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E-pH Diagrams

1. Introduction

This volume is intended to employ E-pH diagrams to describe the inorganic solution chemistry of the chemical elements. Such diagrams are very useful in numerous fields of investigation, including electrochemistry, analytical chemistry, inorganic chemistry, geochemistry, environmental chemistry, corrosion chemistry, hydrometallurgy, water chemistry, agricultural chemistry, toxicology, biochemistry, chemical engineering, materials science, health physics, and nutrition. It is assumed that the reader is acquainted with the following major topics which are treated in elementary chemistry: stoichiometry, equilibrium, acid-base phenomena, solubility, complexation, elementary thermodynamics, and electrochemistry.

In 1923, W. M. Clark and B. Cohen published a paper in which they introduced the idea of plotting the electromotive force as referred to the hydrogen electrode E against the pH for several chemical systems.¹ In 1928, Clark continued to develop this graphical presentation in his text on the determination of pH.² The utility of the method was further extended by numerous other investigators such as M. Pourbaix, G. Valensi, G. Charlot, T. P. Hoar, R. M. Garrels, N. de Zoubov, J. Van Muylder, E. Deltombe, C. Vanleughenaghe, J. Schmets, M. Maraghini, P. Van Rysselberghe, A. Moussard, J. Brenet, F. Jolas, K. Schwabe, J. Besson, W. Kunz, A. L. Pitman, J. N. Butler, P. Delahay, H. Freiser, H. A. Laitinen, L. G. Sillen, P. L. Cloke, and others. In 1963, M. Pourbaix in collaboration with

N. de Zoubov published *Atlas d'équilibres électrochimiques*, a collection of E-pH diagrams for 90 chemical elements. This volume was translated into English in 1966 by J. A. Franklin and published as *Atlas of Electrochemical Equilibria in Aqueous Solutions*.³ Subsequently other investigators published computer programs for constructing the diagrams: L. Santoma; B. G. Williams, and W. H. Patrick; P. B. Linkson, B. D. Phillips, and C. D. Rowles; K. Osseo-Asare, A. W. Asihene, T. Xue, and V. S. T. Ciminellie; D. R. Drewes; M. Mao and E. Peters; H-H. Huang and C. A. Young; J. P. Birk and Laura L. Tayer; G. P. Glasby and H. D. Schulz; and Q. Feng, Y. Ma, and Y. Lu.⁴

2. The Na E-pH Diagram

Figures 1.1 through 1.17 exemplify the general nature of E-pH diagrams. Each E-pH diagram is a plot of E against pH for aqueous solutions.

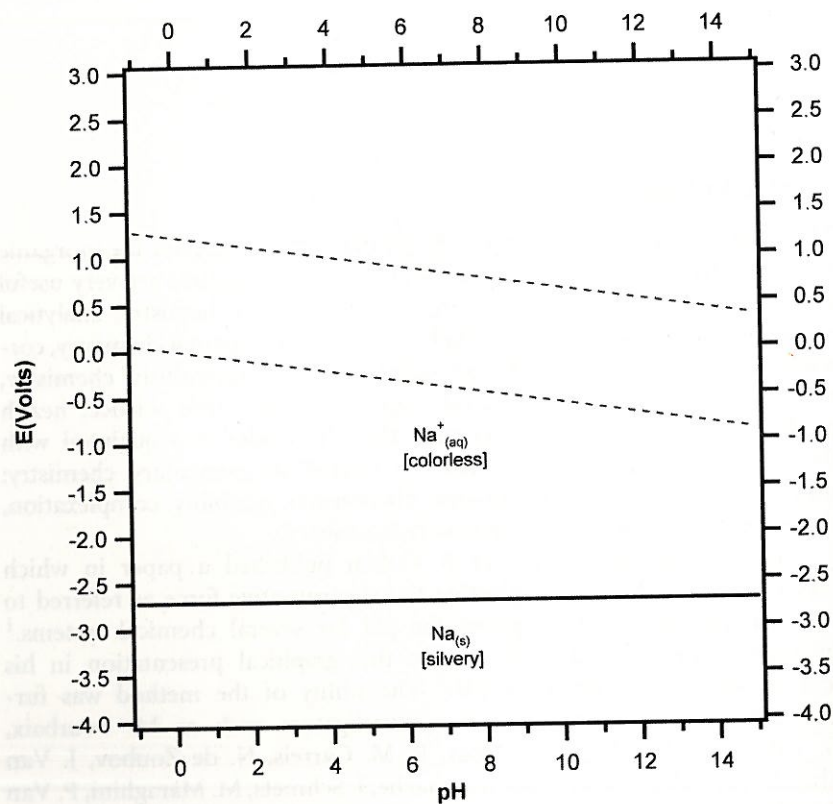


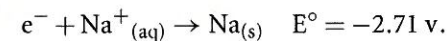
Figure 1.1 E-pH diagram for Na species. Soluble species concentrations (except H^+) = $10^{0.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .

The E (vertical) axis is a reflection of the potential values in volts (v) of reduction half-reactions describing the conditions under which changes in the aqueous oxidation state of the element occur. These E values range from +3.00 v to -4.00 v. The pH (horizontal) axis gives pH values ranging from a pH of -1.0 ($10^{1.0}$ molar hydrogen ion) to a pH of 15.0 ($10^{-15.0}$ molar hydrogen ion). The sloped dashed lines have to do with the behavior of the solvent water. This will be discussed in detail later.

The Na E-pH diagram will now be examined. Figure 1.1 shows the diagram for standard conditions, namely, a temperature T at 298 K (25.0°C), all dissolved species at 1.00 molal activity (the Na^+ ion), and all gases at 1.00 fugacity. In treatments of this system and all systems hereafter, the molar concentration M will be substituted for the molal activity, and the pressure in atmospheres will be substituted for the fugacity. These substitutions will usually introduce only small errors for the concentrations and pressures that will be employed.⁵ The labels for the species (Na^+ and Na) indicate the predominant species under various E and pH conditions. This may be seen by examining the three vertical lines (constant pH values) in Figure 1.2 and the three horizontal lines (constant E values) in Figure 1.3. Take a look at the vertical line at a constant pH of 0.0. Start at the top of the line where E is equal to 3.0 volts (v). As one scans down, the Na^+ species is the predominant one until the line at about -2.7 v is reached. Below this value the predominant species is metallic Na. The same analysis applies to the other two vertical lines at pH values of 7.0 and 14.0.

Now observe the horizontal line in Figure 1.3 at a constant voltage of 2.0 v. Starting at the right and scanning to the left, it can be seen that Na^+ is the predominant species at all pH values. The same is the case for the horizontal line at a constant voltage of 0.0 v. Scanning from right to left across the third horizontal line at a constant voltage of -3.0 v shows that the predominant species is metallic Na at all pH values. Similar analyses may be made for vertical lines at any given constant pH and for horizontal lines at any constant E.

Now, the question arises as to the origin of the horizontal line at about -2.7 v. This is obtained from the reduction half-reaction which relates the two species (Na^+ and Na) on the two sides of the line. A reduction half-reaction is one in which the electron or electrons appear on the left side of the equation. For example, in Figure 1.1 (as well as Figures 1.2 and 1.3), the voltage of the horizontal line comes from the following reduction half-reaction at all pH values:



In this equation, e^- stands for the electron, Na^+ for the sodium ion, (aq) for the aqueous state, Na for elemental sodium, (s) for the solid state, and E° represents the standard electrode potential given in volts (v). The superscript $^\circ$ on E indicates that the reaction is taking place under standard conditions (T = 298 K, Na^+ concentration of 1.00 M). Values of E° may be readily obtained from tables in reference works such as A. J. Bard, R. Parsons, and

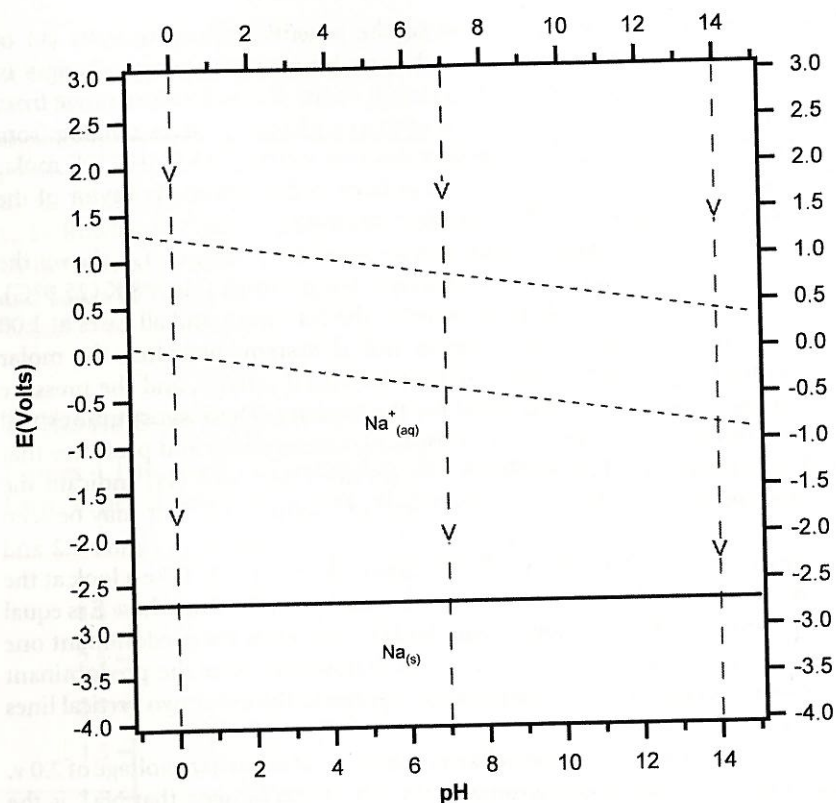


Figure 1.2 E-pH diagram for Na species. Soluble species concentrations (except H^+) = $10^{0.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant pH.

J. Jordan; D. R. Lide; and J. A. Dean.⁶ The potential for a half-reaction, E° or E , may be thought of as the driving force for the electron or electrons in the reaction. The horizontal line at -2.71 v represents this reduction half-reaction. In the region below this line, at E° values more negative than -2.71 v, the half-reaction proceeds to the right such that the predominant species is $\text{Na}_{(s)}$. In the region above this line, at E° values more positive than -2.71 v, the reaction proceeds to the left. As a result, in the region above this line the predominant species is $\text{Na}^+_{(aq)}$.

For Figure 1.4, the $\text{Na}^+_{(aq)}$ concentration has been changed to 0.10 M, and it is to be noted that the E value for the horizontal line between predominant species Na^+ and Na has changed to about -2.8 v. The same sort of remarks as before regarding the three vertical and the three horizontal lines apply to this figure. To ascertain why the E value has changed, it is important to note that the half-reaction of interest is now conducted under non-standard state concentration conditions. The concentration of Na^+ has been altered from

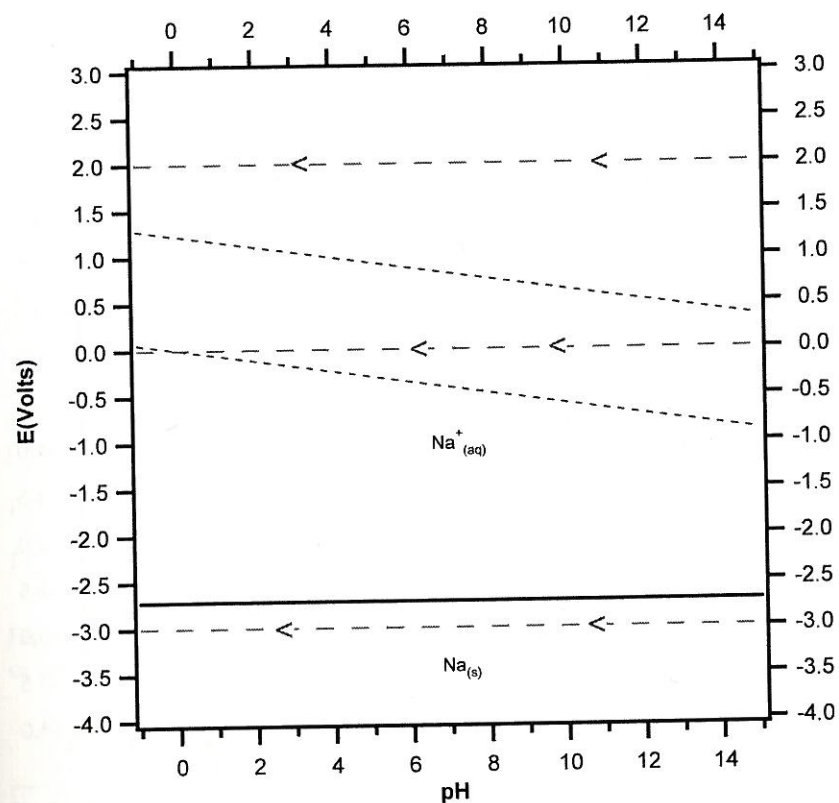
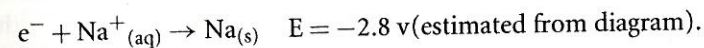


Figure 1.3 E-pH diagram for Na species. Soluble species concentrations (except H^+) = $10^{0.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant E .

1.00 M to 0.10 M. The E° value is therefore not applicable and must be changed to an E value. The half-reaction now reads



The horizontal line at about -2.8 v represents this reduction half-reaction. At E values below (more negative than) -2.8 v, the half-reaction proceeds to the right, and the predominant species in the region below the line is $\text{Na}_{(s)}$. At E values above (more positive than) -2.8 v, the reaction proceeds to the left, and the predominant species in the region above the line is $\text{Na}^+_{(aq)}$. Calculation of the change from E° to E can be made from the Nernst equation, which takes the following form:

$$E = E^\circ - (2.303RT/nF) \log (\Pi [\text{products}]^x / \Pi [\text{reactants}]^y)$$

where $R = 8.314$ J/mol K (joules per mole per degree absolute), $T = 298$ K, $F = 96,490$ C/mole (coulombs per mole), $n =$ moles of electrons involved

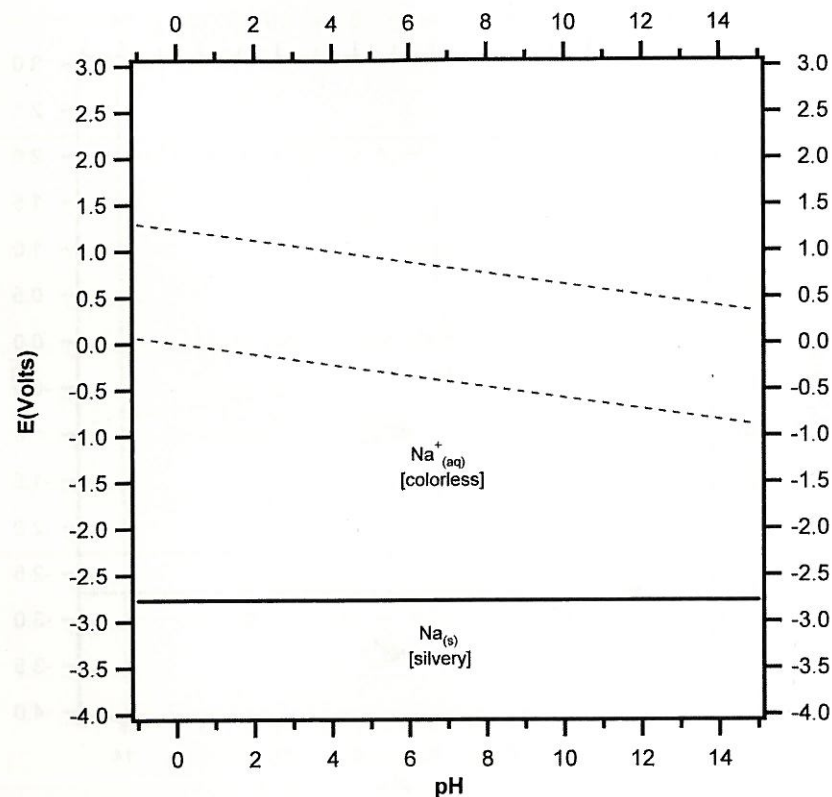


Figure 1.4 E-pH diagram for Na species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .

in the reaction, Π [products]^x signifies the product of the concentrations of the resulting species with each concentration raised to the power x which appears as its prefix in the half-reaction equation, and Π [reactants]^y signifies the product of the concentrations of the reacting species with each concentration raised to the power y which appears as its prefix in the half-reaction equation. Substituting the constants into the above equation yields the following simplified form:

$$E = E^\circ - (0.0591/n) \log (\Pi [\text{products}]^x / \Pi [\text{reactants}]^y) \quad (1)$$

Further substituting into Equation (1) for the specific $\text{Na}^+_{(\text{aq})} \rightarrow \text{Na}_{(\text{s})}$ half-reaction at 0.10 M sodium ion concentration gives:

$$\begin{aligned} E &= E^\circ - (0.0591/n) \log ([\text{Na}]/[e^-][\text{Na}^+]) \\ &= -2.71 - (0.0591/1) \log ([1]/[1][0.10]) = -2.77 \text{ v.} \end{aligned}$$

The reader should recall that the concentrations of the electron, pure solids, and the solvent (water), are defined as 1. The calculated value of -2.77 v matches the value of -2.8 v which was estimated from the diagram. It is interesting to note from the Nernst equation that the reduction potential for the half-reaction is dependent only upon the concentration of the sodium ion, Na^+ . Neither the concentration of the hydrogen ion nor the hydroxide ion influences the potential at which the half-reaction occurs since they do not appear in the above equation. Similar calculations may be made for other concentrations of Na^+ . It will be found that the horizontal line separating Na^+ and Na moves from -2.71 v at 1.00 M Na^+ to -2.89 v at $10^{-3.0}$ M, to -3.06 v at $10^{-6.0}$ M, to -3.24 v at $10^{-9.0}$ M, and so on.

The pH (horizontal) axis in Figures 1.1 through 1.4 is a reflection of both the hydrogen ion concentration, $[\text{H}^+]$, and the hydroxide ion concentration, $[\text{OH}^-]$, of the solution. The pH of the solution is related to these values as:

$$\text{pH} = -\log [\text{H}^+], \text{ or } [\text{H}^+] = 10^{-\text{pH}}, \quad (2)$$

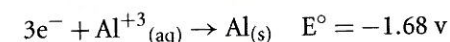
$$\text{pH} = -\log (10^{-14.0}/[\text{OH}^-]) = 14.0 + \log [\text{OH}^-], \text{ or } [\text{OH}^-] = 10^{\text{pH}-14.0}. \quad (3)$$

Equation (3) follows from Equation (2), if one recalls the ion product constant of water:

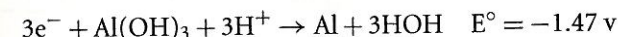
$$[\text{H}^+][\text{OH}^-] = 10^{-14.0}. \quad (4)$$

3. The Al E-pH Diagram

Figure 1.5 is an E-pH diagram for Al under standard conditions. This means that all soluble species are at 1.00 M, the species being Al^{+3} and $\text{Al}(\text{OH})_4^-$. The labels for the four species identify the regions in which they predominate under differing E and pH conditions. These predominance conditions may be seen by examination of the three vertical lines in Figure 1.6 and the three horizontal lines in Figure 1.7. Start at the top of the vertical line at a constant pH of 0.0. As one goes down the line, the predominant species Al^{+3} gives way to the predominant species Al at an E value of about -1.7 v. The reduction half-reaction is written as follows with the E° value as obtained from appropriate tables attached.



