditions on the Colorado Plateau now seems fairly well defined, the manner of deposition of the primary montroseite-uraninite-coffinite ore is still an unsolved problem. Accepting the current hypothesis that the ores were brought in by mineralizing solutions at 55° to 110° C, (Coleman, 1957), it appears probable from the thermodynamic considerations that they could not have been carried in solution in the reduced state in which they were deposited. Trivalent vanadium is too insoluble for transport except at pH values considerably below those

expected for such solutions; a similar situation holds for quadrivalent uranium. Consequently, the vanadium and uranium must have been carried in more oxidized state, and deposited under the action of reducing agents, such as divalent sulfur or the wood debris commonly enclosed in the sandstone. On the other hand, the Eh could not have been sufficiently high to permit all vanadium to be in the quinquevalent state, as the small solubility of carnotite would prevent transport. Therefore, the best estimate is that vanadium was carried as the quadrivalent $V_4O_9^{-2}$, which, so far as is known, does not interact with sexivalent uranium. These considerations suggest, referring to figure 2, that the mineralizing solutions had a pH of about 9 and an oxidation potential of about -0.1 volt. Even if the transport and deposit of vanadium and uranium can be accounted for under these conditions, the presence of pyrite or marcasite, which petrologically appears to be contemporary with montroseite, poses a problem because of the presumably low solubility of iron in this thermodynamic range.

The only certain conclusion that can be made now is that the problem of ore deposition on the Colorado Plateau will be solved at least partly through the further study and refinement of the thermodynamic equilibrium properties, especially in the region suggested above.

SUMMARY

1. The published thermodynamic and chemical data for vanadium have
been used to construct an equilibrium diagram showing the stability
ranges of the various solution and solid phases on the pH-oxidation
potential field. The effects of heat of hydration and elevated temperatures
on the relations determined at 25° C are estimated and found to be minor.

2. The conditions of stability on the equilibrium diagram of the
various vanadium minerals of the Colorado Plateau have been determined
from mineral association and analogy to artificial compounds.

3. The mineralogy of vanadium on the Colorado Plateau,
interpreted in the light of the equilibrium diagram, indicates that nearly
all the vanadium minerals (except some silicates) were derived from the
primary mineral montroseite by weathering processes.

4. The weathering process has been shown to follow two sequences, an
acid branch and an alkaline branch. The acid branch occurs in primary
oxide concentrations where pyrite is present and follows the sequence--
montroseite, paramontroseite, doloresite, corvusite, pascoite, hewettite,
and carnotite. The alkaline branch obtains in regions where pyrite is
absent and follows the sequence--montroseite, paramontroseite, duttonite,
simplotite, melanovanadite, rossite, and carnotite.

5. The hydrothermal deposition of the primary montroseite-coffinite-
uraninite ore has been considered briefly in the light of the equilibrium
diagram.

REFERENCES

Appleman, D. E., and Evans, H. T., Jr., 1958, Crystal structure of carnotite: Acta Crystallographica, v. 10, p. 765.

Baker, H., 1885, The orthovanadates of sodium and their analogs: Chem. Soc. London Jour., v. 47, p. 353-361.

Barton, P. B., Jr., and Appleman, D. E., 1957, Crystal chemistry of carnotite, in Dunning, J. R., and Prentice, B. R., eds., Advances in nuclear engineering, v. II, Proceedings of the Second Nuclear Engineering and Science Congress, Philadelphia, pt. 2: New York, Pergamon Press, p. 294-299.

Christ, C. L., Clark, J. R., and Evans, H. T., Jr., 1954, The crystal structure of potassium metavanadate monohydrate, $KVO_3 \cdot H_2O$: Acta Crystallographica, v. 7, p. 801-807.

Coleman, R. G., 1957, Mineralogical evidence on the temperature of formation of the Colorado Plateau uranium deposits: Econ. Geology, v. 52, p. 1-4.

Deltombe, E., de Zoubov, N., and Pourbaix, M., 1956, Comportement electrochimique du vanadium. Diagramme d'équilibre tension-pH du système $\overline{V}$-H_2O a $25°$ C: Raport technique No. 29, Bruxelles, Centre Belge d'Etude de la Corrosion.

Ducret, L. P., 1951, Contribution a l'étude des ions des valence quatre et cinq du vanadium: Anales de Chimie, v. 6, p. 705-776.

