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

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ABSTRACT

Fields of stability of several vanadium oxides in water solution at 25° C. have been calculated as functions of pH and oxidation potential. The bivalent oxide V_2O_2 is not expected under natural conditions; it should occur only at oxidation potentials below the breakdown potential of water. The oxide corresponding to the mineral montroseite, $V_2O_3 \cdot H_2O$ or VOOH, is predicted to coexist with common metal sulfides and to oxidize to V_2O_4 at about the same potential at which sulfide ion oxidizes to sulfate. Owing to difficulties entailed by the complex chemistry of vanadium, V^{+5}, no attempt was made to calculate a boundary between V_2O_4 and a higher oxide. Diagrams showing the fields of stability of the various oxides have been constructed, and contours showing the activities of the various vanadium ions have been superimposed. The stability fields of the vanadium oxides should be useful in deducing the environment of formation of the carnotite ores and the "blue-black" ores of the Colorado Plateaus.

INTRODUCTION

For many years the chief ore minerals from the uranium-vanadium deposits in the Morrison formation of the Colorado Plateaus have been carnotite and a hydrous vanadium silicate. During the past few years another kind of ore has been found in increasing quantities. It is commonly known as "blue-black" ore. The uranium-bearing mineral is probably uraninite or other quadrivalent uranium oxide; vanadium occurs in a variety of compounds, among them the vanadium (III) oxide, montroseite (Weeks *et al.*, 1953).

In general blue-black ore occurs farther from the surface than carnotite ore; it is typically associated with pyrite-bearing light-colored sandstone, whereas carnotite ore is associated with brown-spotted limonitic sandstone. The implication has been drawn by many workers that the ores are essentially equivalent chemically, but that the carnotite ores reflect an oxidizing environment, whereas the blue-black ores formed under reducing conditions.

The present incomplete data on the mineralogy of the ores support this view. Carnotite ore contains V^{+5} compounds, such as carnotite itself, tyuyamunite, hewettite, hummerite, pascoite, rauvite, and many others; Fe^{+++} oxides; U^{+6} compounds; and S^{+6} and Fe^{+++} compounds. The valence state of the vanadium in the hydrous silicate has not been established. Blue-black ore contains V^{+++}, V^{+4}, and V^{+5} compounds, probably

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largely as oxides; Fe^{++} and $S_2^=$ in pyrite. The valence state of the uranium is probably $+4$.

In anticipation of further mineralogic and geologic work on this problem it seemed worthwhile to summarize present theoretical chemical data on the stability in water solutions of various lower-valence vanadium oxides. Even though the stability fields can be determined only at 25° C. and at atmospheric pressure, they may be useful as general guides to the behavior of the various compounds.

It is shown, for example, in the following, that montroseite ($V_2O_3 \cdot H_2O$) is not stable under ordinary weathering conditions and that V_2O_2 should not be formed at all in ordinary ground water.

Probable Mechanism of Precipitation of Vanadium Oxides

Vanadium oxides probably can be precipitated from water solution according to the following reactions:

$$V^{++} + 2OH^- = V(OH)_2 \tag{1}$$
$$2V(OH)_2 = V_2O_2 + 2H_2O \tag{2}$$
$$V^{+++} + 3OH^- = V(OH)_3 \tag{3}$$
$$2V(OH)_3 = V_2O_3 + 3H_2O \tag{4}$$
$$VO^{++} + 2OH^- = VO(OH)_2 \tag{5}$$
$$2VO(OH)_2 = V_2O_4 + 2H_2O \tag{6}$$

If the free energies of the various reactions are known, equilibrium constants for the ionization of the hydroxides (reactions 1, 3, 5) can be calculated. From these equilibria the maximum activity of V^{++}, V^{+++}, and VO^{++} can be calculated at a stipulated pH. If an oxidation potential (Eh) of the system is also stipulated, the equilibrium ratios of these three ions can be calculated. Therefore, it is possible to designate fields of stability of each of the oxides and to calculate the equilibrium activities of vanadium ions ($a_{V^{++}} + a_{V^{+++}} + a_{VO^{++}} + a_{V(OH)_4^+}$) as functions of pH and Eh.

Table 1. Some Free Energies of Formation

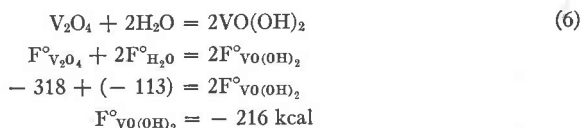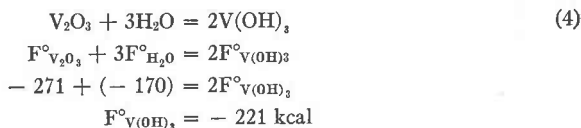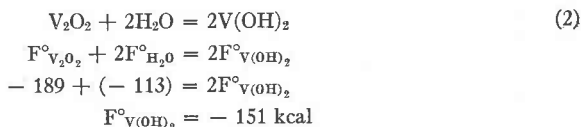| Species	Free Energy of Formation (kilocalories per mol)
V_2O_2	-189
V_2O_3	-271
V_2O_4	-318
H_2O	-56.7
V^{++}aq	-54.7
V^{+++}aq	-60.6
VO^{++}aq	-109
OH^-aq	-37.6