As one scans down the vertical line at a constant pH of 7.0, the predominant species $\text{Al}(\text{OH})_3$ is replaced by the predominant Al at an E value of about -1.9 v. The reduction half-reaction along with its E° value is as follows:



Similar observation of the vertical line at a constant pH of 14.0 shows the transformation from $\text{Al}(\text{OH})_4^-$ to Al as the predominant species at an E of

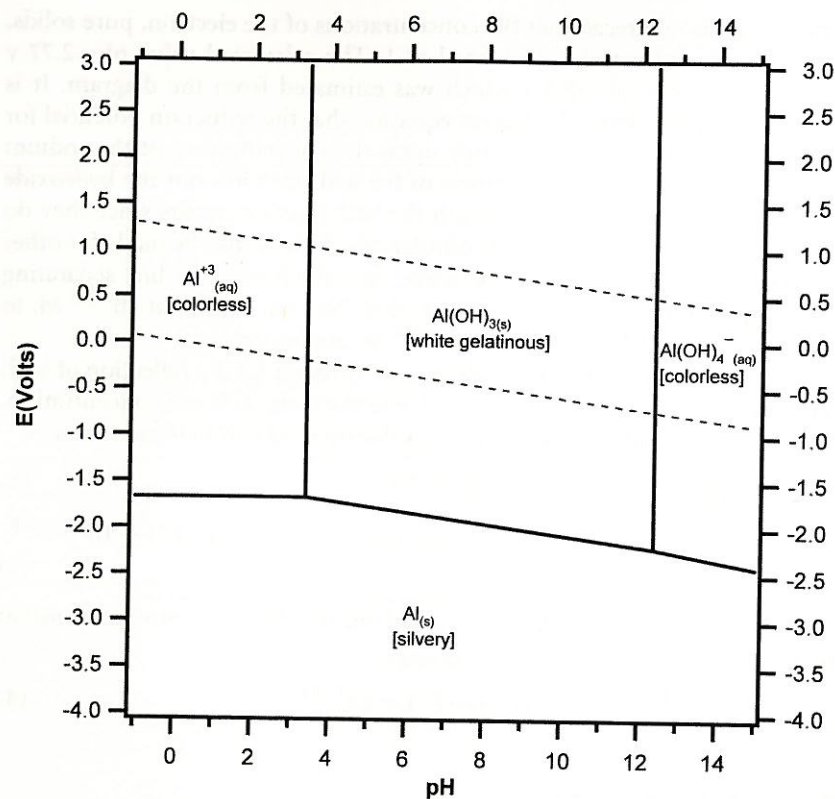
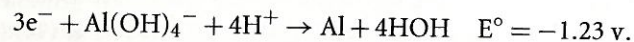


Figure 1.5 E-pH diagram for Al species. Soluble species concentrations (except H^+) = $10^{0.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .

about -2.3 v. The pertinent half-reaction is



Values of E° cannot be used for the last two reactions as given because the H^+ concentration (pH) in both cases is not the standard value of 1.00 M. Hence the Nernst equation must be used to ascertain the applicable values of E when $[H^+]$ is $10^{-7.0}$ M in the $Al(OH)_3$ to Al reaction and $10^{-14.0}$ M in the $Al(OH)_4^-$ reaction.

$$\begin{aligned} E(\text{at pH } 7.0) &= E^\circ - (0.0591/3) \log ([Al][HOH]^3 / [e^-]^3 [Al(OH)_3][H^+]^3) \\ &= -1.47 - (0.0591/3) \log ([1][1]^3 / [1]^3 [1][10^{-7.0}]^3) = -1.88 \text{ v} \end{aligned}$$

$$\begin{aligned} E(\text{at pH } 14.0) &= E^\circ - (0.0591/3) \log ([Al][HOH]^4 / [e^-]^3 [Al(OH)_4^-][H^+]^4) \\ &= -1.23 - (0.0591/3) \log ([1][1]^4 / [1]^3 [1.00][10^{-14.0}]^4) = -2.33 \text{ v} \end{aligned}$$

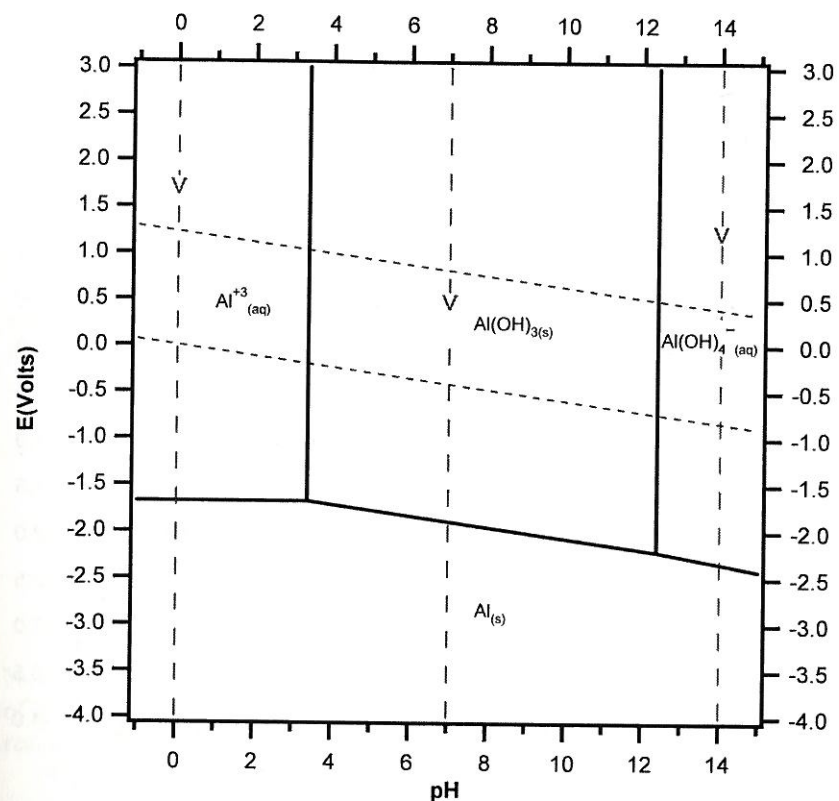
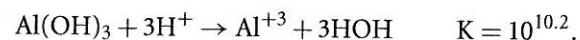


Figure 1.6 E-pH diagram for Al species. Soluble species concentrations (except H^+) = $10^{0.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant pH.

These values of -1.88 v and -2.33 v match the values of -1.9 v and -2.3 v which were estimated from the diagram. Please note also that the line between $Al(OH)_3$ and Al and the line between $Al(OH)_4^-$ and Al are both sloped. This behavior indicates that the lines are functions of both E and pH. This is obvious by virtue of the presence of $[H^+]$ in both equations.

A scan in Figure 1.7 from right to left of the horizontal line at a constant E of 2.00 v indicates a change from $Al(OH)_4^-$ to $Al(OH)_3$ at a pH of 12.4 and a change from $Al(OH)_3$ to Al^{+3} at a pH of 3.4. These transformations are related to the following reactions, to which are appended equilibrium constants obtained from the literature:



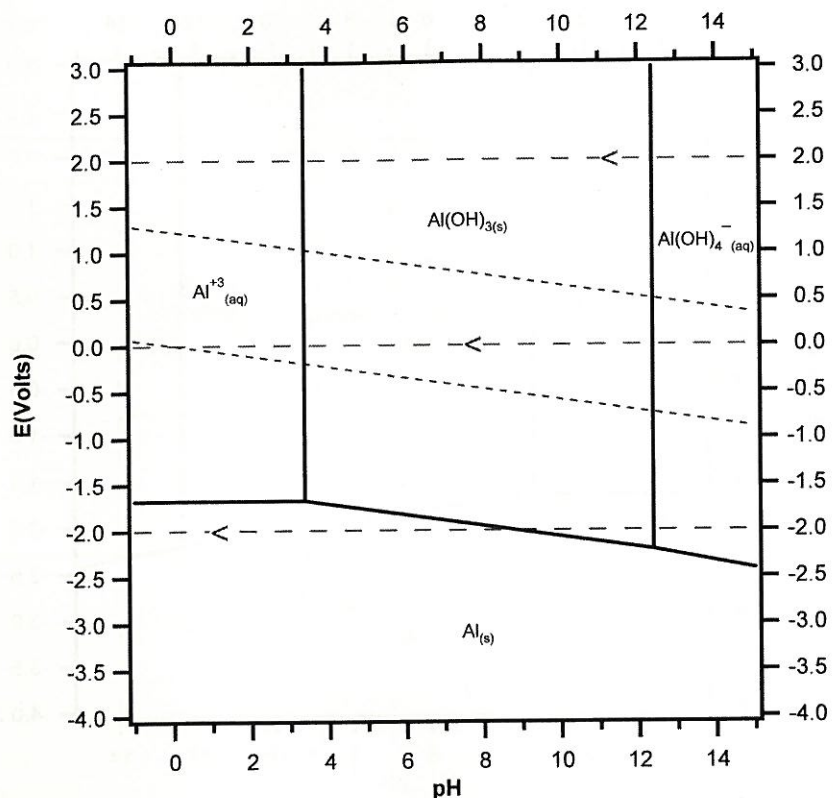


Figure 1.7 E-pH diagram for Al species. Soluble species concentrations (except H^+) = $10^{0.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant E.

It is to be noticed that both of these equilibrium constants are protonation constants, since they apply to the addition of a proton (H^+) to a given species. The pH values for which these reactions occur can be determined using equilibrium constant expressions and the appropriate equilibrium constant, K. Recall that equilibrium expressions take the general form of:

$$K = \frac{\Pi[\text{products}]^x}{\Pi[\text{reactants}]^y} \quad (5)$$

Applying this relationship to these two reactions and solving for the appropriate pH values gives

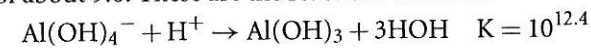
$$K = 10^{12.4} = \frac{[\text{Al}(\text{OH})_3][\text{HOH}]}{[\text{Al}(\text{OH})_4^-][\text{H}^+]} = \frac{[1][1]}{[1.00][\text{H}^+]}$$

$$[\text{H}^+] = 10^{-12.4} \quad \text{pH} = 12.4$$

$$K = 10^{10.2} = \frac{[\text{Al}^{3+}][\text{HOH}]^3}{[\text{Al}(\text{OH})_3][\text{H}^+]^3} = \frac{[1.00][1]^3}{[1][\text{H}^+]^3}$$

$$[\text{H}^+] = 10^{-3.4} \quad \text{pH} = 3.4$$

The same considerations apply to the horizontal line at a constant E of 0.0 v. However, the horizontal line at a constant E of -2.0 v involves two changes as one proceeds from right to left: $\text{Al}(\text{OH})_4^-$ to $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ to Al. The first transition occurs at a pH of about 12.4 and the second change occurs at a pH of about 9.0. These are the reactions involved:



The equilibrium constant is used for the first of these reactions since no electrons are involved in the equation, that is, no change of oxidation state is occurring. But since there are electrons in the second reaction, the Nernst equation which handles reduction reactions must be used.

$$K = 10^{12.4} = \frac{[\text{Al}(\text{OH})_3][\text{HOH}]}{[\text{Al}(\text{OH})_4^-][\text{H}^+]} = \frac{[1][1]}{[1.00][\text{H}^+]}$$

$$[\text{H}^+] = 10^{-12.4} \quad \text{pH} = 12.4$$

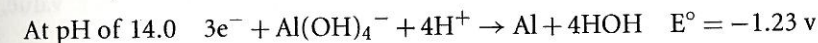
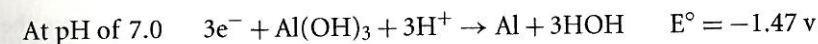
$$E = E^\circ - (0.0591/n) \log \left(\frac{[\text{Al}][\text{HOH}]^3}{[e^-]^3 [\text{Al}(\text{OH})_3][\text{H}^+]^3} \right)$$

$$-2.00 = -1.47 - (0.0591/3) \log \left(\frac{[1][1]^3}{[1]^3 [1][\text{H}^+]^3} \right)$$

$$[\text{H}^+] = 10^{-9.0} \quad \text{pH} = 9.0$$

Notice that the line dividing $\text{Al}(\text{OH})_3$ and Al is sloped, this being characteristic of a reaction that is dependent upon both E and pH. Equations of such reactions show both H^+ and electrons.

Figure 1.8 is an E-pH diagram for Al with the soluble species at 0.10 M except for the hydrogen ion concentration. This changed concentration applies to both Al^{3+} and $\text{Al}(\text{OH})_4^-$. By observation of Figure 1.9, these transition equations can be seen for the descending vertical lines at constant pH values of 0.0, 7.0, and 14.0:



Entering the altered concentrations of the soluble species (Al^{3+} and $\text{Al}(\text{OH})_4^-$) into the Nernst equation as written for these three reactions will yield values of E which will be found comparable to the ones observed in Figure 1.8. These Nernst relationships are as follows:

$$\text{At pH of 0.0, } E = -1.68 - (0.0591/3) \log \left(\frac{[1][1]^3}{[1][1]^3 [0.10]} \right) = -1.70 \text{ v}$$

$$\text{At pH of 7.0, } E = -1.47 - (0.0591/3) \log \left(\frac{[1][1]^3}{[1]^3 [1][10^{-7.0}]^3} \right) = -1.88 \text{ v}$$

$$\text{At pH of 14.0, } E = -1.23 - (0.0591/3) \log \left(\frac{[1][1]^4}{[1]^3 [0.10][10^{-14.0}]^4} \right) = -2.35 \text{ v}$$

Further considering Figure 1.10 in which the concentrations of Al^{3+} and $\text{Al}(\text{OH})_4^-$ have both been altered to 0.10 M, these reactions reflect the changes

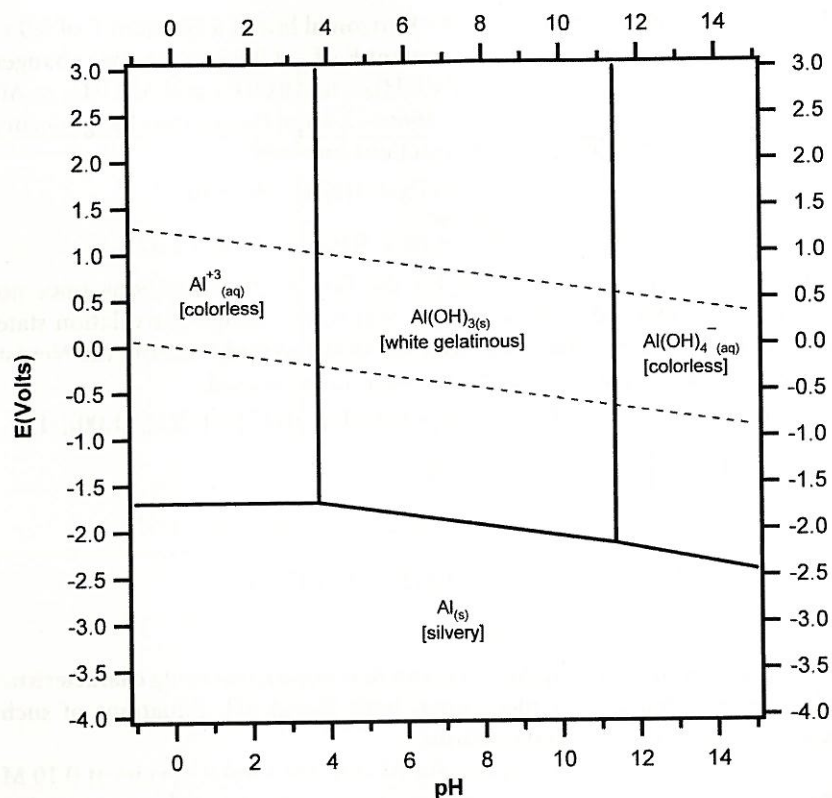
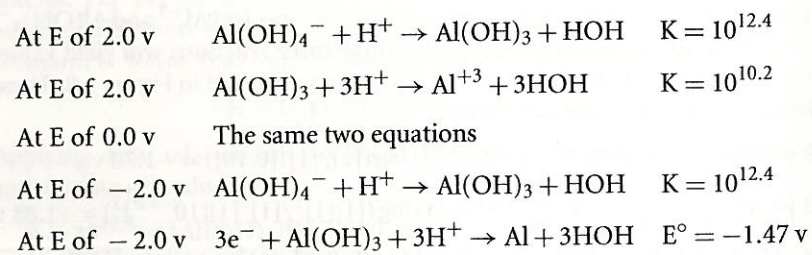


Figure 1.8 E-pH diagram for Al species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .

in species that can be observed as one moves from right to left across the three horizontal lines. Attached to each reaction is its E° value or its K value, whichever is pertinent.