Evans, H. T., Jr., and Mrose, M. E., 1955, A crystal chemical study of montroseite and paramontroseite: Am. Mineralogist, v. 40, p. 861-875.

Evans, H. T., Jr., Mrose, M. E., and Marvin, R., 1955, Constitution of the natural and artificial decavanadates (abs.): Am. Mineralogist, v. 40, p. 314.

Fischer, R. P., and Hilpert, L. S., 1952, Geology of the Uravan mineral belt: U. S. Geol. Survey Bull. 988-A, 13 p.

Garrels, R. M., 1953, Some thermodynamic relations among the vanadium oxides, and their relation to the oxidation state of the uranium ores of the Colorado Plateaus: Am. Mineralogist, v. 38, p. 1251-1265.

_____ 1955, Some thermodynamic relations among the uranium oxides and their relation to the oxidation states of the uranium ores of the Colorado Plateaus: Am. Mineralogist, v. 40, p. 1004-1021.

Gruner, J. W., Gardiner, L., and Smith, D. K., Jr., 1953, Annual report
    for July 1, 1952 to March 31, 1953: U. S. Atomic Energy Comm.,
    RME-3044, 58 p., issued by U. S. Atomic Energy Comm., Tech. Inf.
    Service Extension, Oak Ridge, Tenn.

Hess, F. L., 1933, Uranium, vanadium, radium, gold, silver, and
    molybdenum sedimentary deposits, in Ore deposits of the Western
    States, Lindgren Memorial Volume: New York, Am. Inst. Mining Metall.
    Engineers, p. 450-481.

Jander, G., and Jahr, K. F., 1933, Aufbau und Abbau Nohermolekularer
    anorganischer Verbindungen in Losung an Beispiel der Vanadinsaure,
    Polyvanadate und Vanadansalze: Zeitschr. für anorg. allg. Chemie,
    v. 212, p. 1-20.

Krumbein, W. C., and Garrels, R. M., 1952, Origin and classification of
    chemical sediments in terms of pH and oxidation-reduction potentials:
    Jour. Geology, v. 60, p. 1-33.

Latimer, W. M., 1952, Oxidation potentials, 2d ed.: New York, Prentice-Hall,
    Inc. 392 p.

McKelvey, V. E., Everhart, D. L., and Garrels, R. M., 1955, Origin of
    uranium deposits, Fiftieth Anniversary Volume, Pt. 1: Econ. Geology,
    p. 464-533.

Palache, C., Berman, H., and Frondel, C., 1951, Dana's system of
    mineralogy, 7th ed., v. 2: New York, John Wiley and Sons, Inc., 1124 p.

Pourbaix, M. J. N., 1949, Thermodynamics of dilute aqueous solutions:
    London, Edward Arnold and Co.

Rossotti, F. J. C., and Rossotti, H., 1955, Studies on the hydrolysis of
    metal ions, XII: The hydrolysis of vanadium (IV) ion: Acta Chemica
    Scandinavica, v. 9, p. 1177-1192.

_____ 1956, Equilibrium studies of polyanions: I. Isopolyvanadates in
    acidic media: Acta Chemica Scandinavica, v. 10, p. 957-984.

Stern, T. W., Stieff, L. R., Evans, H. T., Jr., and Sherwood, A. M., 1957,
    Doloresite, a new vanadium oxide mineral from the Colorado Plateau:
    Am. Mineralogist, v. 42, p. 587-593.

Stieff, L. R., Stern, T. W., and Sherwood, A. M., 1956, Coffinite, a
    uranous silicate with hydroxyl substitution: a new mineral: Am.
    Mineralogist, v. 41, p. 675-688.

Sundberg, I., and Sillén, L. G., 1949, On the crystal structure of KUO_2VO_4
    (synthetic anhydrous carnotite): Arkiv för Kemi, v. 1, p. 337-351.

Syneček, V., and Hanic, F., 1954, The crystal structure of ammonium metavanadate: Czechoslovak Jour. Physics, v. 4, p. 120-130.

Thompson, M. E., Roach, C. H., and Meyrowitz, R., 1957, Duttonite, a new quadrivalent vanadium oxide from the Peanut mine, Montrose County, Colorado: Am. Mineralogist, v. 42, p. 455-460.