FREE ENERGY OF FORMATION OF IONS AND COMPOUNDS INVOLVED IN PRECIPITATION OF VANADIUM OXIDES

The free energy changes of reactions 1 through 6 have not been determined, but they can be calculated if the free energy of formation of the chemical species involved are known. Available data are listed in Table 1 (Latimer, 1952).
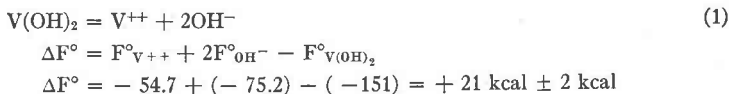
FREE ENERGY CHANGE FOR FORMATION OF HYDROXIDES FROM CONSTITUENT IONS

The free energy change of reactions 2, 4, and 6 cannot be computed directly because the free energy of formation of the hydroxides is not known (Table 1). However, the free energy change in the reaction from hydrate or hydroxide to oxide plus water is very small in other cases where data are available. For the reactions from $Pb(OH)_2$ to PbO and H_2O, for $Cu(OH)_2$ to $CuO+H_2O$, and $Ni(OH)_2$ to $NiO+H_2O$, the free energy changes are all less than 2 kcal. Similar values are not available for hydroxides of trivalent metals, but for the reactions $Al_2O_3 \cdot H_2O$ to Al_2O_3 and H_2O and for $Al_2O_3 \cdot 3H_2O$ to Al_2O_3 and $3H_2O$, the same rule holds. Therefore the free energy of formation of the various vanadium hydroxides is equal to the sum of the free energies of formation of oxides plus the necessary water, with a probable uncertainty of about 2 kcal.

At 25° C.:

$$V_2O_2 + 2H_2O = 2V(OH)_2 \tag{2}$$
$$F^\circ_{V_2O_2} + 2F^\circ_{H_2O} = 2F^\circ_{V(OH)_2}$$
$$- 189 + (- 113) = 2F^\circ_{V(OH)_2}$$
$$F^\circ_{V(OH)_2} = - 151 \text{ kcal}$$

$$V_2O_3 + 3H_2O = 2V(OH)_3 \tag{4}$$
$$F^\circ_{V_2O_3} + 3F^\circ_{H_2O} = 2F^\circ_{V(OH)3}$$
$$- 271 + (- 170) = 2F^\circ_{V(OH)_3}$$
$$F^\circ_{V(OH)_3} = - 221 \text{ kcal}$$

$$V_2O_4 + 2H_2O = 2VO(OH)_2 \tag{6}$$
$$F^\circ_{V_2O_4} + 2F^\circ_{H_2O} = 2F^\circ_{VO(OH)_2}$$
$$- 318 + (- 113) = 2F^\circ_{VO(OH)_2}$$
$$F^\circ_{VO(OH)_2} = - 216 \text{ kcal}$$

From these values of the free energy of formation of the hydroxides, and the values for formation of the ions in Table 1, the free energy change for the ionization of the hydroxides in water can be determined:

$$V(OH)_2 = V^{++} + 2OH^- \tag{1}$$
$$\Delta F^\circ = F^\circ_{V^{++}} + 2F^\circ_{OH^-} - F^\circ_{V(OH)_2}$$
$$\Delta F^\circ = - 54.7 + (- 75.2) - (-151) = + 21 \text{ kcal} \pm 2 \text{ kcal}$$

$$V(OH)_3 = V^{+++} + 3OH^- \tag{3}$$
$$\Delta F^\circ = F^\circ_{V^{+++}} + 3F^\circ_{OH^-} - F^\circ_{V(OH)_3}$$
$$\Delta F^\circ = -60.6 + (-113) - (-221) = +47 \text{ kcal} \pm 2 \text{ kcal}$$

$$VO(OH)_2 \rightarrow VO^{++} + 2OH^- \tag{5}$$
$$\Delta F^\circ = F^\circ_{VO^{++}} + 2F^\circ_{OH^-} - F^\circ_{VO(OH)_2}$$
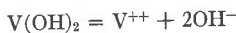$$\Delta F^\circ = -109 + (-75.2) - (-216) = +32 \text{ kcal} \pm 2 \text{ kcal}$$

IONIZATION CONSTANTS FOR VANADIUM HYDROXIDES

The free energy change for the ionization of the hydroxides is related to the ionization constant K by the equation:

$$\Delta F^\circ = -RT \ln K.$$

At 25° C, RT ln K can be replaced by 1.364 log K when ΔF° is given in kcal.