The pH values at which the transformations occur may be calculated by use of the equilibrium constant K or the Nernst equation, the latter being applicable to reactions in which the oxidation state changes, that is, reaction equations

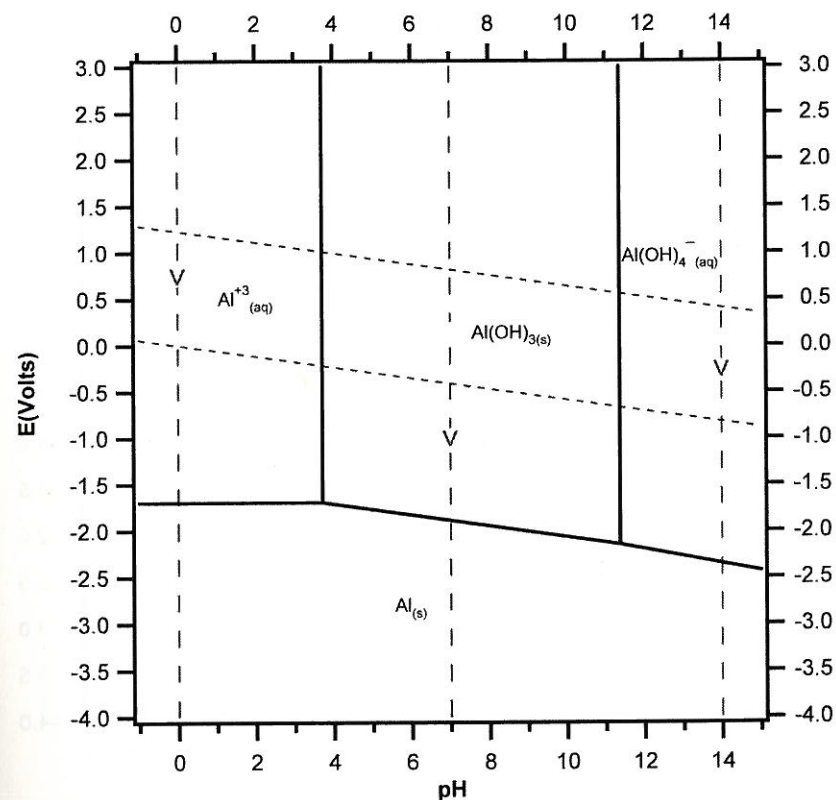


Figure 1.9 E-pH diagram for Al species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant pH.

in which electrons appear.

$$K = 10^{12.4} = \frac{[1][1]}{[0.10][\text{H}^+]} \quad [\text{H}^+] = 10^{-11.4} \quad \text{pH} = 11.4$$

$$K = 10^{10.2} = \frac{[0.10][1]^3}{[1][\text{H}^+]^3} \quad [\text{H}^+] = 10^{-3.7} \quad \text{pH} = 3.7$$

$$E = E^\circ - (0.0591/3) \log \left(\frac{[1][1]^3}{[1]^3[1][\text{H}^+]^3} \right)$$

$$-2.00 = -1.47 - (0.0591/3) \log \left(\frac{[1][1]^3}{[1]^3[1][\text{H}^+]^3} \right)$$

$$[\text{H}^+] = 10^{-9.0} \quad \text{pH} = 9.0$$

The estimated pH values observed on Figure 1.10 for these transformations are 11.5 and 3.8 at a constant E of 2.0 v, the same values at a constant E of 0.0 v, and 11.4 and 9.0 at a constant E of -2.0 v. These fit very well with the calculated values given that the initial values from the figure are estimates. The general procedure presented here can be applied to any number of vertical

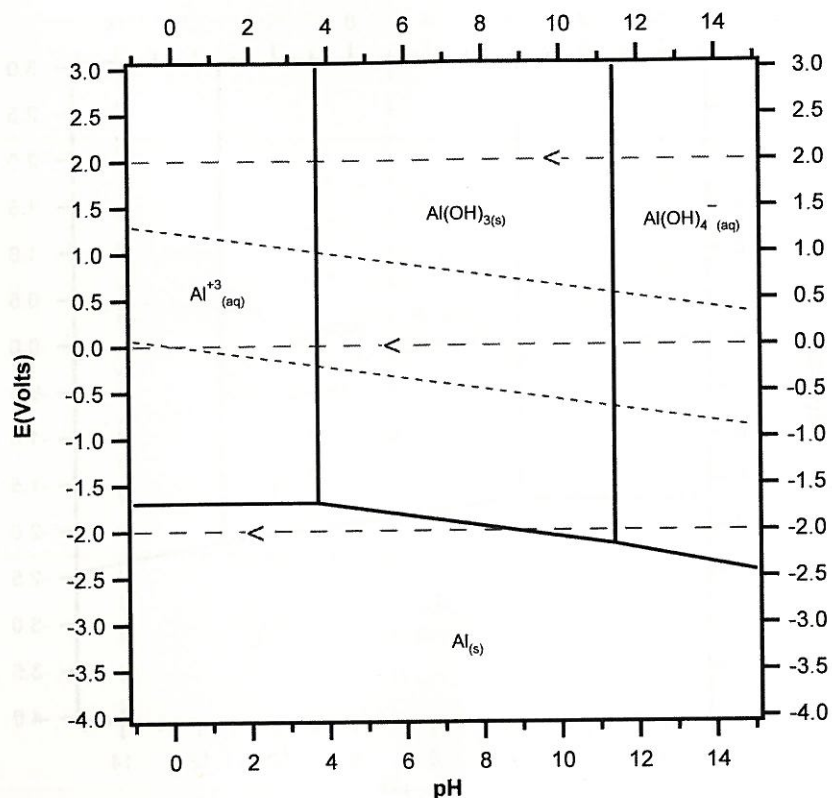


Figure 1.10 E-pH diagram for Al species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant E.

lines and horizontal lines across the E-pH diagram using any soluble species concentrations.

4. The Fe E-pH Diagram

In Figure 1.11, the E-pH diagram for iron, the predominant species is again determined by the combined effect of the potential E and the pH of the solution. The concentrations of all dissolved species in Figure 1.11 have been adjusted to 0.10 M, except for the hydrogen ion concentration. First, consider the three vertical lines in Figure 1.12 at constant pH values of 0.0, 7.0, and 14.0. The species transformations seen at a constant pH of 0.0 are Fe^{+3} to Fe^{+2} at an E of about 0.8 v, and Fe^{+2} to Fe at an E of about -0.4 v. At a constant pH of 7.0, the transformations are $FeO(OH)$ to $Fe(OH)_2$ at an E of

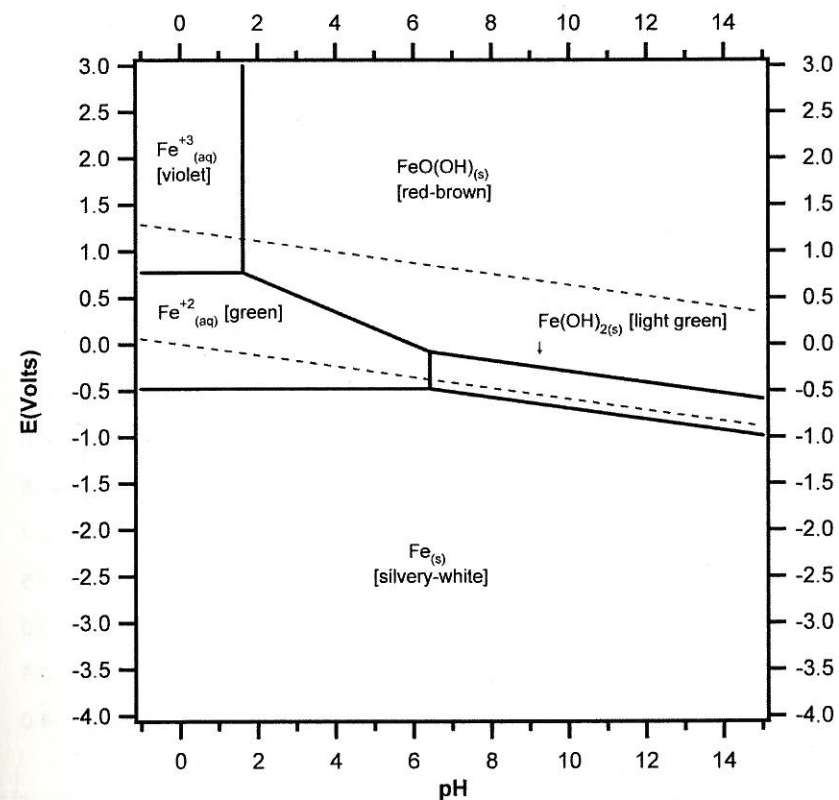
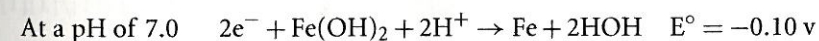
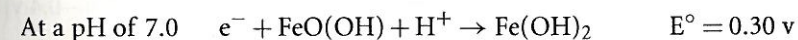
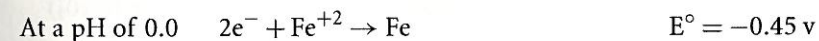
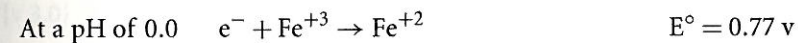


Figure 1.11 E-pH diagram for Fe species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .

about -0.1 v, and $Fe(OH)_2$ to Fe at an E of about -0.5 v. At a constant pH of 14.0, the changes are $FeO(OH)$ to $Fe(OH)_2$ at an E of about -0.5 v, and $Fe(OH)_2$ to Fe at an E of about -0.9 v. The reactions describing these changes are represented by the following equations. Values of E° are attached to the equations.



At a pH of 14.0 Same as the two previous equations

Accurate values of E for comparison with the values estimated from the diagram may be calculated from the Nernst equation as follows. The values

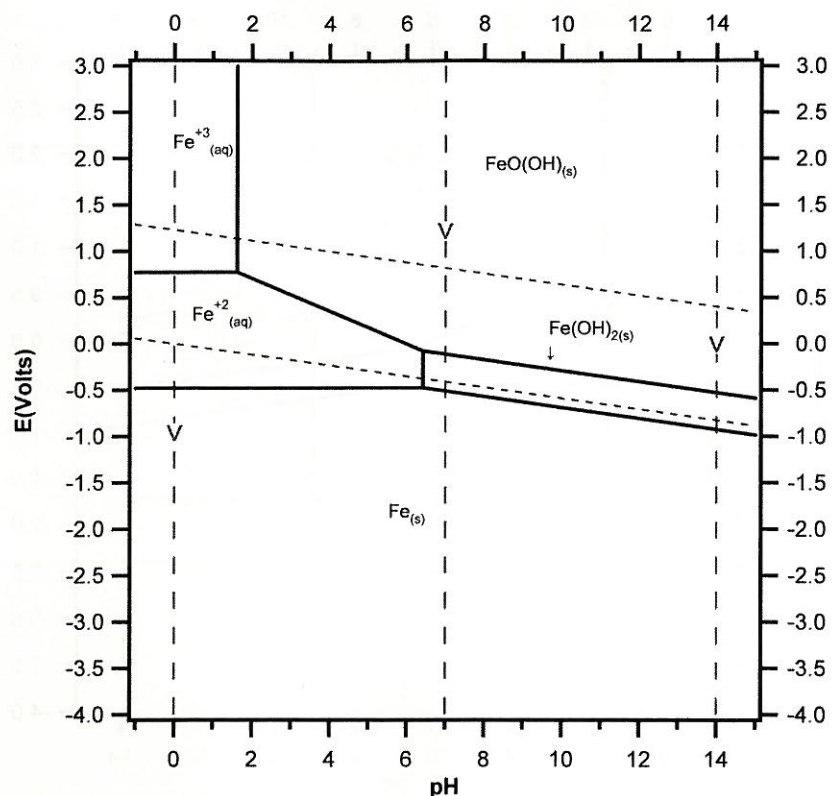


Figure 1.12 E-pH diagram for Fe species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant pH.

estimated by observation of the E-pH diagram are presented in brackets.

$$\begin{aligned} \text{At a pH of 0.0, } E(\text{Fe}^{+3}/\text{Fe}^{+2}) &= 0.77 - (0.0591/1) \log ([0.10]/[1][0.10]) \\ &= 0.77 \text{ v} \quad \{0.8 \text{ v}\} \end{aligned}$$

$$\begin{aligned} \text{At a pH of 0.0, } E(\text{Fe}^{+2}/\text{Fe}) &= -0.45 - (0.0591/2) \log ([1]/[1]^2[0.10]) \\ &= -0.48 \text{ v} \quad \{-0.4 \text{ v}\} \end{aligned}$$

$$\begin{aligned} \text{At a pH of 7.0, } E(\text{FeO(OH)}/\text{Fe(OH)}_2) &= 0.30 - (0.0591/1) \log ([1]/[1][1] \\ &[10^{-7.0}]) = -0.11 \text{ v} \quad \{-0.1 \text{ v}\} \end{aligned}$$

$$\begin{aligned} \text{At a pH of 7.0, } E(\text{Fe(OH)}_2/\text{Fe}) &= -0.10 - (0.0591/2) \log ([1][1]^2/[1]^2[1] \\ &[10^{-7.0}]^2) = -0.51 \text{ v} \quad \{-0.5 \text{ v}\} \end{aligned}$$

$$\begin{aligned} \text{At a pH of 14.0, } E(\text{FeO(OH)}/\text{Fe(OH)}_2) &= 0.30 - (0.0591/1) \log ([1]/[1][1] \\ &[10^{-14.0}]) = -0.53 \text{ v} \quad \{-0.5 \text{ v}\} \end{aligned}$$

$$\begin{aligned} \text{At a pH of 14.0, } E(\text{Fe(OH)}_2/\text{Fe}) &= -0.10 - (0.0591/2) \log ([1][1]^2/[1]^2[1] \\ &[10^{-14.0}]^2) = -0.93 \text{ v} \quad \{-0.9 \text{ v}\} \end{aligned}$$

Now, consider the three horizontal lines in Figure 1.13. Moving from right to left, the line at a constant E of 2.0 v shows the change of FeO(OH) to Fe^{+3} at a pH of about 1.5. The line at a constant E of 0.0 v indicates a change from FeO(OH) to Fe^{+2} at a pH of about 6.0. The horizontal line at a constant E of -2.0 v shows no change, the predominant species at all pH values being Fe. The reactions for the transformations are as follows:

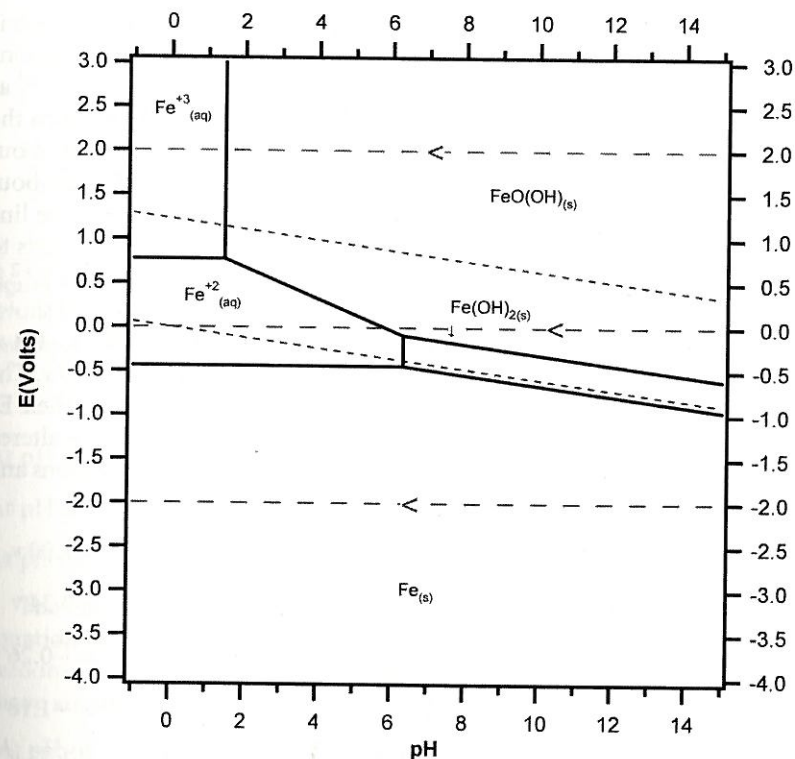
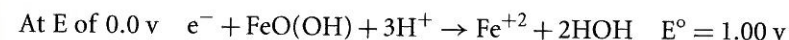
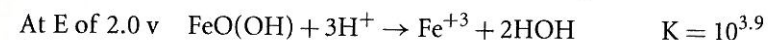


Figure 1.13 E-pH diagram for Fe species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant E.

Application of the equilibrium constant equation along with the value for $[\text{Fe}^{+3}]$ and then the Nernst equation containing values for E and E° and the concentration changes (0.10 M for all other soluble species) will give accurate pH values for comparison with the estimates from the diagram. The estimated values from the diagram are again presented in brackets.

$$K = 10^{3.9} = [\text{Fe}^{+3}][\text{HOH}]^2/[\text{FeO}(\text{OH})][\text{H}^+]^3 = [0.10][1]^2/[1][\text{H}^+]^3$$

$$[\text{H}^+] = 10^{-1.6} \quad \text{pH} = 1.6 \quad \{\text{pH} = 1.5\}$$

$$E = E^\circ - (0.0591/n) \log ([\text{Fe}^{+2}][\text{HOH}]^2/[e^-][\text{FeO}(\text{OH})][\text{H}^+]^3)$$

$$0.00 = 1.00 - (0.0591/1) \log ([0.10][1]^2/[1][1][\text{H}^+]^3)$$

$$[\text{H}^+] = 10^{-6.0} \quad \text{pH} = 6.0 \quad \{\text{pH} = 6.0\}$$

5. The V E-pH Diagram

A further, slightly more complicated, E-pH diagram is the one for V which is depicted in Figure 1.14. This diagram is based upon aqueous concentrations of all soluble species (other than H^+) being at $10^{-3.0}$ M. In Figure 1.15, as before, the three vertical lines will be observed. As one goes down from the top of the line at a constant pH of 1.5, VO_2^+ changes to VO^{+2} at about 0.8 v, VO^{+2} changes to V^{+3} at about 0.2 v, V^{+3} goes over to V^{+2} at about -0.3 v, and V^{+2} transforms into V at about -1.3 v. Coming down the line at a pH of 5.0, H_2VO_4^- changes into V_2O_4 at about 0.5 v, V_2O_4 converts to $\text{V}(\text{OH})_3$ at about -0.1 v, $\text{V}(\text{OH})_3$ is altered to V^{+2} at about -0.5 v, and V^{+2} is replaced by V at about -1.3 v. The vertical line at a constant pH of 11.0 shows these changes as one scans downward: HVO_4^{-2} to $\text{V}(\text{OH})_3$ at about -0.4 v, $\text{V}(\text{OH})_3$ to $\text{V}(\text{OH})_2$ at about -1.2 v, and $\text{V}(\text{OH})_2$ to V at about -1.5 v. The half-reactions corresponding to these changes in species along with their E° values are as follows. Please remember that the E° values will need to be altered to E values by proper consideration of the soluble species concentrations and the hydrogen ion concentrations.