_____1958, Simplotite, a new quadrivalent vanadium mineral from the Colorado Plateau: Am. Mineralogist, v. 43, p. 16-24.

Wadsley, A. D., 1955, The crystal structure of $Na_{2-x}V_6O_{15}$: Acta Crystallographica, v. 8, p. 695-701.

Weeks, A. D., Cisney, E., and Sherwood, A. M., 1953, Montroseite, a new vanadium oxide from the Colorado Plateaus: Am. Mineralogist, v. 38, p. 1235-1241.

Weeks, A. D., and Thompson, M. E., 1954, Identification and occurrence of uranium and vanadium minerals from the Colorado Plateaus: U. S. Geol. Survey Bull. 1009-B, p. 13-62.

Weeks, A. D., Thompson, M. E., and Sherwood, A. M., 1955, Navajoite, a new vanadium oxide from Arizona: Am. Mineralogist, v. 40, p. 207-215.
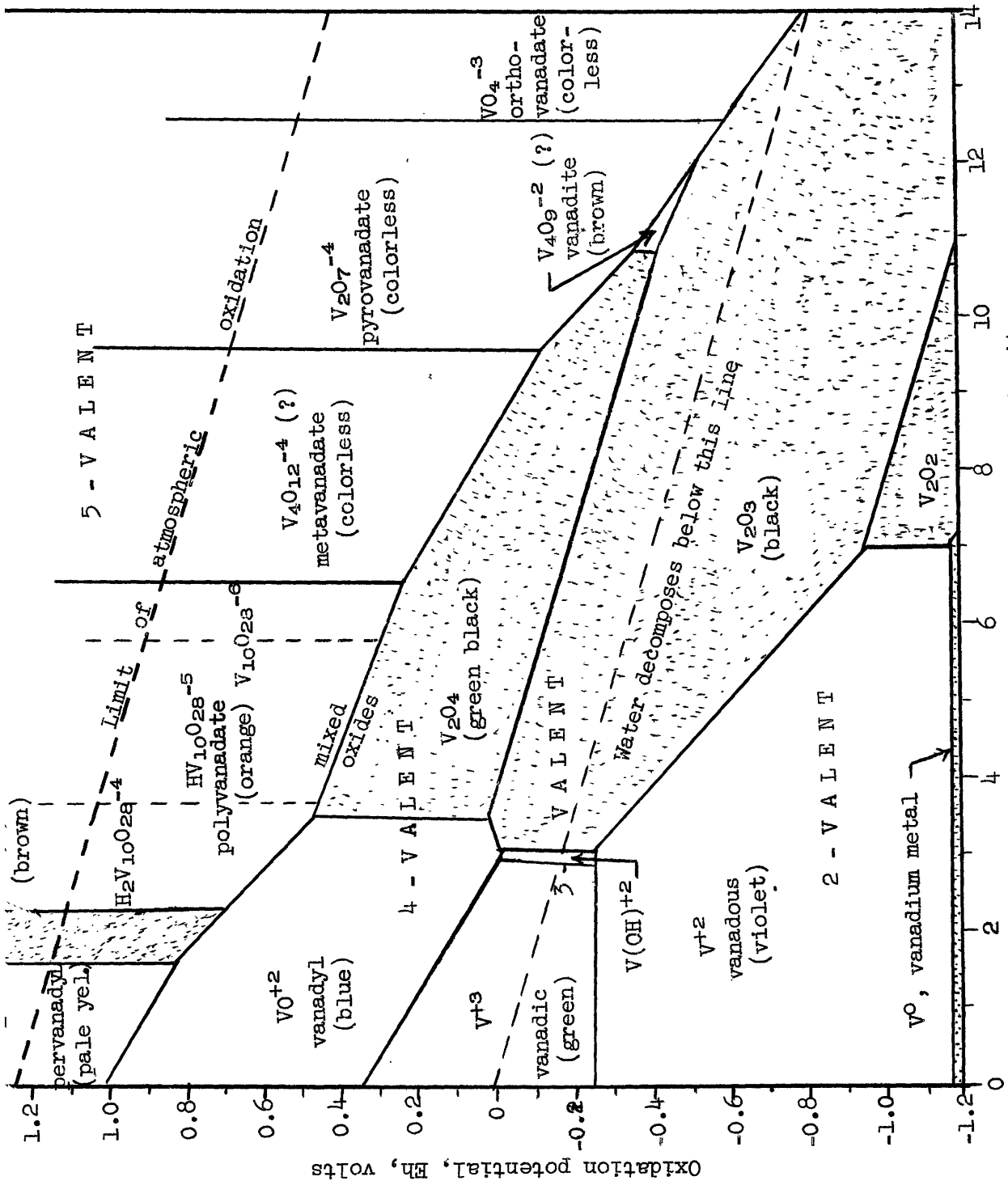
Figure 1.—Aqueous equilibrium diagram showing stability ranges of various solid and solution phases as explained in the text. In stippled areas, the solubility of vanadium is less