For equation 1:

$$V(OH)_2 = V^{++} + 2OH^-$$
$$K_{V(OH)_2} = \frac{a_{V^{++}} a^2_{OH^-}}{a_{V(OH)_2}}$$

Because the activity of the precipitated $V(OH)_2$ is unity:

$$\Delta F^\circ = -1.364 \log a_{V^{++}} a^2_{OH^-}$$
$$21 = -1.364 \log a_{V^{++}} a^2_{OH^-}$$
$$K_{V(OH)_2} = a_{V^{++}} a^2_{OH^-} = 10^{-15.4} \tag{7}$$

For equation 3:

$$\Delta F^\circ = -1.364 \log a_{V^{+++}} a^3_{OH^-}$$
$$47 = -1.364 \log a_{V^{+++}} a^3_{OH^-}$$
$$K_{V(OH)_3} = a_{V^{+++}} a^3_{OH^-} = 10^{-34.4} \tag{8}$$

For equation 5:

$$\Delta F^\circ = -1.364 \log a_{VO^{++}} a^2_{OH^-}$$
$$32 = -1.364 \log a_{VO^{++}} a^2_{OH^-}$$
$$K_{VO(OH)_2} = a_{VO^{++}} a^2_{OH^-} = 10^{-23.5} \tag{9}$$

OXIDATION POTENTIAL RELATIONS AMONG THE VANADIUM IONS

The oxidation potential (Eh) of a system can be measured by obtaining the electromotive force generated by the system relative to the standard hydrogen electrode. This can be done by using a circuit containing a hydrogen electrode and an inert electrode, usually platinum. The reaction involved can be described as follows:

$$2H^+ + \text{reduced system} \rightarrow H_2 + \text{oxidized system}.$$
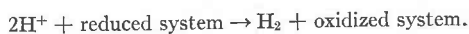
From the standard electrochemical equation for galvanic cells:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_{H_2} \text{ (oxidized system)}}{a^2_{H^+} \text{ (reduced system)}}.$$

Where E is the measured emf, $E°$ is the emf at unit activity of all constituents, R the gas constant, T the absolute temperature, nF the number of Faradays of electricity involved in the reaction. At 25° C,

$$\frac{RT}{F} \log \cdots = 0.059 \log \cdots$$

Because the activity of H_2 and H^+ are unity by definition of the standard hydrogen electrode, the equation reduces to:

$$E = E° - \frac{RT}{nF} \ln \frac{\text{(oxidized system)}}{\text{(reduced system)}}$$

By convention, $Eh = -E$, so that:

$$Eh = -E° + \frac{RT}{nF} \ln \frac{\text{(oxidized system)}}{\text{(reduced system)}}$$

$E°$ is not known for complex natural systems, but if each chemical reaction in the system is in equilibrium with the system as a whole,

$$Eh = -E° + \frac{RT}{nF} \ln Q$$

Where Q is the product of the activities (or fugacities) of the resulting substances, divided by the product of the activities of the reacting substances, each activity raised to that power whose exponent is the coefficient of the substance in the chemical equation.

For the vanadium ions, the various reactions involved are (Latimer, 1952):

$$V° = V^{++} + 2e \qquad\qquad E° = 1.18$$
$$V^{++} = V^{+++} + e \qquad\qquad E° = 0.255$$
$$V^{+++} + H_2O = VO^{++} + 2H^+ + e \qquad E° = -0.361$$
$$VO^{++} + 3H_2O = V(OH)_4^+ + 2H^+ + e \qquad E° = -1.00.$$
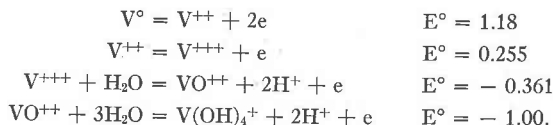
The corresponding Eh equations are:

$$Eh = -1.18 + \frac{0.059}{2} \log \frac{a_{V^{++}}}{a_{V°}} \tag{10}$$

$$Eh = -0.255 + 0.059 \log \frac{a_{V^{+++}}}{a_{V^{++}}} \tag{11}$$

$$Eh = +0.361 + 0.059 \log \frac{a_{VO^{++}} a^2_{H^+}}{a_{V^{+++}}} \tag{12}$$

$$Eh = +1.00 + 0.059 \log \frac{a_{V(OH)_4^+} a^2_{H^+}}{a_{VO^{++}}} \tag{13}$$

Thus the great value of Eh measurements stems from their application to the determination of ionic ratios for all pairs present for which $E°$ values are known; the great danger in using Eh values is in the assumption that the individual reactions are in equilibrium with the system as a whole.

Vanadium Ion Activities as Functions of Eh and pH

If the Eh and pH ($-\log a_{H^+}$) of an environment are stipulated, the ratios of the various vanadium ions are fixed. Designation of a pH value also fixes the OH$^-$ activity as $a_{H^+}a_{OH^-} = K_{H_2O}$. Knowledge of OH$^-$ activity in turn fixes the activity of V^{++} in equilibrium with V(OH)$_2$, V^{+++} in equilibrium with V(OH)$_3$, and VO^{++} in equilibrium with VO(OH)$_2$ (equations 7, 8, 9).