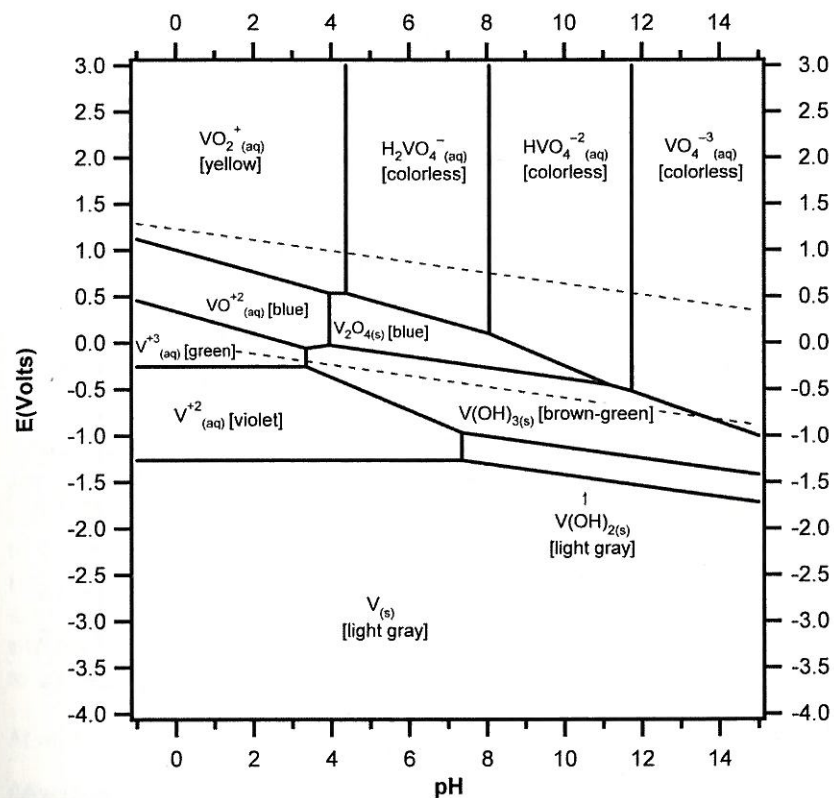
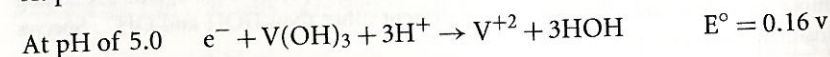
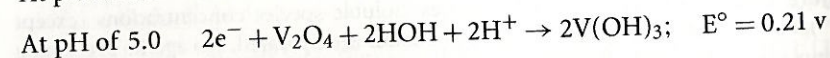
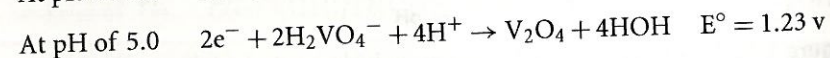
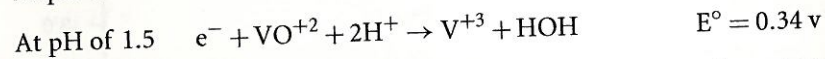
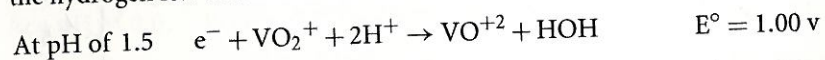
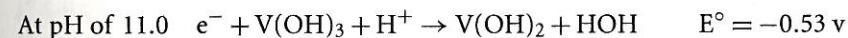


Figure 1.14 E-pH diagram for V species. Soluble species concentrations (except H^+) = $10^{-3.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .



The equations in the previous paragraph may be treated with the Nernst equation to arrive at the calculated values of E at which the changes in predominant species occur. The values estimated from the diagram as given above are shown in brackets.

$$\text{At pH of 1.5} \quad E(\text{VO}_2^+/\text{VO}^{+2}) =$$

$$1.00 - (0.0591/1) \log ([10^{-3.0}][1]/[1][10^{-3.0}][10^{-1.5}]^2) = 0.82 \text{ v} \quad \{0.8 \text{ v}\}$$

$$\text{At pH of 1.5} \quad E(\text{VO}^{+2}/\text{V}^{+3}) =$$

$$0.34 - (0.0591/1) \log ([10^{-3.0}][1]/[1][10^{-3.0}][10^{-1.5}]^2) = 0.16 \text{ v} \quad \{0.2 \text{ v}\}$$

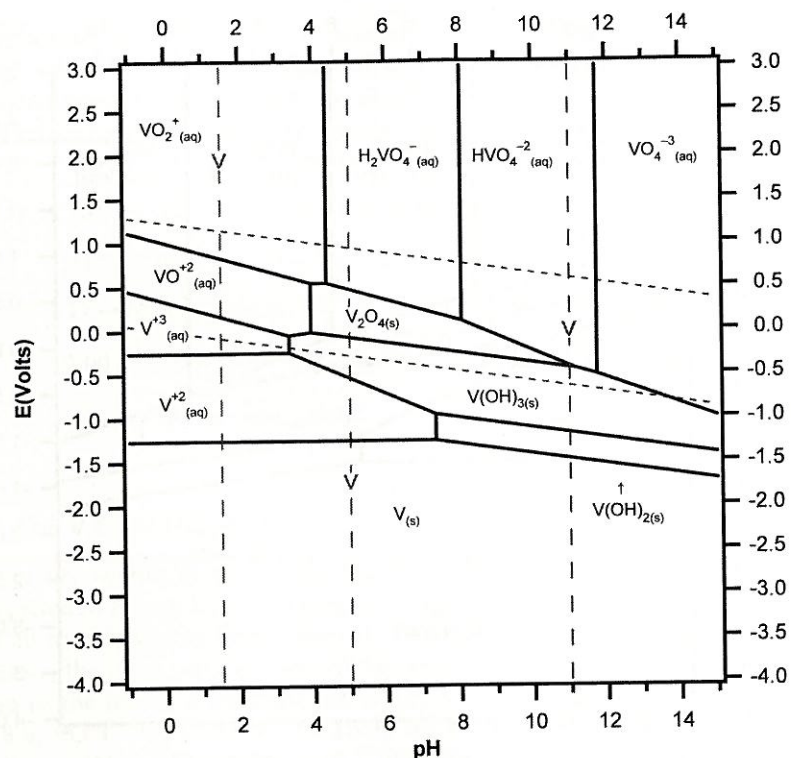


Figure 1.15 E-pH diagram for V species. Soluble species concentrations (except H^+) = $10^{-3.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant pH.

$$\text{At pH of 1.5 } E(V^{+3}/V^{+2}) =$$

$$-0.26 - (0.0591/1) \log ([10^{-3.0}]/[1][10^{-3.0}]) = -0.26 \text{ v} \quad \{-0.3 \text{ v}\}$$

$$\text{At pH of 1.5 } E(V^{+2}/V) =$$

$$-1.18 - (0.0591/2) \log ([1]/[1]^2[10^{-3.0}]) = -1.27 \text{ v} \quad \{-1.3 \text{ v}\}$$

$$\text{At pH of 5.0 } E(H_2VO_4^-/V_2O_4) =$$

$$1.23 - (0.0591/2) \log ([1][1]^4/[1]^2[10^{-3.0}]^2[10^{-5.0}]^4) = 0.46 \text{ v} \quad \{0.5 \text{ v}\}$$

$$\text{At pH of 5.0 } E(V_2O_4/V(OH)_3) =$$

$$0.21 - (0.0591/2) \log ([1]^2/[1]^2[1][1]^2[10^{-5.0}]^2) = -0.09 \text{ v} \quad \{-0.1 \text{ v}\}$$

$$\text{At pH of 5.0 } E(V(OH)_3/V^{+2}) =$$

$$0.16 - (0.0591/1) \log ([10^{-3.0}][1]^3/[1][1][10^{-5.0}]^3) = -0.55 \text{ v} \quad \{-0.5 \text{ v}\}$$

$$\text{At pH of 1.5 } E(V^{+2}/V) =$$

$$-1.18 - (0.0591/2) \log ([1]/[1]^2[10^{-3.0}]) = -1.27 \text{ v} \quad \{-1.3 \text{ v}\}$$

$$\text{At pH of 11.0 } E(HVO_4^{-2}/V(OH)_3) =$$

$$0.96 - (0.0591/2) \log ([1][1]/[1]^2[10^{-3}][10^{-11.0}]^4) = -0.43 \text{ v} \quad \{-0.4 \text{ v}\}$$

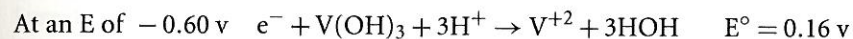
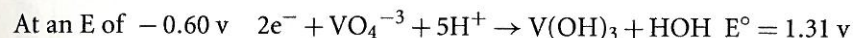
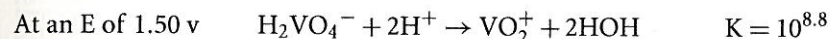
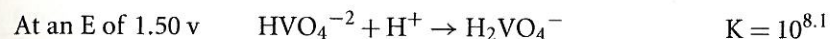
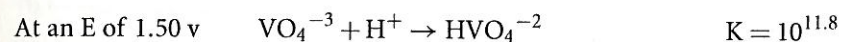
$$\text{At pH of 11.0 } E(V(OH)_3/V(OH)_2) =$$

$$-0.53 - (0.0591/1) \log ([1][1]/[1][1][10^{-11.0}]) = -1.18 \text{ v} \quad \{-1.2 \text{ v}\}$$

$$\text{At pH of 11.0 } E(V(OH)_2/V) =$$

$$-0.83 - (0.0591/2) \log ([1][1]^2/[1]^2[1][10^{-11.0}]^2) = -1.48 \text{ v} \quad \{-1.5 \text{ v}\}$$

There are two horizontal lines in Figure 1.16 which represent changes in pH at constant E values. Observation of the topmost one which occurs at a constant E of 1.50 v shows the following changes as one proceeds from right to left: from VO_4^{-3} to HVO_4^{-2} at a pH of about 11.8, from HVO_4^{-2} to $H_2VO_4^-$ at a pH of about 8.1, and from $H_2VO_4^-$ to VO_2^+ at a pH of about 4.3. Consideration of the other horizontal line at a constant E of -0.60 v shows a transformation of VO_4^{-3} to $V(OH)_3$ at a pH of about 12.5 and of $V(OH)_3$ to V^{+2} at a pH of about 5.2.



The first three equations above lend themselves to treatment by equilibria expressions and the last two by the Nernst expression. In all five cases it is the pH that is being solved for. The estimated values taken from the E-pH diagram are presented in brackets for comparison.

$$\text{At an E of 1.50 v} \quad K = 10^{11.8} = [10^{-3.0}]/[10^{-3.0}][H^+]$$

$$[H^+] = 10^{-11.8} \quad \text{pH} = 11.8 \quad \{\text{pH} = 11.8\}$$

$$\text{At an E of 1.50 v} \quad K = 10^{8.1} = [10^{-3.0}]/[10^{-3.0}][H^+]$$

$$[H^+] = 10^{-8.1} \quad \text{pH} = 8.1 \quad \{\text{pH} = 8.1\}$$

$$\text{At an E of 1.50 v} \quad K = 10^{8.8} = [10^{-3.0}][1]^2/[10^{-3.0}][H^+]^2$$

$$[H^+] = 10^{-4.4} \quad \text{pH} = 4.4 \quad \{\text{pH} = 4.3\}$$

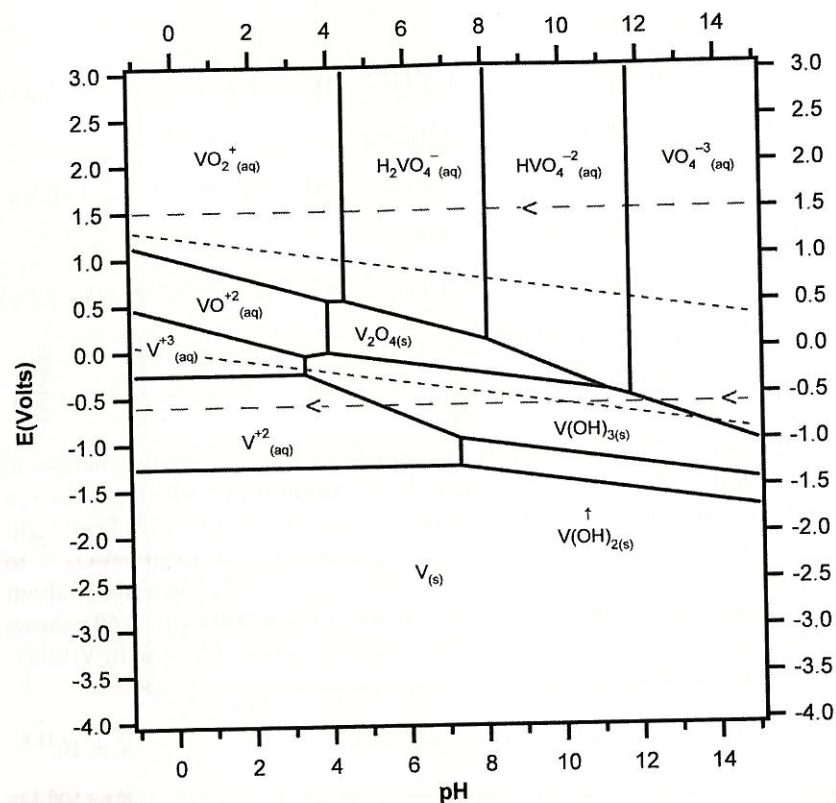


Figure 1.16 E-pH diagram for V species. Soluble species concentrations (except H^+) = $10^{-3.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant E.

$$\text{At an E of } -0.60 \text{ v} \quad -0.60 = 1.31 - (0.0591/2) \log ([1][1]/[1]^2[10^{-3.0}][\text{H}^+]^5)$$

$$[\text{H}^+] = 10^{-12.3} \quad \text{pH} = 12.3 \quad \{\text{pH} = 12.5\}$$

$$\text{At an E of } -0.60 \text{ v} \quad -0.60 = 0.16 - (0.0591/1) \log ([10^{-3.0}][1]^3/[1][1][\text{H}^+]^3)$$

$$[\text{H}^+] = 10^{-5.3} \quad \text{pH} = 5.3 \quad \{\text{pH} = 5.2\}$$

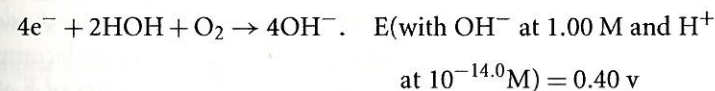
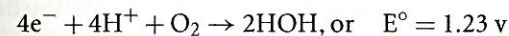
At this juncture, four different E-pH diagrams have been empirically examined in detail. Several important points are to be noted. First, an E-pH diagram shows the regions of species predominance under conditions of E and pH. Second, the regions of predominance are separated by lines which show the transformations of predominant species. Third, these lines are reflections of transformation reactions which can be represented by equations. Fourth, when the transformation equation does not show the hydrogen ion, the

line is horizontal. Fifth, when the transformation equation does not show electrons, the line is vertical. Sixth, when the transformation equation shows both the hydrogen ion and electrons, the line is sloped. Seventh, E values for transformation equations which contain electrons may be ascertained through use of the Nernst relationship along with pertinent E° values. Eighth, pH values for transformation equations which do not contain electrons may be ascertained through use of equilibrium expressions and appropriate equilibrium constant values.

With regard to the lines which show transformations of predominant species, it is of interest to know what the concentration gradients are on each side of the line. For example, consider the line which separates Fe^{+3} from Fe^{+2} in Figure 1.11. On the line the molar amounts of iron are equal: 50% Fe^{+3} and 50% Fe^{+2} . Just 0.07 v below the line, there is 10% Fe^{+3} and 90% Fe^{+2} . For a second illustration, consider the line which separates VO_4^{-3} and HVO_4^{-2} in Figure 1.14. On the line, the molar amounts of vanadium are equal: 50% HVO_4^{-2} and 50% VO_4^{-3} . One pH unit to the right of the line, there is 10% HVO_4^{-2} and 90% VO_4^{-3} . These illustrations indicate that species change is quite sensitive to voltage but less sensitive to pH.

6. The HOH E-pH Diagram

The reader will have seen in all the E-pH diagrams described so far that there are two dashed lines running respectively from 1.29 v to -0.34 v and from 0.06 v to -0.89 v on every diagram. These are the species change lines for water. And since the E-pH diagrams are for aqueous solutions, water is involved in all cases and its behavior under all E and pH conditions must be taken into account. Figure 1.17 shows only the water E-pH diagram. In between the dotted lines the species H^+ and HOH appear, represented hereafter in the text as $\text{HOH} \equiv \text{H}^+$. The HOH represents water and the H^+ represents the hydrogen ion. Since water ionizes slightly into H^+ and OH^- , and the two ions are interdependent, then OH^- is tacitly included in this area. If one observes any vertical line (constant pH) and moves down from the top O_2 is seen to transform into $\text{HOH} \equiv \text{H}^+$ and then $\text{HOH} \equiv \text{H}^+$, is seen to transform into H_2 . The equation for the first transformation may be written in two ways



Since E-pH diagrams involve the pH which is a representation of the hydrogen ion concentration, the first of these equations is preferred.

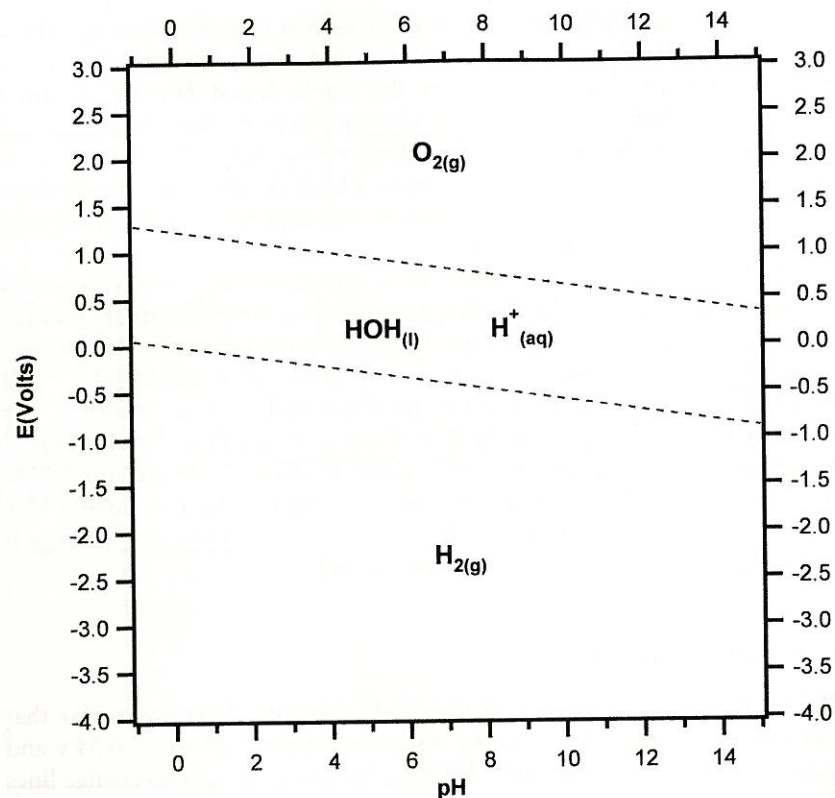
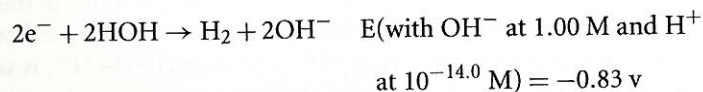
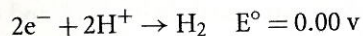


Figure 1.17 E-pH diagram for HOH.