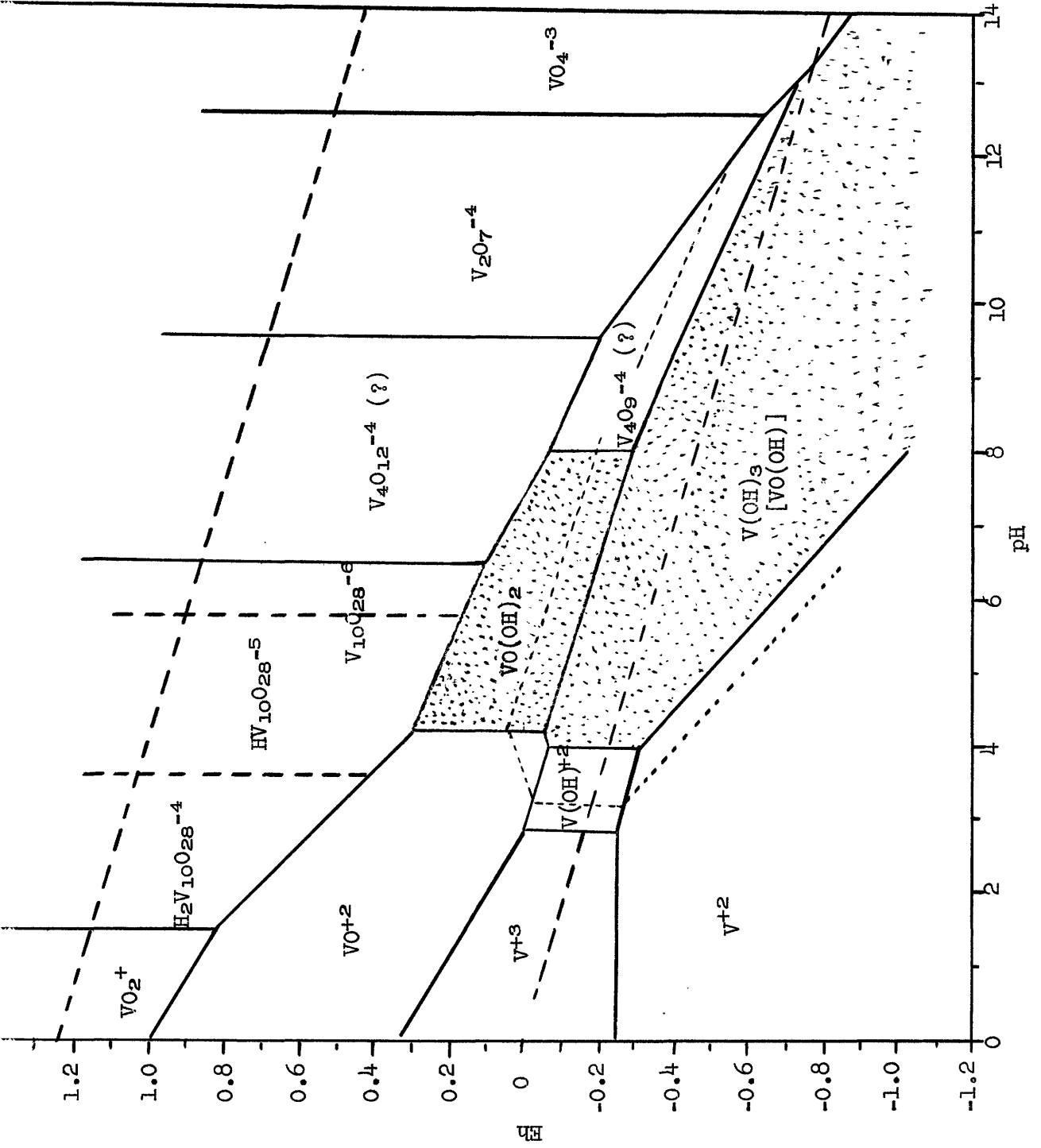
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Figure 2.—The diagram of figure 1 modified according to the estimated free energies of hydration of the oxides. The dotted boundary indicates the estimated region of stability of
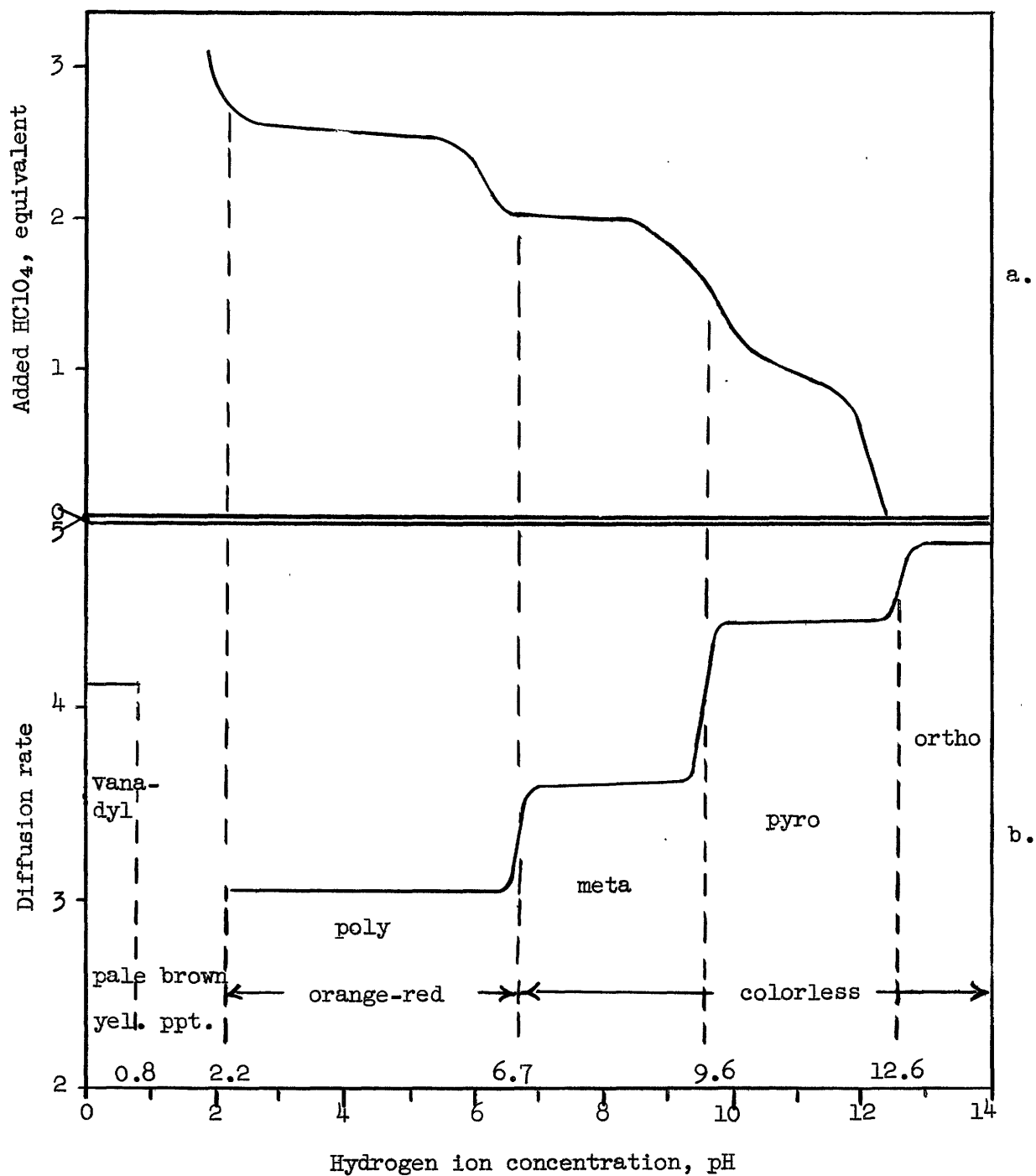
Figure 3.--Diagrams showing the behavior of quinquevalent vanadium in solution. Upper curve (a) shows the titration curve of Ducret (1951); lower curve (b) shows the results of diffusion experiments of Jander and Jahr (1933).