Consequently if a pair of pH and Eh values are chosen arbitrarily, the concentration of each vanadium ion in equilibrium with its hydroxide can be calculated, and the stable hydroxide also can be determined. For example, on a qualitative basis, V^{++} would be expected to be the predominant species at low Eh values, and V(OH)$_2$ the stable hydroxide. This prediction can be checked quantitatively at a given pair of pH and Eh values by calculating $a_{V^{++}}$ in equilibrium with V(OH)$_2$, then calculating $a_{V^{+++}}$ and $a_{VO^{++}}$ from the Eh equations (11 and 12), and finally testing if these activities are too small to be in equilibrium with either V(OH)$_3$ or VO(OH)$_2$. Calculations of this type show that it is possible to delineate fields of stability of the three vanadium hydroxides of interest here.

A sample calculation may suffice to illustrate the method used.[*] At the arbitrary values pH 5 and Eh$+0.20$, the activities of vanadium ion in equilibrium with the hydroxides are:

$$\text{A. } a_{VO^{++}}a^2_{OH^-} = K_{VO(OH)_2} = 10^{-23.5} \tag{9}$$

$$a_{VO^{++}} = \frac{10^{-23.5}}{(10^{-9})^2} = 10^{-5.5}$$

$$\text{B. } a_{V^{+++}}a^3_{OH^-} = K_{V(OH)_3} = 10^{-34.4} \tag{8}$$

$$a_{V^{+++}} = \frac{10^{-34.4}}{10^{-27.0}} = 10^{-7.4}$$

$$\text{C. } a_{V^{++}}a^2_{OH^-} = K_{V(OH)_2} = 10^{-15.4} \tag{7}$$

$$a_{V^{++}} = \frac{10^{-15.4}}{10^{-18.0}} = 10^{2.6}$$

Both $a_{VO^{++}}$ and $a_{V^{+++}}$ are small relative to $a_{V^{++}}$, so it seems likely that either VO(OH)$_2$ or V(OH)$_3$ is the stable hydroxide under the conditions given. Assuming that VO(OH)$_2$ is the stable form, then:

$$Eh = 0.361 + 0.059 \log \frac{a_{VO^{++}}a^2_{H^+}}{a_{V^{+++}}} \tag{12}$$

$$0.20 = 0.361 + 0.059 \log \frac{10^{-5.5} \times 10^{-10}}{a_{V^{+++}}}$$

$$a_{V^{+++}} = 10^{-12.8}$$

[*] For examples of similar calculations see Krumbein and Garrels (1952), and Delahay, Roe, and Rysselberghe (1950).
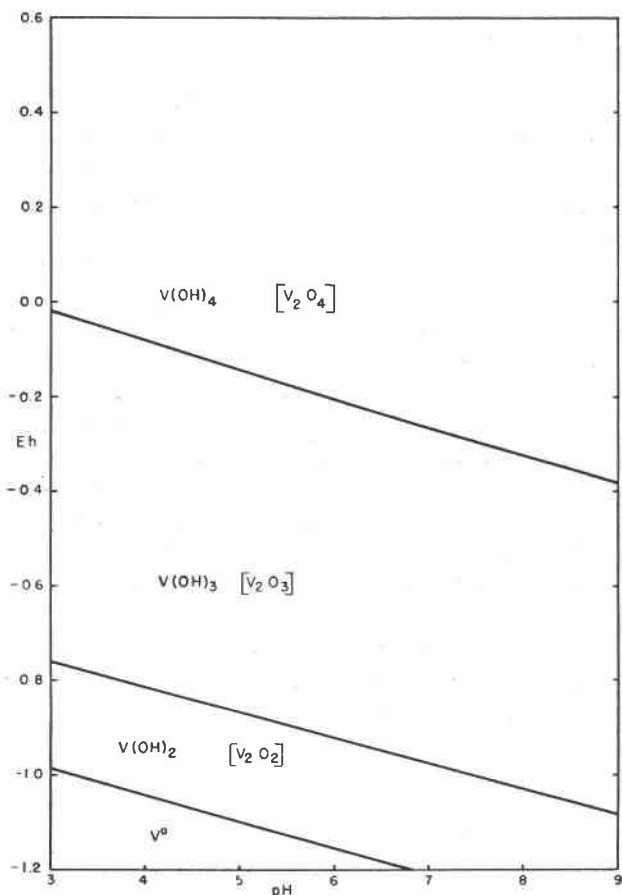
F$_{\text{IG}}$. 1. Stability fields of vanadium hydroxides as functions of Eh and pH.

This result shows that, at Eh 0.2 and pH 5, $VO(OH)_2$ is, as assumed, the stable hydroxide, because the activity of V^{+++} in solution under the assumed condition $(10^{-12.8})$ is far less than that required for equilibrium with V $(OH)_3(10^{-7.4})$.