The second transition from $HOH \rightleftharpoons H^+$ may also be written in two ways:



Once again, the equation showing H^+ is preferred because one of the variables for the E-pH diagram is the pH.

As is the pattern with other E-pH diagrams the area above the top dotted line shows the predominance of O_2 , the area below the lower dashed line shows the predominance of H_2 , and the area in between the dashed lines shows the predominance of HOH. In other words, at high potentials water decomposes into O_2 and at low potentials water decomposes into H_2 . Values of E at H^+ concentrations other than 1.00 M may be readily calculated by introducing the above equations and the appropriate E° values into the Nernst relation.

2

The Construction of E-pH Diagrams

1. Introduction

In order to construct an E-pH diagram one needs to follow eight basic steps:

- (1) Select the species of the element involved which contain one or more of the following entities: the element, oxygen, and hydrogen. This is best done by reading the descriptive chemistry of the element in a good inorganic text and identifying the species, both soluble and insoluble, which persist, at least for several minutes, in aqueous solution.
- (2) Starting at the lower left-hand corner of an E-pH framework, arrange the selected species in vertical order of increasing oxidation number of the element. Then, if there are different species with the same oxidation number, arrange them in horizontal order of decreasing protonation (increasing hydroxylation). If there is only one species of a given oxidation number, this species extends across the entire pH range for the purposes of diagram construction.
- (3) Draw in border lines between the species, that is, the lines representing the transformation of a species to another species. You will not know exactly where these lines occur but the approximate regions are sufficient for the purposes of diagram construction.

- (4) Write equations for the transformations that have been indicated. Some of them will involve electrons and therefore will be half-reactions. Such equations must always be written as reductions, that is, with the electrons on the left. In addition, no reaction should contain the OH^- ion; only the H^+ and/or HOH instead.
- (5) From appropriate tabulations, obtain the standard free energy values (ΔG° in kJ/mole) of every species in the equations. These ΔG° values are to be employed in the following relationship which applies to each of the above equations.

$$\Delta G^\circ (\text{reaction}) = \Sigma \Delta G^\circ (\text{products}) - \Sigma \Delta G^\circ (\text{reactants}) \quad (6)$$

- (6) The ΔG° (reaction) values for each equation are to be converted into E° values for those equations containing electrons and into K values for those equations which do not. This is done by use of the following expressions:

$$E^\circ = \Delta G^\circ / -96.49n \quad \log K = \Delta G^\circ / -5.7 \quad (7/8)$$

where n represents the number of electrons in an equation.

- (7) For each reduction half-reaction, the Nernst equation is written with the proper E° , and the relationship is solved for E as a function of pH and the concentrations of the soluble species. For each reaction which does not involve electrons, the equilibrium expression is written with the pertinent K and is solved for pH as a function of the concentrations of the soluble species.
- (8) The above equations of E or K are straight line relationships and either are or can be rewritten in the familiar $y = ax + b$ or $y = b + ax$ form. The lines can then be drawn on the E - pH framework and portions of them can be erased when overlaps occur.

2. Constructing the Ga E-pH Diagram

The eight steps described in the previous section will now be applied to the construction of a Ga E-pH diagram.

Step (1). *Species identification.* Perusal of descriptive inorganic chemistry texts will lead to the discovery of the Ga-, O-, and H-containing species which persist in water. These species consist of the solids Ga and $\text{Ga}(\text{OH})_3$ and the soluble ions Ga^{+3} and $\text{Ga}(\text{OH})_4^-$. It should be noted that $\text{Ga}(\text{OH})_3$ should occur in the basic region and that Ga will sit low on the E-pH diagram because it is the most highly reduced species.

Step (2). *Species placement.* In accordance with the procedure, the most reduced species Ga (oxidation number 0) is placed in the lower left-hand corner. There are no other species with a 0 oxidation number, and therefore Ga is to be assumed to extend all across the bottom of the diagram. The other

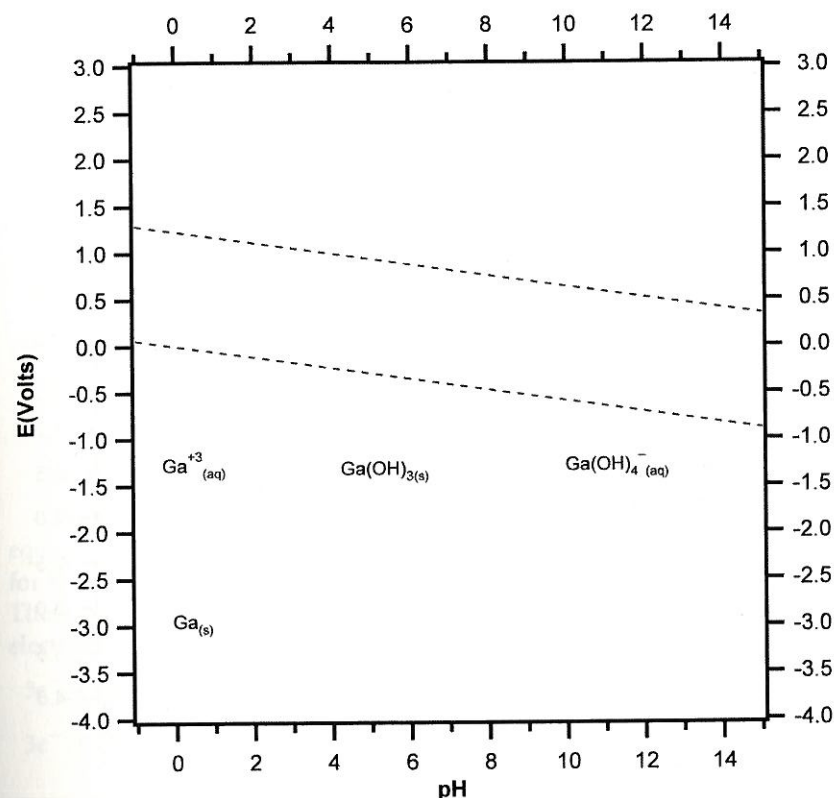
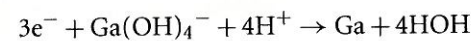
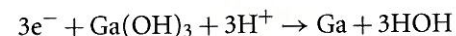
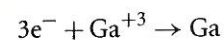


Figure 2.1 E-pH diagram for Ga species. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species placement approximation.

three species are all seen to have a Ga oxidation number of III. Ga^{+3} is likely to exist in the acidic region (low pH) and the other two toward the basic region. Of these other two, $\text{Ga}(\text{OH})_4^-$ will exist farthest toward the basic region because it involves four OH^- whereas $\text{Ga}(\text{OH})_3$ involves only three. These species have been placed on the E-pH framework in Figure 2.1.

Step (3). *Drawing in transformation lines.* A line is now drawn in between every contiguous pair of species. These lines are preliminary placements of transformations from one predominant species to another. See Figure 2.2.

Step (4). *Writing equations.* Each line on the diagram symbolizes a species transformation. The following equations represent these reactions.



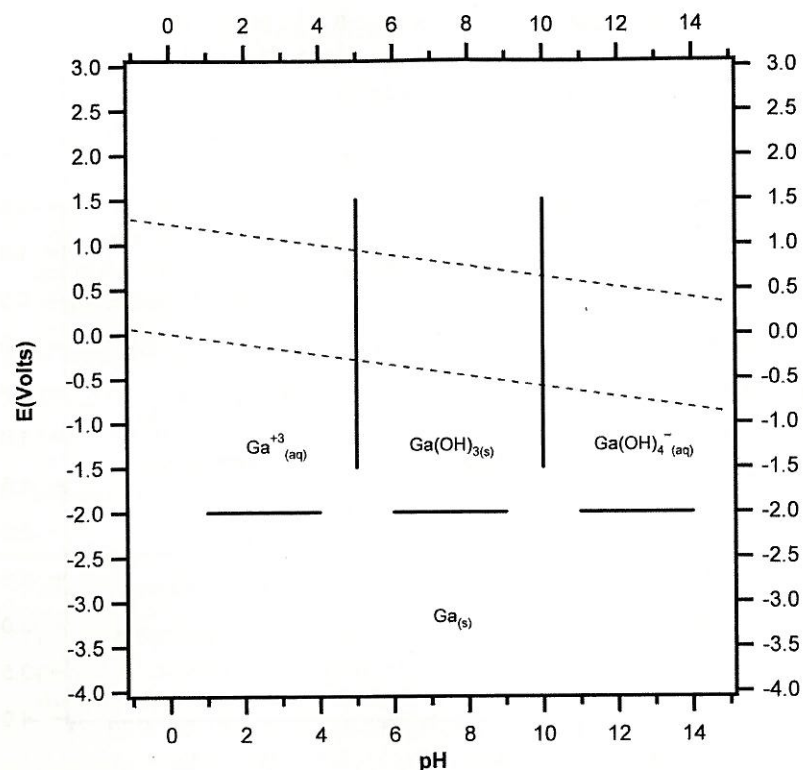
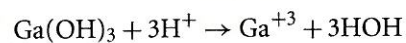
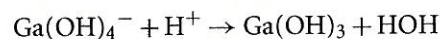
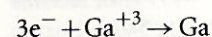


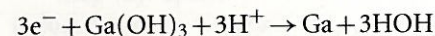
Figure 2.2 E-pH diagram for Ga species. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH⁻. Species with initial line separations.



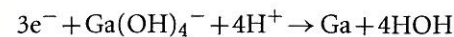
Step (5). *Free energy calculations.* Consultation of standard free energy value tables gives the following ΔG° values in kJ/mole for the four species being considered: Ga (0.0), Ga⁺³ (-159.4), Ga(OH)₃ (-831.4), and Ga(OH)₄⁻ (-982.4). These values are attached to the above equations and ΔG° (reaction) values have been calculated using Equation (6). The ΔG° values for the electron and for H⁺ are both 0.00 kJ/mole and that for HOH is -237.2 kJ/mole.



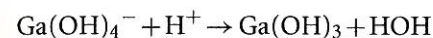
$$0 \quad -159.4 \quad 0 \quad \Delta G^\circ(\text{Ga}^{+3}/\text{Ga}) = 159.4 \text{ kJ/mole}$$



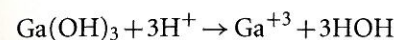
$$0 \quad -831.4 \quad 0 \quad 0 \quad 3(-237.2) \quad \Delta G^\circ(\text{Ga(OH)}_3/\text{Ga}) \\ = 119.8 \text{ kJ/mole}$$



$$0 \quad -982.4 \quad 0 \quad 0 \quad 4(-237.2) \quad \Delta G^\circ(\text{Ga(OH)}_4^-/\text{Ga}) \\ = 33.6 \text{ kJ/mole}$$



$$-982.4 \quad 0 \quad -831.4 \quad -237.2 \quad \Delta G^\circ(\text{Ga(OH)}_4^-/\text{Ga(OH)}_3) \\ = -86.2 \text{ kJ/mole}$$



$$-831.4 \quad 0 \quad -159.4 \quad 3(-237.2) \quad \Delta G^\circ(\text{Ga(OH)}_3/\text{Ga}^{+3}) \\ = -39.6 \text{ kJ/mole}$$

Step (6). *Conversions into E° or K values.* Values of ΔG° for the first three equations are converted into E° values using Equation (7). Values of ΔG° for the last two equations are converted into K values using Equation (8). These conversions are appropriate because the first three equations contain electrons whereas the last two do not.

$$3e^- + \text{Ga}^{+3} \rightarrow \text{Ga} \quad E^\circ = \Delta G^\circ / -96.49n = 159.4 / -96.49(3) = -0.55 \text{ v}$$

$$3e^- + \text{Ga(OH)}_3 + 3\text{H}^+ \rightarrow \text{Ga} + 3\text{HOH} \quad E^\circ = \Delta G^\circ / -96.49n \\ = 119.8 / -96.49(3) = -0.41 \text{ v}$$

$$3e^- + \text{Ga(OH)}_4^- + 4\text{H}^+ \rightarrow \text{Ga} + 4\text{HOH} \quad E^\circ = \Delta G^\circ / -96.49n \\ = 33.6 / -96.49(3) = -0.12 \text{ v}$$

$$\text{Ga(OH)}_4^- + \text{H}^+ \rightarrow \text{Ga(OH)}_3 + \text{HOH} \quad \log K = \Delta G^\circ / -5.7 \\ = -86.2 / -5.7 = 15.1 \quad K = 10^{15.1}$$

$$\text{Ga(OH)}_3 + 3\text{H}^+ \rightarrow \text{Ga}^{+3} + 3\text{HOH} \quad \log K = \Delta G^\circ / -5.7 \\ = -39.6 / -5.7 = 6.9 \quad K = 10^{6.9}$$

Step (7). *Writing E and pH equations.* For each of the above three equations, the Nernst expression is written out, then the equation is solved for E as a function of pH. For each of the last two equations, the equilibrium constant is written out, the equation is put into logarithmic form, and is then solved for the pH.

$$E = E^\circ - (0.0591/n) \log(\Pi[\text{products}]^x / \Pi[\text{reactants}]^y) \quad (1)$$

$$E(\text{Ga}^{+3}/\text{Ga}) = -0.55 - (0.0591/3) \log([1]/[1]^3[\text{Ga}^{+3}]) \\ = -0.55 + 0.020 \log[\text{Ga}^{+3}]$$

$$E(\text{Ga}(\text{OH})_3/\text{Ga}) = -0.41 - (0.0591/3) \log ([1][1]^3/[1]^3[1][\text{H}^+]^3)$$

$$= -0.41 - 0.059 \text{ pH}$$

$$E(\text{Ga}(\text{OH})_4^-/\text{Ga}) = -0.12 - (0.0591/3) \log ([1][1]^4/[1]^3[\text{Ga}(\text{OH})_4^-][\text{H}^+]^4)$$

$$= -0.12 - 0.079 \text{ pH} + 0.020 \log [\text{Ga}(\text{OH})_4^-]$$

$$K(\text{Ga}(\text{OH})_4^-/\text{Ga}(\text{OH})_3) = 10^{15.1} = [1][1]/[\text{Ga}(\text{OH})_4^-][\text{H}^+]$$

$$\text{pH} = 15.1 + \log [\text{Ga}(\text{OH})_4^-]$$

$$K(\text{Ga}(\text{OH})_3/\text{Ga}^{+3}) = 10^{6.9} = [\text{Ga}^{+3}][1]^3/[1][\text{H}^+]^3$$

$$3\text{pH} = 6.9 - \log [\text{Ga}^{+3}]$$

Step (8). *Drawing lines.* The five expressions above represent straight lines. They have been drawn in Figure 2.3. The lines have not been extended

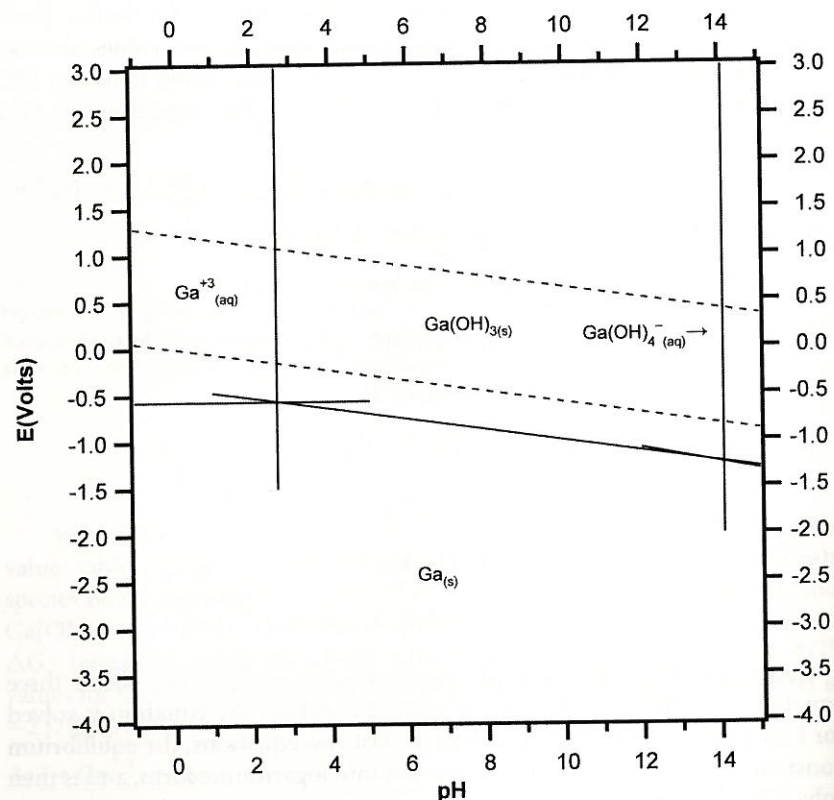


Figure 2.3 E-pH diagram for Ga species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Preliminary line placements.

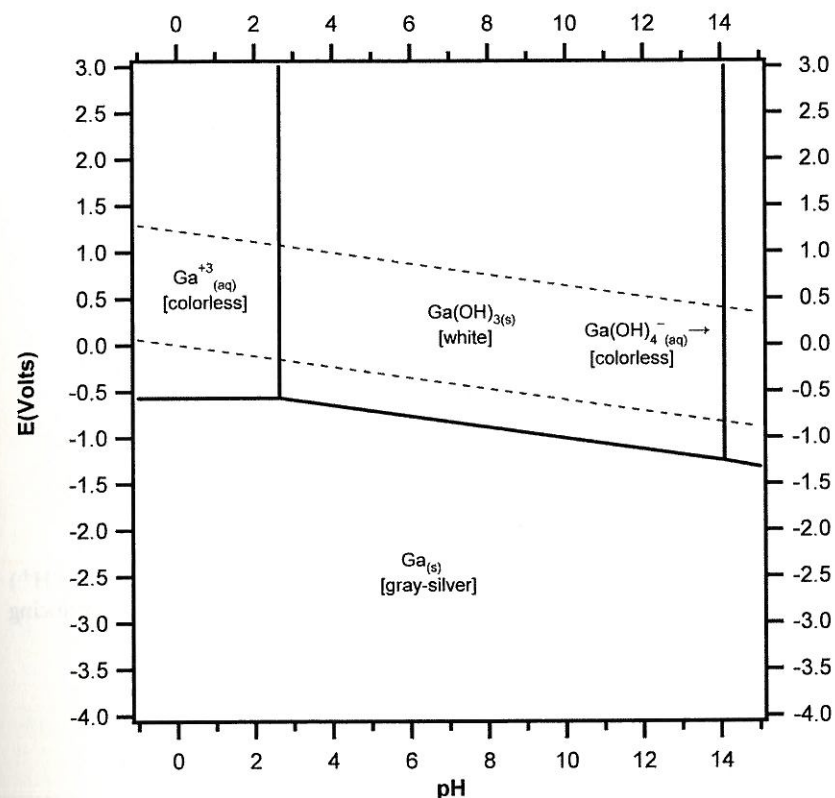


Figure 2.4 E-pH diagram for Ga species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Final diagram.

into regions where the species involved are not pertinent. For example, the Ga^{+3}/Ga line has not been extended into the basic region. The portions of the lines which invade regions of predominant species then have been erased to produce the completed E-pH diagram as displayed in Figure 2.4. Note that the five expressions given above can be used to make detailed calculations of the exact values of E and pH for species transformations.