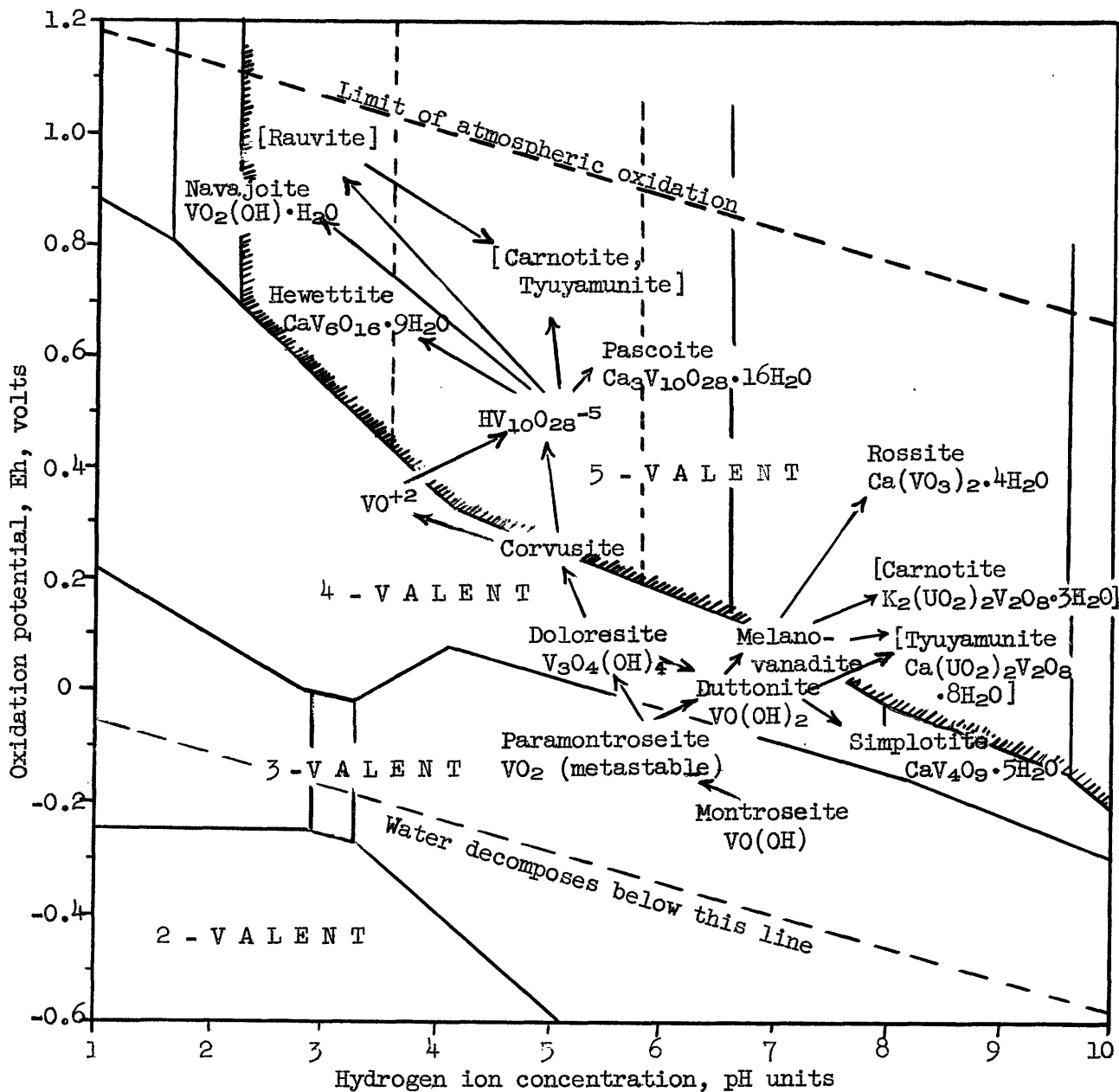
Figure 4.—Aqueous equilibrium diagram for vanadium with the stability regions of various vanadium minerals indicated. Arrows show expected and observed alteration sequences under weathering conditions. Shaded boundary indicates stability region of carnotite and tyuyamunite, which supersede all other vanadium species in the presence of sexivalent uranium.