The results of a series of such calculations are shown in Figure 1. The position of the boundaries was determined quickly and easily by using the condition that at a boundary both activity products must be satisfied. Therefore at a given pH the ratio of the vanadium ion activities in equilibrium with the two stable solids is fixed. From this known ratio the Eh was determined from the appropriate equation (11 or 12).

Figures 2, 3, 4, and 5 show contours of the activities of V^{++}, V^{+++}, VO^{++}, and $V(OH)^+_4$, respectively, in relation to the stability fields of the
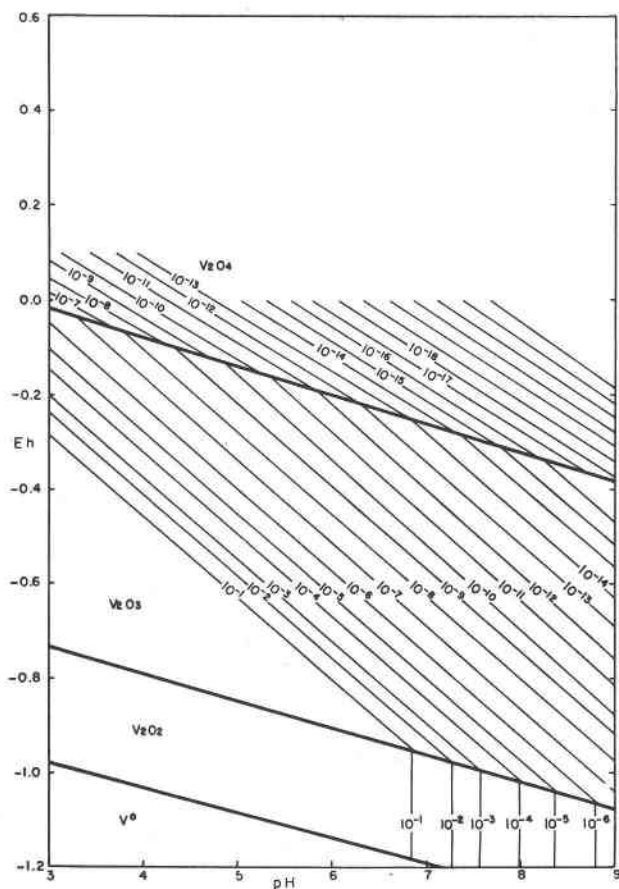
FIG. 2. V^{++} ion activity in equilibrium with various vanadium oxides.

various hydroxides. The calculated values fit the expected general relation that VO^{++} is the most abundant ion in solutions of higher Eh, V^{+++} at intermediate Eh, and V^{++} at lower Eh.

These values represent maximum activities of the various ions in equilibrium with the solid hydroxides at 25° C and at atmospheric pressure, and the values are essentially independent of the composition of the system. The values are, of course, accurate only within the limitations of knowledge of E° and of K values.

Relation of Vanadium Ion Activities and Vanadium Solubility

Although it is possible to calculate vanadium ion activities with reasonable confidence in the order of magnitude of the results, it is very difficult
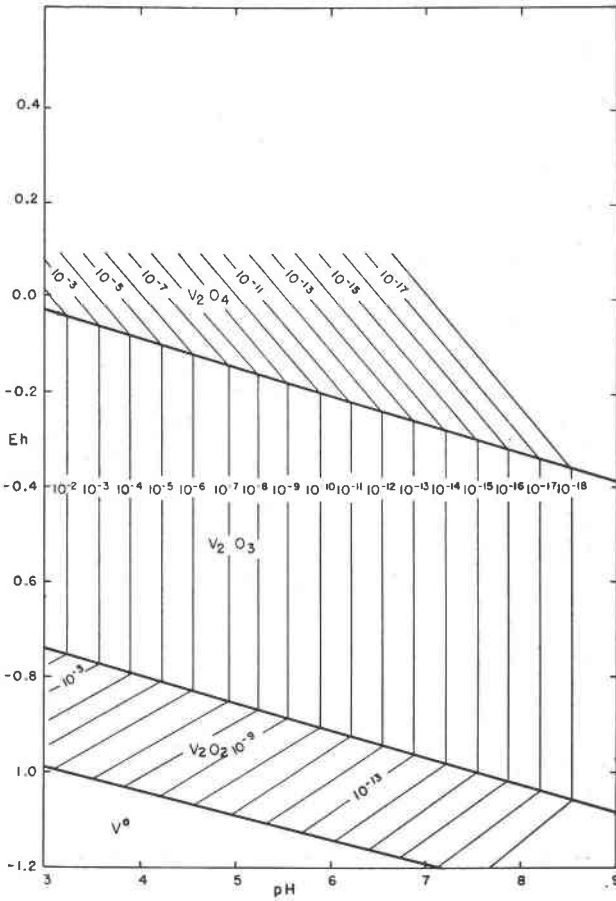
FIG. 3. V^{+++} ion activity in equilibrium with various vanadium oxides.