3. Constructing the Ga E-pH Diagram with Concentration Variations

By using the above procedures, Ga E-pH diagrams at soluble species concentrations of $10^{-1.0}$ M, $10^{-4.0}$ M, and $10^{-7.0}$ M can be made. Individual diagrams for the three concentrations are presented in Figures 2.4–2.6. These three figures have been combined to give Figure 2.7. Notice that E transition

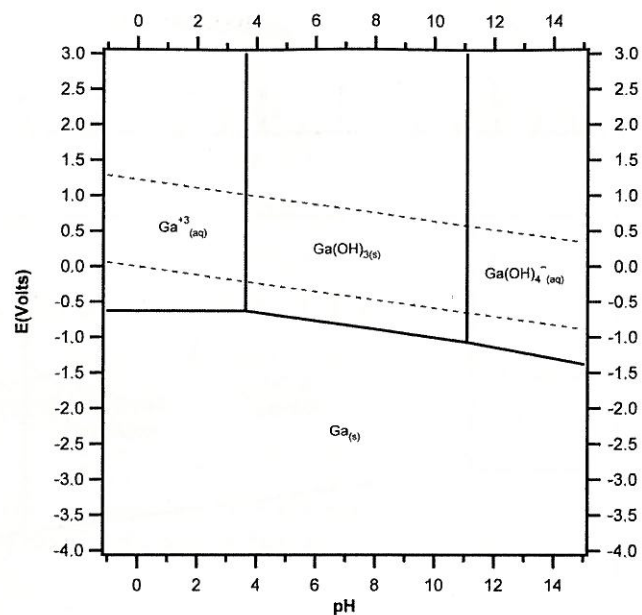


Figure 2.5 E-pH diagram for Ga species. Soluble species concentrations (except H^+) = $10^{-4.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .

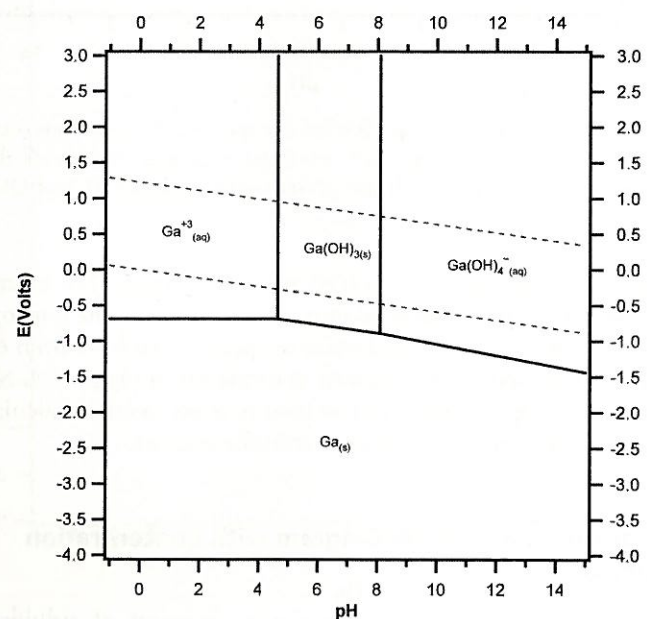


Figure 2.6 E-pH diagram for Ga species. Soluble species concentrations (except H^+) = $10^{-7.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .

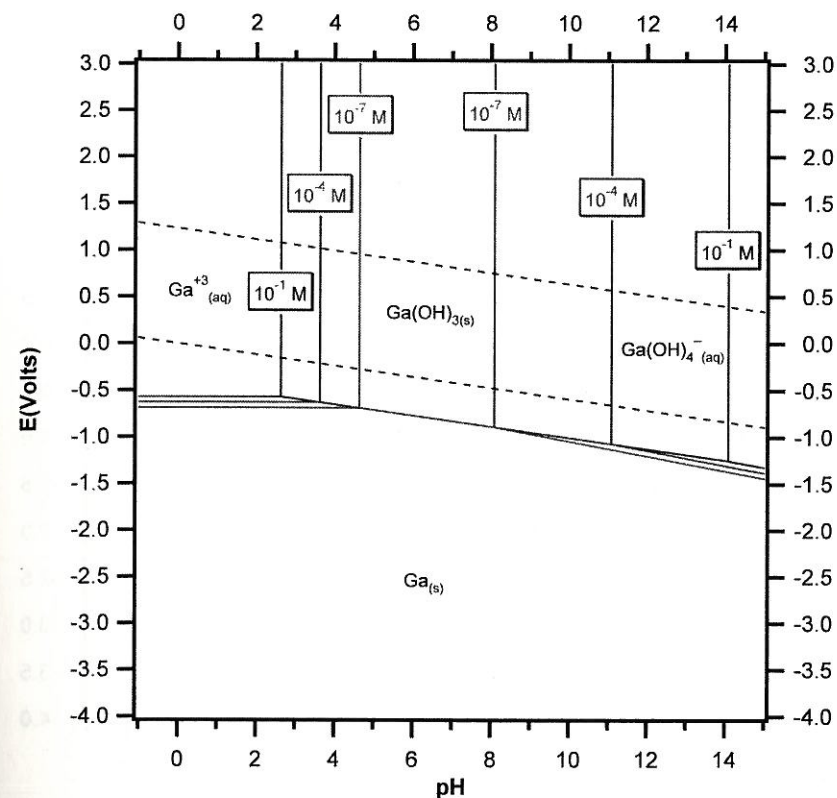


Figure 2.7 E-pH diagram for Ga species. Soluble species concentrations (except H^+) = $10^{-1.0}$, $10^{-4.0}$, and $10^{-7.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Combined diagram.

values are not highly sensitive to concentration variations, for example the Ga^{3+}/Ga line moves from -0.57 v to -0.63 v to -0.69 v with the above concentration changes. However, the pH transition values are quite sensitive to concentration variations, as the values go from $\text{pH} = 14.1$ to $\text{pH} = 11.1$ to $\text{pH} = 8.1$ for the $\text{Ga}(\text{OH})_4^-/\text{Ga}(\text{OH})_3$ line when the above concentrations decrease.

4. Constructing the Mn E-pH Diagram

The eight steps described in the first section of this chapter will now be applied to the construction of an Mn E-pH diagram.

Step (1). *Species identification.* Consultation of a good descriptive inorganic chemistry textbook will indicate that the major species of Mn which

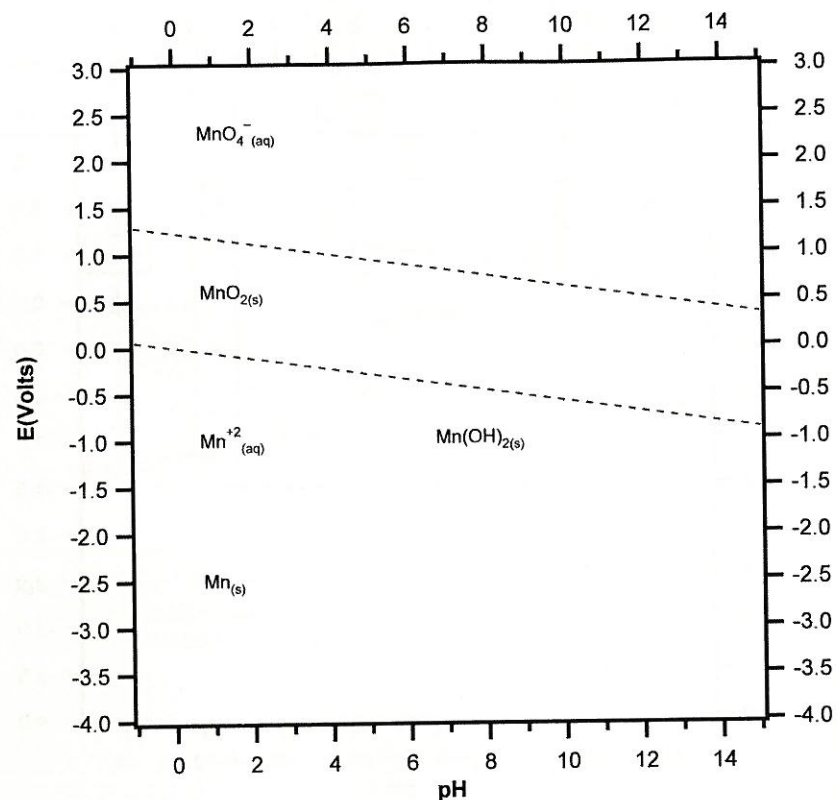


Figure 2.8 E-pH diagram for Mn species. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH⁻. Species placement approximation.

need to be considered for an E-pH diagram are Mn, Mn⁺², Mn(OH)₂, MnO₂, and MnO₄⁻. Several points should be noted: Mn and MnO₂ are solids and Mn⁺² and MnO₄⁻ are solution species; Mn is the only species with an Mn oxidation number of 0 and MnO₄⁻ is the only species with an Mn oxidation number of VII; both Mn⁺² and Mn(OH)₂ have Mn oxidation numbers of II; and Mn⁺² is likely to be an acidic-region species whereas Mn(OH)₂ is a basic-region species.

Step (2). *Species placement.* In accordance with the procedure, the most reduced species Mn (oxidation number 0) is placed on Figure 2.8 in the lower left-hand corner. There are no other species with a 0 oxidation number, and therefore Mn is to be assumed to extend all across the bottom of the diagram. The two species with an Mn oxidation number of II are next added to the figure, with Mn⁺² above Mn and Mn(OH)₂ placed to the right (the basic direction). Then MnO₂ is placed above the Mn⁺² and extended all the

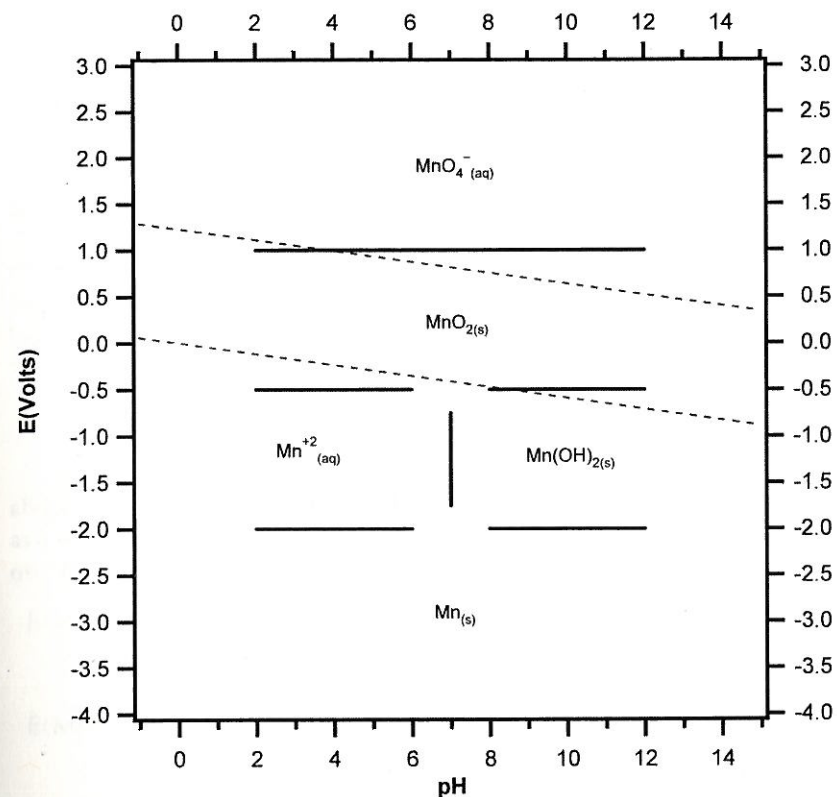
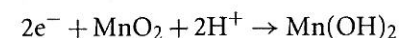
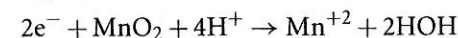


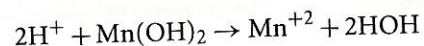
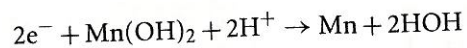
Figure 2.9 E-pH diagram for Mn species. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH⁻. Species with initial line separations.

way across the diagram, and MnO₄⁻ above the MnO₂ and all across the diagram.

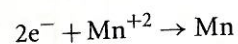
Step (3). *Drawing in transformation lines.* A line is now drawn in between every contiguous pair of species. These lines are preliminary placements of transformations from one predominant species to another. See Figure 2.9.

Step (4). *Writing equations.* Each line on the diagram symbolizes a species transformation. The following equations represent these reactions.

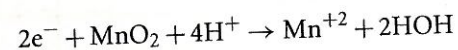




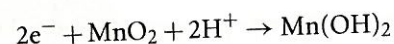
Step (5). *Free energy calculations.* Consultation of standard free energy value tables gives the following ΔG° values in kJ/mole for the five species being considered: Mn (0.0), Mn^{+2} (-228.4), $\text{Mn}(\text{OH})_2$ (-615.0), MnO_2 (-465.3), and MnO_4^- (-447.3). These values are attached to the above equations and $\Delta G^\circ(\text{reaction})$ values have been calculated using Equation (6). The ΔG° values for the electron and for H^+ are both 0.00 kJ/mole and that for HOH is -237.2 kJ/mole.



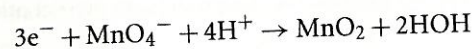
$$0 \quad -228.4 \quad 0 \quad \Delta G^\circ(\text{Mn}^{+2}/\text{Mn}) = 228.4 \text{ kJ/mole}$$



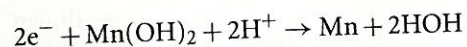
$$0 \quad -465.3 \quad 0 \quad -228.4 \quad 2(-237.2) \quad \Delta G^\circ(\text{MnO}_2/\text{Mn}^{+2}) \\ = -237.5 \text{ kJ/mole}$$



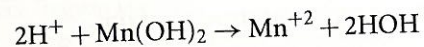
$$0 \quad -465.3 \quad 0 \quad -615.0 \quad \Delta G^\circ(\text{MnO}_2/\text{Mn}(\text{OH})_2) \\ = -149.7 \text{ kJ/mole}$$



$$0 \quad -447.3 \quad 0 \quad -465.3 \quad 2(-237.2) \quad \Delta G^\circ(\text{MnO}_4^-/\text{MnO}_2) \\ = -492.4 \text{ kJ/mole}$$



$$0 \quad -615.0 \quad 0 \quad 0 \quad 2(-237.2) \quad \Delta G^\circ(\text{Mn}(\text{OH})_2/\text{Mn}) \\ = 140.6 \text{ kJ/mole}$$



$$0 \quad -615.0 \quad -228.4 \quad 2(-237.2) \quad \Delta G^\circ(\text{Mn}(\text{OH})_2/\text{Mn}^{+2}) \\ = -87.8 \text{ kJ/mole}$$

Step (6). *Conversions into E° or K values.* Values of ΔG° for the first five equations are converted into E° values using Equation (7). The values of ΔG° for the last equation is converted into a K value using Equation (8). These

conversions are appropriate because the first five equations contain electrons whereas the last one does not.



$$K = 10^{15.4}$$

Step (7). *Writing E and pH equations.* For each of the first five equations above, the Nernst expression is written out, then the equation is solved for E as a function of pH. For the last equation, the equilibrium constant is written out, the equation is put into logarithmic form, and is then solved for the pH.

$$E(\text{Mn}^{+2}/\text{Mn}) = -1.18 - (0.0591/2) \log [1]/[1][\text{Mn}^{+2}] \\ = -1.18 + 0.030 \log [\text{Mn}^{+2}]$$

$$E(\text{MnO}_2/\text{Mn}^{+2}) = 1.23 - (0.0591/2) \log ([\text{Mn}^{+2}][1]^2/[1]^2[1][\text{H}^+]^4) \\ = 1.23 - 0.030 \log [\text{Mn}^{+2}] - 0.118 \text{ pH}$$

$$E(\text{MnO}_2/\text{Mn}(\text{OH})_2) = 0.78 - (0.0591/2) \log ([1]/[1]^2[1][\text{H}^+]^2) \\ = 0.78 - 0.059 \text{ pH}$$

$$E(\text{MnO}_4^-/\text{MnO}_2) = 1.70 - (0.0591/3) \log ([1][1]^2/[1]^3[\text{MnO}_4^-][\text{H}^+]^4) \\ = 1.70 + 0.020 \log [\text{MnO}_4^-] - 0.079 \text{ pH}$$

$$E(\text{Mn}(\text{OH})_2/\text{Mn}) = -0.73 - (0.0591/2) \log ([1][1]^2/[1]^2[1][\text{H}^+]^2) \\ = -0.73 - 0.059 \text{ pH}$$

$$K(\text{Mn}(\text{OH})_2/\text{Mn}^{+2}) = 10^{15.4} = [\text{Mn}^{+2}][1]^2/[1][\text{H}^+]^2 \\ 2\text{pH} = 15.4 - \log [\text{Mn}^{+2}]$$

Step (8). *Drawing lines.* The six expressions above represent straight lines. They have been drawn into Figure 2.10. The lines have not been extended into regions where the species involved are not pertinent. For example, the Mn^{+2}/Mn line has not been extended into the basic region. The portions of the lines which invade regions of predominant species then have been erased to produce the completed E-pH diagram as displayed in Figure 2.11. Note that the six expressions given above can be used to make detailed calculations of the exact values of E and pH for species transformations.

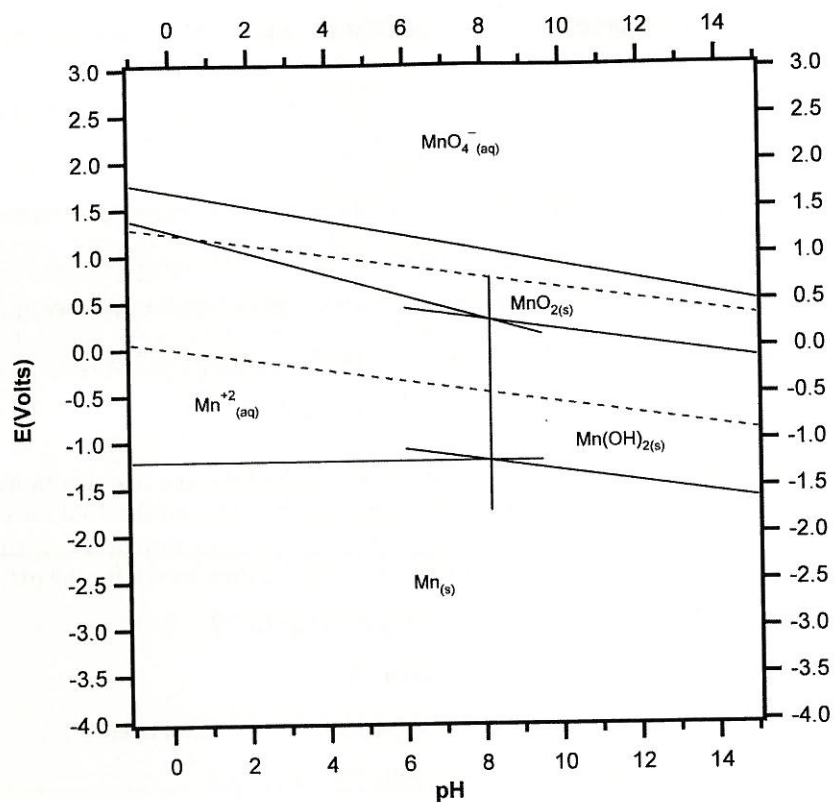


Figure 2.10 E-pH diagram for Mn species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Preliminary line placements.