to relate the values obtained to the stoichiometric solubility. The solubility of vanadium in equilibrium with the hydroxides is equal to the sum of the molalities of all species in solution and can be represented as the sum of the known plus the unknown species:

$$\text{Solubility}_V = \sum m_{V^{++}} + m_{V^{+++}} + m_{VO^{++}} + m_{V(OH)_4^+} + m_{X_1} + m_{X_2} + m_{X_3} \cdots.$$

The activities of V^{++}, V^{+++}, VO^{++}, and $V(OH)_4^+$ are related to the molalities as follows:

$$a_{V^{++}} = \gamma_{V^{++}} m_{V^{++}}$$
$$a_{V^{+++}} = \gamma_{V^{+++}} m_{V^{+++}}$$
$$a_{VO^{++}} = \gamma_{VO^{++}} m_{VO^{++}}$$
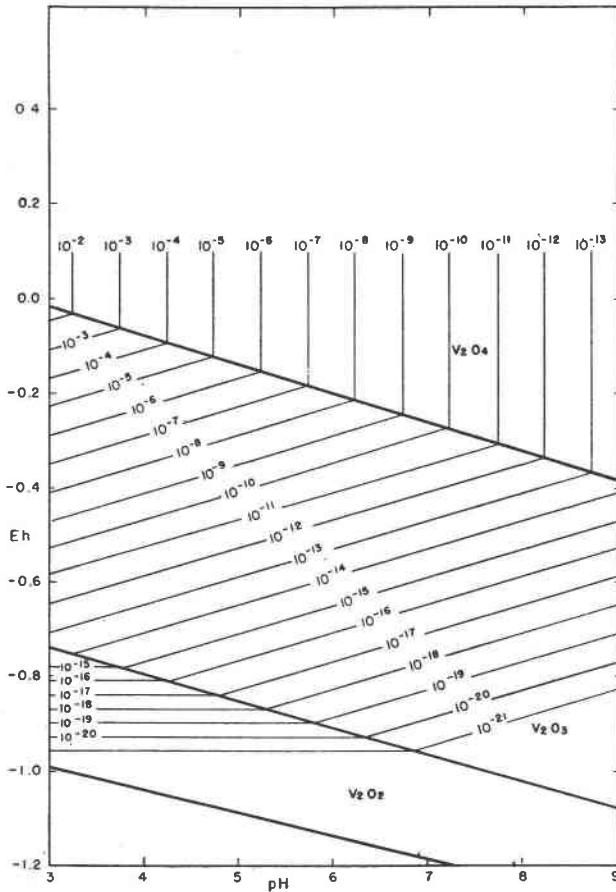$$a_{V(OH)_4^+} = \gamma_{V(OH)_4^+} m_{V(OH)_4^+}$$

FIG. 4. VO^{++} ion activity in equilibrium with various vanadium oxides.

Therefore $a_i \cong m_i$ only under conditions where $\gamma_i \cong 1$. γ_i is a function of the ionic strength, usually decreasing with increasing ionic strength up to values of ionic strength of 0.1 or 0.2, and then increasing again to unity or more at values of ionic strength of about 1.0. Values of γ_i may drop as low as 0.01 or 0.02 in the range of ionic strength between 0.1 and 1.0. Consequently, because activity usually approximates molality only in very dilute solutions or at specific values of the ionic strength of about 1.0, the error introduced by assuming $a_i = m_i$ is usually an underestimation of the actual value, and the corrective factor may be as large as 100-fold.

The presence of ionic complexes increases solubility; in the vanadium system involved, there is no indication in the literature of the presence
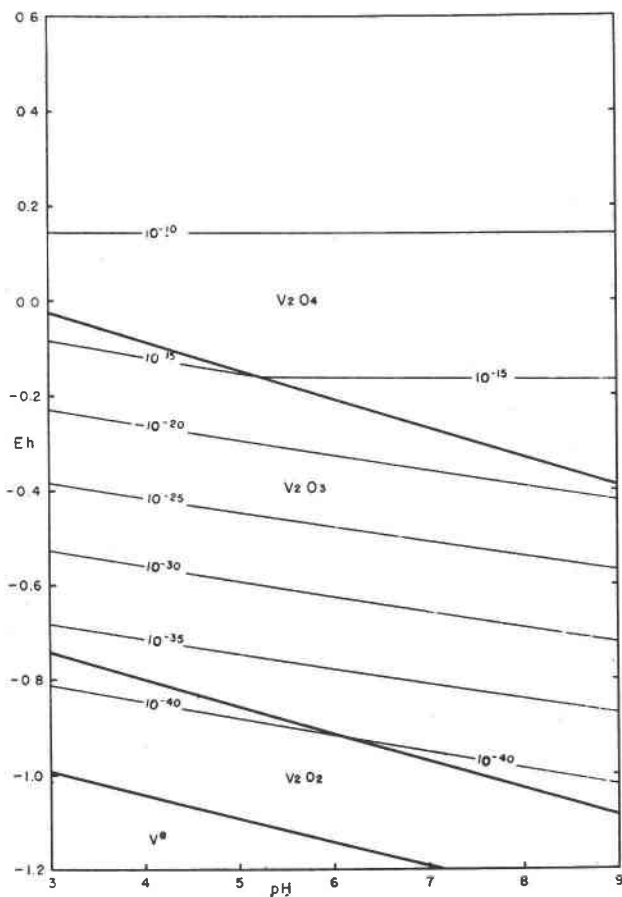
Fig. 5. $V(OH)_4{}^+$ ion activity in equilibrium with various vanadium oxides.