5. E-pH Computer Programs

The above calculations, being algebraic, can be readily incorporated into a computer program which quickly makes them, generates the lines, and then presents the resulting E-pH diagram. However, the species must be specified. A further advantage of a computer program is that it can be set up to minimize the free energy of the complete system involving any number of species. Such free energy minimizations by hand are tedious and time consuming, but the program can carry them out rapidly. Hence, species which do not exist under competition with other species will be omitted. Several such programs are available commercially, some from universities, and some in the public domain.

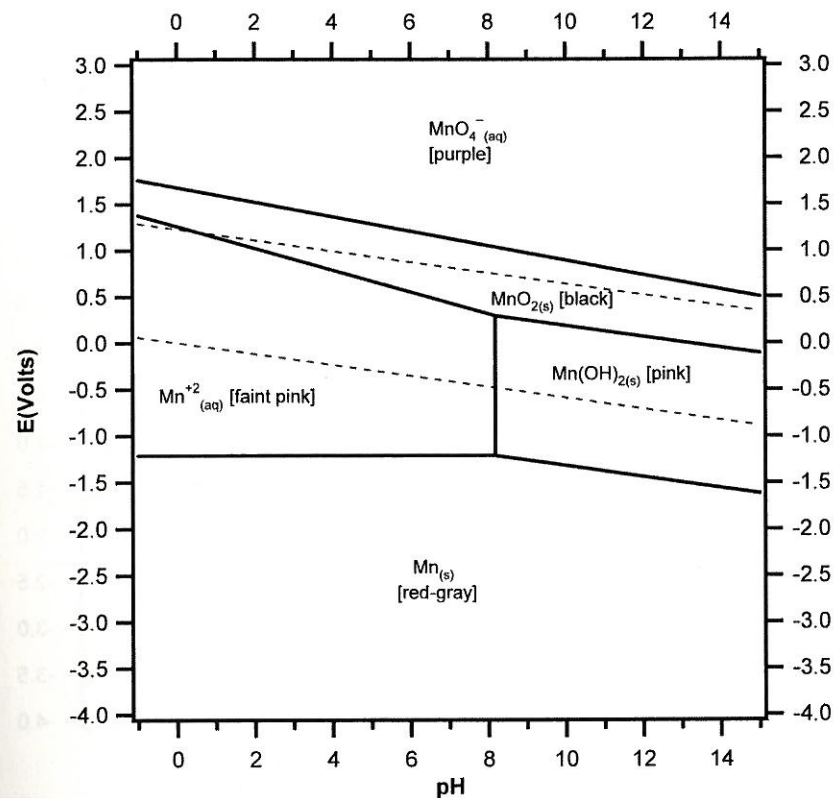


Figure 2.11 E-pH diagram for Mn species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Final diagram.

6. Species Selection and Treatment

All of the solution and solid Mn/O/H species which persist in water (for at least several minutes) and for which standard free energy values are available are as follows (with the ΔG° values in kJ/mole in parentheses): Mn (0.0), MnO (-362.8), MnO₂ (-465.3), Mn₂O₃ (-878.9), Mn₃O₄ (-1283.0), Mn(OH)₂ (-615.0), MnO(OH) (-567.1), HMnO₂⁻ (-506.1), Mn⁺ (-85.0), Mn²⁺ (-228.4), MnO₂⁻² (-429.0), MnO₄⁻ (-447.3), MnO₄⁻² (-503.7), and Mn(OH)⁺ (-407.0). The very fact that ΔG° values are available for these species is an indicator that they are probably important to the aqueous chemistry of Mn. When all these species are employed to construct an E-pH diagram, Figure 2.12 results. Notice that free energy minimization has

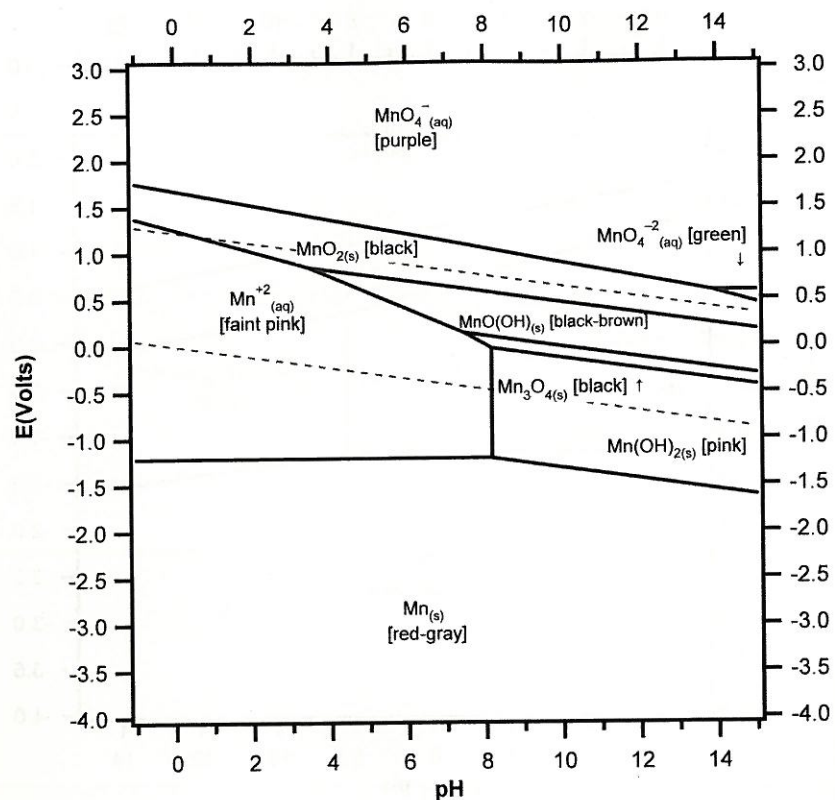


Figure 2.12 E-pH diagram for Mn species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species include Mn, Mn^{+2} , $Mn(OH)_2$, Mn_3O_4 , $MnO(OH)$, MnO_2 , MnO_4^- , and MnO_4^{2-} .

excluded several of the species, indicating that they are not as stable as the competing species which remain.

The species remaining in Figure 2.12 are Mn, Mn^{+2} , $Mn(OH)_2$, Mn_3O_4 , $MnO(OH)$, MnO_2 , MnO_4^{2-} , and MnO_4^- . Notice that Mn_3O_4 has a very narrow range of existence on the E scale, so it might be difficult to maintain under experimental conditions. If it is omitted, the diagram presented as Figure 2.13 is obtained. However, it will be important to include it if geochemical systems are being treated, since it occurs in nature as the mineral hausmannite. Further, the species MnO_4^{2-} also has a very narrow area of existence, and again might be difficult to maintain. Should it be omitted, Figure 2.14 is obtained.

Attention is now directed to the species $MnO(OH)$. This compound, in which Mn is in an oxidation state of III, in a water system could be written as Mn_2O_3 , $MnO(OH)$, or $Mn(OH)_3$, the only differences between them being

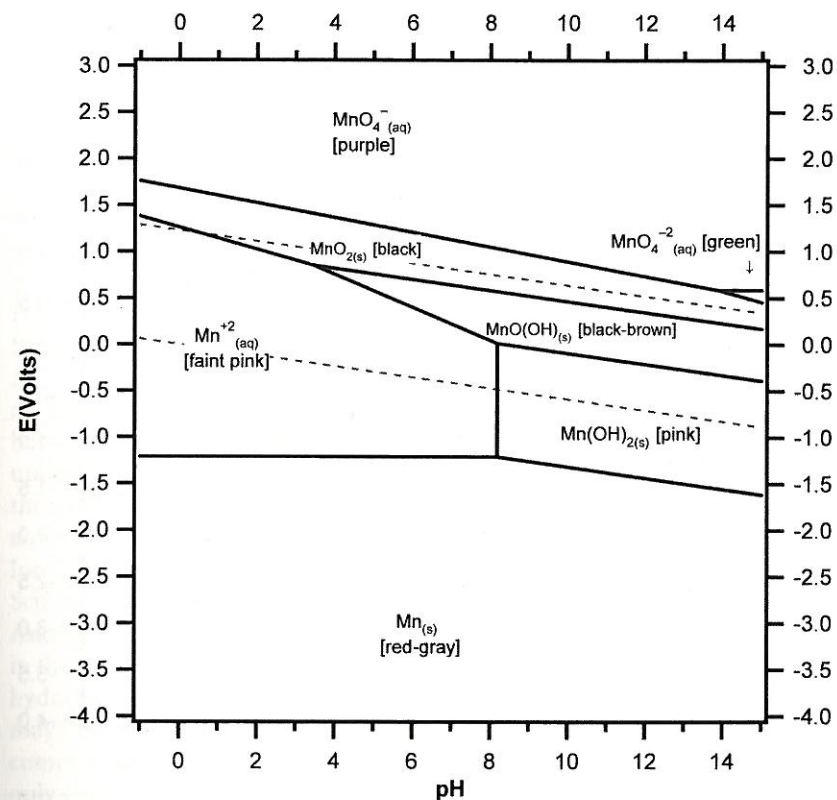


Figure 2.13 E-pH diagram for Mn species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species include Mn, Mn^{+2} , $Mn(OH)_2$, $MnO(OH)$, MnO_2 , MnO_4^- , and MnO_4^{2-} .

the state of hydration [$Mn(OH)_3 - HOH = MnO(OH)$ and $2Mn(OH)_3 - 3HOH = Mn_2O_3$]. Among inorganic hydroxides of metals carrying a III or greater charge, there is a tendency for a freshly precipitated metal ion to be the hydroxide, for example $Mn(OH)_3$. As this compound ages or is heated, it tends to dehydrate, going first to $MnO(OH)$, then perhaps to Mn_2O_3 . In general, the rate of this transformation increases as the charge on the metal ion gets larger (IV or greater). Many investigators believe that for many of the more-highly charged cations, the species with hydroxide ions never occur, the oxide being formed even upon fresh precipitation. For the Mn compounds, it is instructive to consider the ΔG° values of the following reactions:



$$2(-757.3) \quad 2(-567.1) \quad 2(-237.2) \quad \Delta G^\circ(\text{reaction}) = -94.0 \text{ kJ}$$

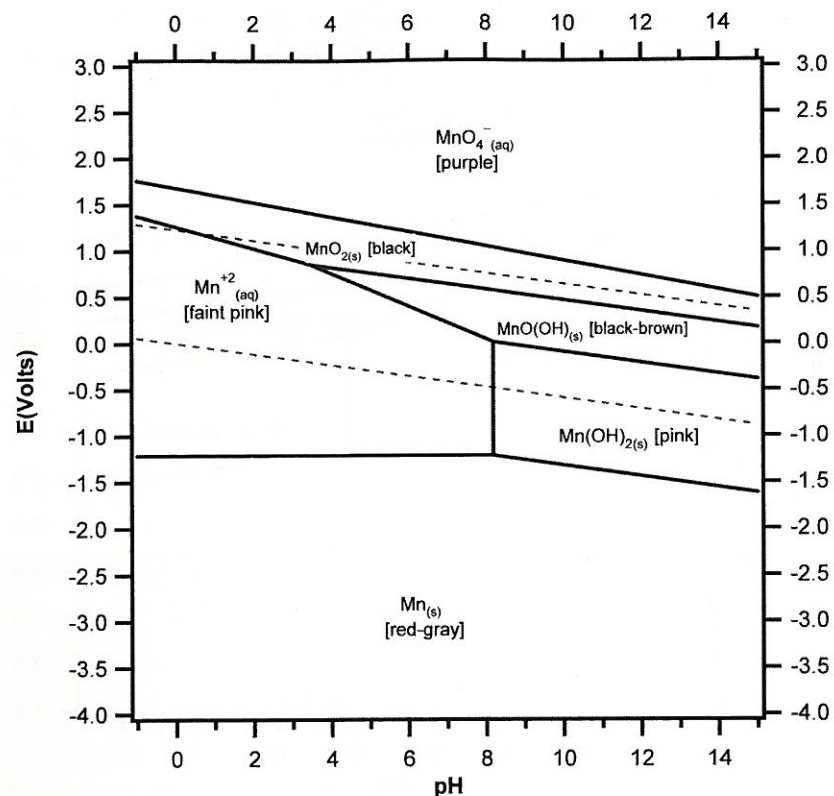
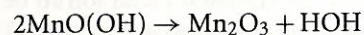


Figure 2.14 E–pH diagram for Mn species. Soluble species concentrations (except H^+) = $10^{-1.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species include Mn, Mn^{+2} , $\text{Mn}(\text{OH})_2$, $\text{MnO}(\text{OH})$, MnO_2 , and MnO_4^- .



$$2(-757.3) \quad -878.9 \quad 3(-237.2) \quad \Delta G^\circ(\text{reaction}) = -75.9 \text{ kJ}$$



$$2(-567.1) \quad -878.9 \quad -237.2 \quad \Delta G^\circ(\text{reaction}) = +18.1 \text{ kJ (Note: +)}$$

Since the $\text{Mn}(\text{OH})_3$ system seeks the lowest (most stable) free energy, the preferred form of the Mn(III) oxide/hydroxide is $\text{MnO}(\text{OH})$ as the E–pH diagram shows. In other words, the most stable is the partially dehydrated species. In other systems, for example, the Al system, possible species would be $\text{Al}(\text{OH})_3$, $\text{AlO}(\text{OH})$, and Al_2O_3 . Analysis of the free energy relations of these species indicates that Al_2O_3 is the preferred species at equilibrium, but chemical experimentation shows that $\text{Al}(\text{OH})_3$ precipitates. The $\text{Al}(\text{OH})_3$ species then undergoes transformation to Al_2O_3 over time or with heating.

In many other cases, free energy values will lead to conclusions regarding which species is the most stable. A further illustration of the importance of species which differ by hydration is AlO_2^- and $\text{Al}(\text{OH})_4^-$, the latter being preferred by free energy calculations ($\text{AlO}_2^- + 2\text{HOH} \rightarrow \text{Al}(\text{OH})_4^-$).

Another important aspect of E–pH diagrams is the oversimplification of species. For example, the Mn^{+2} species in water solution is more properly written as $\text{Mn}(\text{HOH})_6^{+2}$ which reflects the coordination number of the ion. The coordination numbers of +1, +2, and +3 cations for water in solution are generally 6, except for those which show 4 (Li^+ , Be^{+2} , Ag^+ , Pd^{+2} , Pt^{+2} , Sn^{+2}), those which show 8 (K^+ and Rb^+ sometimes, Cs^+ , Sr^{+2} , Ba^{+2} , Y^{+3} , Gd^{+3} to Lu^{+3}), and those which show 9 (La^{+3} to Eu^{+3} , Ac^{+3}). In a similar simplification, $\text{Al}(\text{OH})_4^-$ is more accurately written as $\text{Al}(\text{HOH})_2(\text{OH})_4^-$, again the coordination number of 6 for the cation being recognized. Another example is afforded by the Be^{+2} ion which undergoes hydrolysis (addition of hydroxide ion) at low pH values to give the predominant species $\text{Be}_3(\text{HOH})_6(\text{OH})_3^{+3}$. Details on actual species in aqueous solution can be found in D. T. Richens, *The Chemistry of Aqua Ions*, Wiley, New York, NY, 1997 and in the chemical literature as indexed on SciFinder, a facility provided to libraries by the American Chemical Society. Another oversimplification that will be made is that solid species will be written in the anhydrous form even though in many cases they commonly exist in the hydrated form. Details on the hydration of commonly existing compounds may be obtained from catalogs of suppliers. For example, CuSO_4 commonly comes as the pentahydrate $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, but it will be treated by writing only CuSO_4 . It is very important that these oversimplifications be constantly borne in mind when dealing with E–pH diagrams and when reading listings of compounds.

A further characteristic of E–pH diagrams is one which involves species which are thermodynamically unstable but kinetically are slow to decompose. Consider a piece of Mn metal placed in acid. The reaction is slow because of the limited surface area. However, if the Mn is powdered the reaction is faster due to a marked increase in surface area. Or, consider the MnO_4^- ion in water solution. This ion is known to decompose under these conditions, however, the reaction is ordinarily quite slow. Further, a piece of Al metal will not readily dissolve in dilute acid even though a thermodynamic prediction indicates it will. The reason is that there usually is a thin coating of refractory (non-reactive) Al_2O_3 on the surface. A similar situation is seen, at least in a portion of the pH range, for numerous other metals, particularly those that form highly stable oxides, such as Ti, Zr, Sn, Hf, Be, In, and Cr. Another consideration with regard to rates relates to the following ions: Ir^{+3} , Rh^{+3} , Cr^{+3} , Ru^{+3} , and Pt^{+2} . These ions are referred to as inert, because they and their complexes tend to react slowly, in contradistinction to labile ions which consist of most other ions and which usually react rapidly.

Finally, some considerations with regard to standard free energy values must be taken into account. Many ΔG° values are well known, some have

sizable error limits, and some are estimated from chemical trends and behavior. When an E-pH diagram is derived and then seen to be in contradiction to chemical behavior, the cause may be various including kinetics (slow decomposition), erroneous species identification, or an erroneous ΔG° value. Certain aspects of an E-pH diagram are especially sensitive to ΔG° values, particularly pH values at which a hydroxide precipitates. Consider, for example, the precipitation of $\text{La}(\text{OH})_3$ from a 1.00 M solution of La^{+3} . The accepted value of the ΔG° for $\text{La}(\text{OH})_3$ is -1272.8 kJ/mole, that for La^{+3} is -686.1 kJ/mole, and that for HOH is -237.2 kJ/mole. These values lead to the following equation for the line on the E-pH diagram which separates $\text{La}(\text{OH})_3$ from La^{+3} : $3\text{pH} = 21.9 - \log [\text{La}^{+3}]$. This gives a pH value of 7.3 for the precipitation of the hydroxide. Now let us suppose there is a 13 kJ error (about 1%) in the ΔG° for the $\text{La}(\text{OH})_3$. Using a value of -1259.8 kJ/mole gives this relationship: $3\text{pH} = 24.2 - \log [\text{La}^{+3}]$, which predicts a precipitation pH value of 8.1. Similar calculations show that a difference of 2 kJ (about 0.16%) in the ΔG° of $\text{La}(\text{OH})_3$ results in a 0.1 change in the pH value for precipitation. It is to be noted that many ΔG° values are derived from measured E° values, and many E° values are derived from measured ΔG° values. Equation (7) is used to convert one to the other.