of soluble complexes with low dissociation constants for the 2-, 3-, and 4-valent ions, at least in solutions containing the typical inorganic ions present in natural waters. Vanadium, V^{+5}, on the other hand, is notorious for the complexity and number of the ions it forms. To a large extent it was this complex behavior of vanadium, V^{+5}, that led to the restriction of this study to the region in which the lower-valent ions are the vastly predominant species. A second consideration is the uncertainty of the reaction mechanism for the precipitation of V_2O_5 in nature.

Figure 6 shows contours of $\sum a_{V^{++}} + a_{V^{+++}} + a_{VO^{++}} + a_{V(OH)_4^+}$ superimposed on the stability fields of the various hydroxides. It can be used as a solubility diagram only for solutions of very low ionic strength with no other ionic species containing vanadium present.
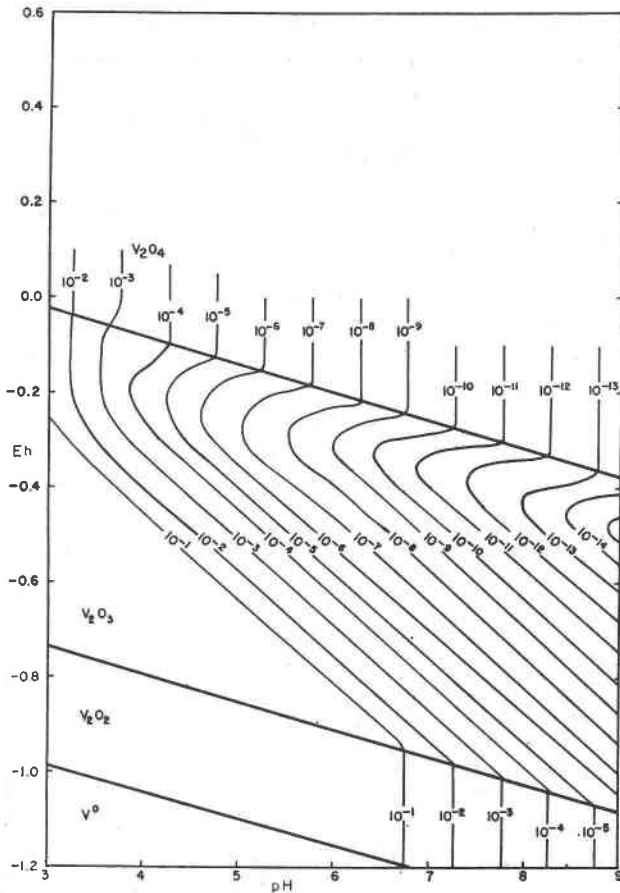
FIG. 6. Equilibrium fields of some vanadium oxides in water. Contours are for activities of vanadium ions in solution $\sum a_{V^{++}} + a_{V^{+++}} + a_{VO^{++}} + a_{V(OH)_4}^{+}$.

In spite of the restrictions imposed on using such diagrams as guides to solubility, it should be reemphasized that phase boundaries are independent of solution composition and are functions only of temperature and pressure. This means, for example, that in spite of the unknown compositional factors in the geologic environment of deposition of these vanadium compounds, there is no escaping the fact that equilibrium conditions for formation of $VO(OH)_2$ and $V(OH)_2$ are mutually exclusive.

Another relation should be emphasized. It is probable that, with various compositional variations, parts of the fields of stability of the compounds shown would be replaced by those of other compounds. This can occur, however, only if the ionic activity in equilibrium with these new

compounds is less than that in equilibrium with those shown. Therefore the diagrams show the approximate activity of vanadium ions in equilibrium with the oxides considered and the maximum activity in any other reasonably dilute aqueous system from which other vanadium compounds are formed at equilibrium.

GEOLOGIC IMPLICATIONS

Natural Limits of pH and Eh

Mason (1952, pp. 142–147) points out that the upper and lower limits of Eh for natural waters are determined by the potentials at which oxygen and hydrogen are liberated at atmospheric pressure by decomposition of the waters. The release of oxygen occurs at Eh values well above any shown in this paper; that of hydrogen, however, is well within the range considered, and actually removes the field of stability of $V(OH)_2$ from
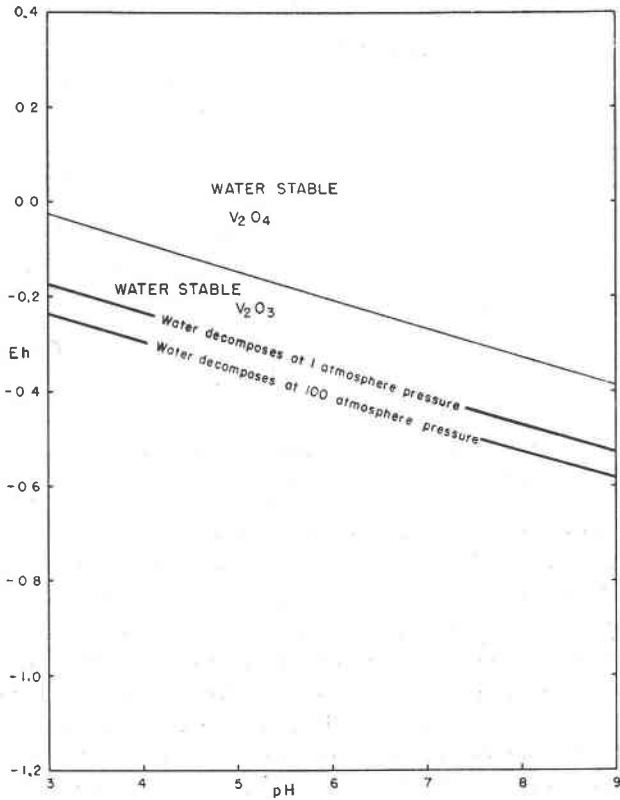
FIG. 7. Conditions for decomposition of water at 1 atmosphere and 100 atmospheres pressure.

the system. Mason points out that equilibrium is not always attained, and somewhat lower than theoretical Eh values may be achieved experimentally without releasing appreciable H_2 from water. Latimer (1952, p. 43) indicates that Eh values a full half volt lower than theoretical may be necessary to release hydrogen. Figure 7 shows the equilibrium values for decomposition of water at 1 atmosphere and at 100 atmospheres pressure at 25° C.

The natural pH range (Mason, 1952) is from 0 to 10 or somewhat higher. The low values usually are achieved under weathering conditions where sulfides are being oxidized to sulfates, with consequent production of hydrogen ion, or in the waters of some volcanic areas, where the source of the H^+ is less well known. Most ground waters range in pH from 4 to 8.

Unfortunately relatively few Eh measurements have been made of natural waters, as opposed to the copious pH data, but surface waters in equilibrium with oxygen under the partial pressure of the atmosphere commonly give empirical Eh values of $+0.1$ to $+0.3$. Eh values of deoxygenated ground waters in the zone of rock-pore saturation ordinarily range from zero to slightly minus values. In the presence of abundant carbonaceous material values as low as -0.5 have been measured. Mason (1952, p. 145) suggests that hydrogen actually may be released from water under such conditions.

Relation of Vanadium Oxide Stability Fields to Natural Conditions

In terms of the range of natural conditions, the theoretical fields of the vanadium oxides show that V_2O_3 (or its hydrate) is the lowest-valent vanadium oxide expected. It should occur under reducing conditions common in nature. It would be expected to oxidize to the next higher-valent vanadium oxide at about the same potential necessary to convert sulfide ion to sulfate. To put this relation in another way, V_2O_3 would be expected to coexist in equilibrium with various metal sulfides, such as pyrite or galena, and to oxidize at about the same potential.

It seems that V_2O_4 would be a transitory phase in most natural situations. The general tendency in nature is to produce either moderate to strong reducing conditions or moderate to strong oxidizing conditions. For example, V_2O_3 below the water table would probably remain indefinitely, but if raised above to a place where moist air or aerated water had free access to it, it would eventually oxidize all the way up to a 5-valent species. Surface conditions would thus ordinarily produce vanadates from V_2O_3. Little is known about the rate of the reaction, but oxidation probably is slow, and many mixed 3–4 valent and 4–5 valent vanadium oxides might have "half-lives" measured in months or years.

Unlike the reaction from sulfide to sulfate, which is essentially irre-

versible in natural inorganic systems at low temperature, the reaction $V^{+++} \leftrightarrows V^{4+} \leftrightarrows V^{5+}$ apparently goes either way at a finite rate under appropriate conditions.

CONCLUSION

These theoretical equilibrium relations among the vanadium oxides fit well into the concept that the carnotite ore and the blue-black ore are equivalent chemical expressions of differences in oxidation potential of their environment of formation. Whether the blue-black ores represent pre-vanadate stages of oxidation of an original montroseite-pyrite-pitchblende type of ore, or a reduced form of an original carnotite ore, or whether the two types were introduced simultaneously into different environments must be deduced from detailed geologic, mineralogic, and geochemical studies of the field relations. Even at this stage of knowledge, however, there is a surprising correlation between theoretical and observed associations. There seems to be a good possibility that laboratory studies of oxidation and reduction of natural and synthetic materials will be helpful in solving the problem.

ACKNOWLEDGMENTS

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