3

Reactions and Applications

1. Introduction

E-pH diagrams involve two types of reactions: (1) Non-redox full reactions and (2) Redox half-reactions. Non-redox full reactions are exemplified by ones such as $\text{Mn}(\text{OH})_2 + 2\text{H}^+ \rightarrow \text{Mn}^{+2} + 2\text{HOH}$. This is not a redox (reduction-oxidation) reaction, since there are no changes in oxidation numbers of the elements. Such reactions are reflected as vertical lines on E-pH diagrams. An example of a redox half-reaction is $2e^- + \text{Mn}^{+2} \rightarrow \text{Mn}$. As can be seen, this is a redox reaction, since electrons appear in the equation, and there is an oxidation number change (II to 0 for Mn). Such reactions are represented by horizontal or sloped lines in an E-pH diagram. In order to write complete reactions in which oxidation numbers change, two half-reactions must be combined. One half reaction will represent a reduction ($2e^- + \text{Mn}^{+2} \rightarrow \text{Mn}$) and the other will represent an oxidation ($\text{Mg} \rightarrow \text{Mg}^{+2} + 2e^-$). These half-reactions are combined such that the electrons cancel out and a complete redox equation is obtained ($\text{Mn}^{+2} + \text{Mg} \rightarrow \text{Mn} + \text{Mg}^{+2}$). Each of the two half-reactions has an E value, and the E value of the resulting complete redox equation is obtained by the difference in the E values of the contributing half-reactions. E-pH diagrams may be employed to predict non-redox full reactions and complete redox reactions and to ascertain E values of the latter. This will be the subject matter of the next few sections.

2. Reactions with HOH

Dashed lines in every E-pH diagram represent the E values for changes in HOH-related species (HOH, H^+ , H_2 , O_2 , and implicitly OH^-). The upper dashed sloped line represents the reaction $4e^- + 4H^+ + O_2 \rightarrow 2HOH$ and is described by the equation $E = 1.23 - 0.059 \text{ pH}$. The lower dashed sloped line represents the reaction $2e^- + 2H^+ \rightarrow H_2$ and is described by the equation $E = 0.00 - 0.059 \text{ pH}$. Figure 3.1 shows the E-pH diagram for HOH, and Figure 3.2 shows the E-pH diagram for Mg with all soluble species at 1.00 M except H^+ . The solid horizontal line represents the reaction $2e^- + Mg^{+2} \rightarrow Mg$, and the equation for the line is $E = -2.36 + 0.030 \log [Mg^{+2}]$.

In order to predict the interaction of Mg with HOH at a pH of 2.0, a vertical cut is made at this pH on the Mg diagram and another at this pH on the HOH diagram. See the dashed vertical lines on Figures 3.1 and 3.2.

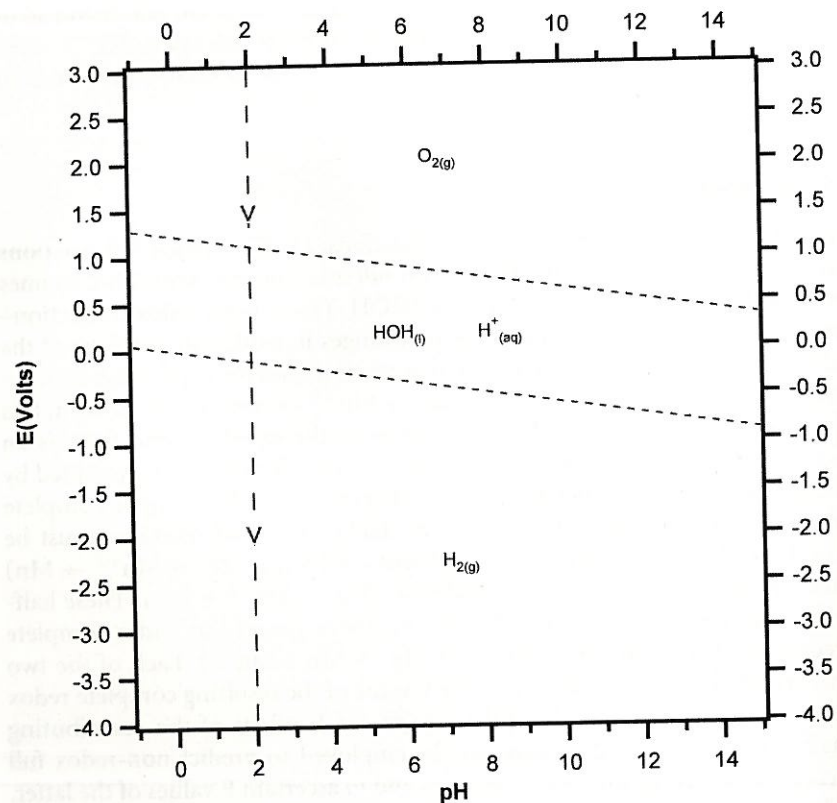


Figure 3.1 E-pH diagram for HOH. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant pH.

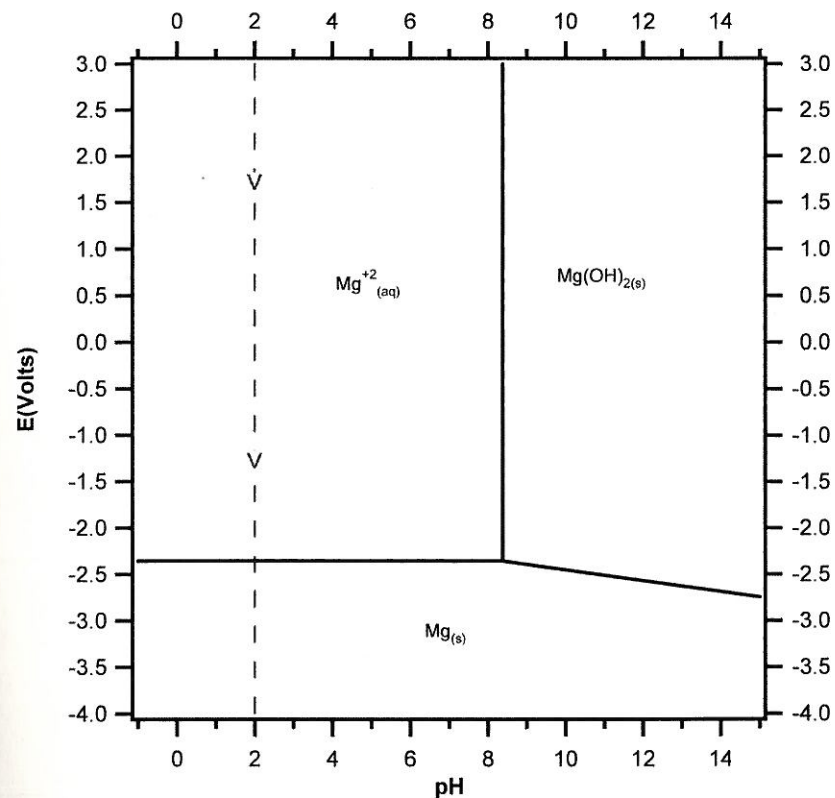


Figure 3.2 E-pH diagram for Mg species. Soluble species concentrations (except H^+) = $10^{0.0}$ M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- . Species transformations take place at constant pH.

These vertical cuts are called electron ladders. Rungs are placed on them at the proper E values, and proper species are indicated below and above the rungs. These are shown in Figure 3.3. The exact values of E for the HOH ladder have been calculated from the equations given above, and that for the Mg ladder from $E = -2.36 + 0.030 \log [Mg^{+2}]$, which is the equation that describes the line between Mg^{+2} and Mg on the Mg E-pH diagram.

Once these electron ladders have been written out (using the E-pH diagrams and the equations that describe the lines), the two ladders are combined as in Figure 3.4. The interaction between Mg and $HOH \equiv H^+$ at a pH of 2.0 can now be described using these rules: (1) Identify the two reacting species, Mg and $HOH \equiv H^+$, (2) Identify the lowest rung which contains one of the reacting species, -2.36 v with Mg, (3) Identify the rung above it which contains the other reacting species, -0.12 v with $HOH \equiv H^+$, (4) Write an equation showing the reaction of the lower species of the lower

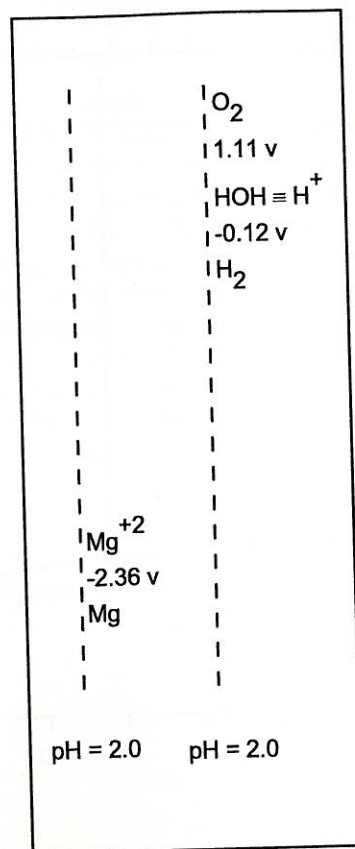
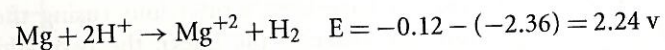


Figure 3.3 Electron ladders for Mg and H₂O at pH = 2.0. Soluble species concentrations (except H⁺) = 10^{0.0} M.

rung (Mg) with the upper species of the upper rung (HOH ≡ H⁺) to give the two intermediate species, Mg⁺² and H₂, (5) Balance the equation, (6) Subtract the E value of the lower rung from the E value of the upper rung to give the E value of the complete equation. These steps lead to this complete redox reaction:



When the E for a reaction is positive, as this one is, the reaction will proceed to the right. A positive E value corresponds to a negative ΔG value as indicated by $\Delta G = -96.49nE$.

A similar procedure can be carried out at any desired pH. When such is done for a pH of 10.0, the following equations can be used to define the values

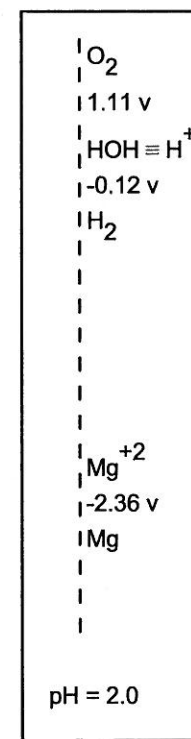


Figure 3.4 Combined electron ladder for Mg and H₂O at pH = 2.0. Soluble species concentrations (except H⁺) = 10^{0.0} M.

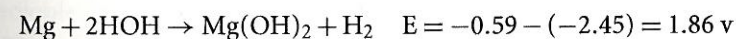
and species at the three rungs:

$$E(\text{O}_2/\text{HOH} \equiv \text{H}^+) = 1.23 - 0.059 \text{ pH} = 0.64 \text{ v,}$$

$$E(\text{HOH} \equiv \text{H}^+/\text{H}_2) = 0.00 - 0.059 \text{ pH} = -0.59 \text{ v, and}$$

$$E(\text{Mg}(\text{OH})_2/\text{Mg}) = -1.86 - 0.059 \text{ pH} = -2.45 \text{ v.}$$

The consequent electron ladder is shown in Figure 3.5. The reaction which results by the combination of the lower species at the lower rung with the upper species at the upper rung to give the intermediate species is:



Another variation on the theme would be to alter the concentration of the Mg in the Mg E-pH diagram. This would give a different value for the rung separating the two Mg species. Let us suppose that the Mg soluble species concentrations be designated as 10^{-4.0} M and that the pH be specified as 4.0.

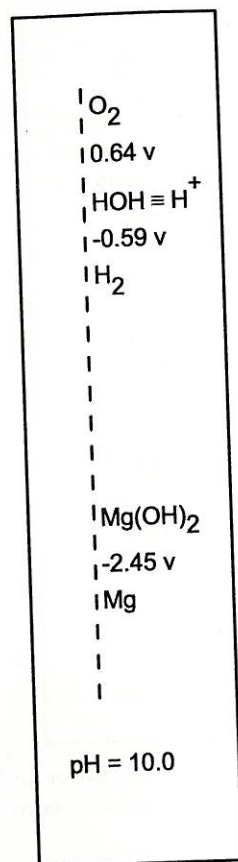


Figure 3.5 Combined electron ladder for Mg and H₂O at pH = 10.0. Soluble species concentrations (except H⁺) = 10^{0.0} M.

The pertinent equations for the rungs on the electron ladder are as follows:

$$E(\text{O}_2/\text{HOH} \equiv \text{H}^+) = 1.23 - 0.059 \text{ pH} = 1.23 - 0.059(4.0) = 0.99 \text{ v}$$

$$E(\text{HOH} \equiv \text{H}^+/\text{H}_2) = 0.00 - 0.059 \text{ pH} = 0.00 - 0.059(4.0) = -0.24 \text{ v}$$

$$E(\text{Mg}^{+2}/\text{Mg}) = -2.36 + 0.03 \log [\text{Mg}^{+2}] = -2.36 + 0.03 \log [10^{-4.0}] = -2.48 \text{ v}$$

The electron ladder which shows these interrelationships is pictured in Figure 3.6. And the reaction which takes place along with its potential is

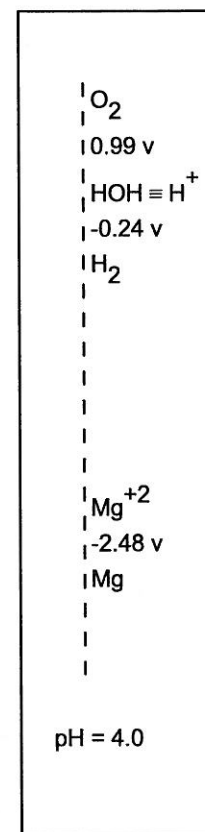
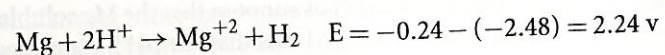


Figure 3.6 Combined electron ladder for Mg and H₂O at pH = 4.0. Soluble species concentrations (except H⁺) = 10^{-4.0} M.

3. The Mn-Fe-HOH System (Excess Mn Species)

Consideration will now be paid to the Mn-Fe-HOH system. The E-pH diagrams for Mn and Fe at soluble species concentrations of 1.00 M (except H⁺) are given in Figures 3.7 and 3.8. Remember that the HOH E-pH diagram is involved in each of these. Electron ladders have been abstracted at a pH of 1.0, the Mn soluble species concentrations have been left at 1.00 M, and the Fe species have been set at 10^{-3.0} M. These diagrams appear as Figures 3.9 and 3.10, with a combined diagram as Figure 3.11. Recognizing the soluble species concentrations as 1.00 M for Mn, and 10^{-3.0} M for Fe, and the pH as 1.0, the exact values of E for each of the rungs on the ladders have been calculated from these equations:

$$E(\text{MnO}_4^-/\text{MnO}_2) = 1.70 - 0.079 \text{ pH} + 0.020 \log [\text{MnO}_4^-] = 1.62 \text{ v}$$

$$E(\text{MnO}_2/\text{Mn}^{+2}) = 1.23 - 0.118 \text{ pH} - 0.030 \log [\text{Mn}^{+2}] = 1.11 \text{ v}$$

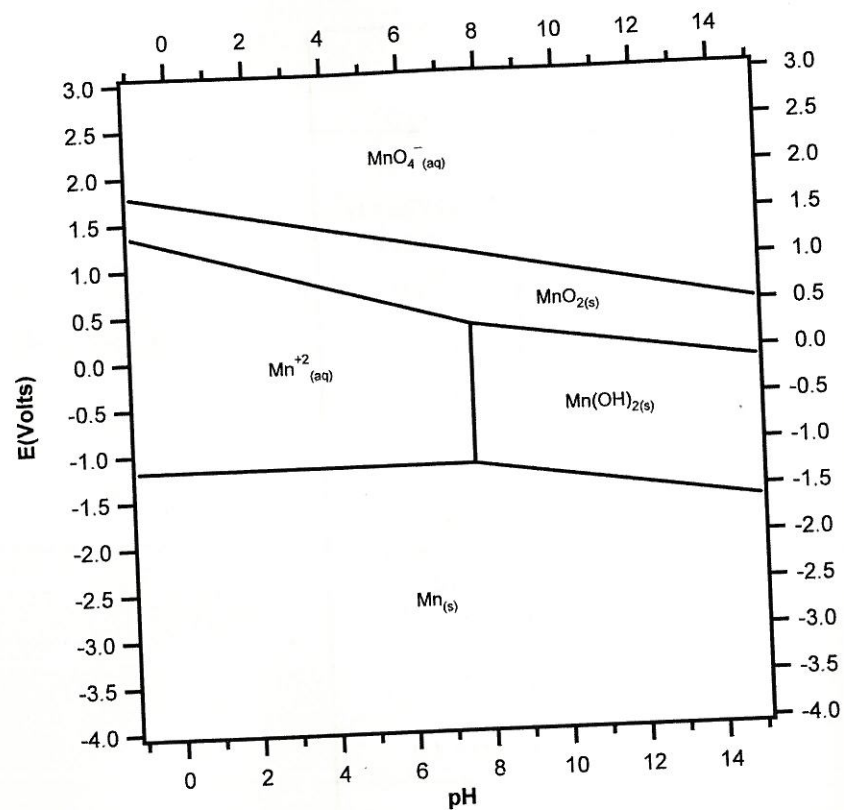


Figure 3.7 E-pH diagram for Mn species. Soluble species concentrations (except H⁺) = 10^{0.0} M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH⁻.

$$E(\text{Mn}^{+2}/\text{Mn}) = -1.18 + 0.030 \log [\text{Mn}^{+2}] = -1.18 \text{ v}$$

$$E(\text{O}_2/\text{HOH} \equiv \text{H}^+) = 1.23 - 0.059 \text{ pH} = 1.17 \text{ v}$$

$$E(\text{HOH} \equiv \text{H}^+/\text{H}_2) = 0.00 - 0.059 \text{ pH} = -0.06 \text{ v}$$

$$E(\text{Fe}^{+3}/\text{Fe}^{+2}) = 0.77 \text{ v}$$

$$E(\text{Fe}^{+2}/\text{Fe}) = -0.45 + 0.030 \log [\text{Fe}^{+2}] = -0.54 \text{ v}$$

Now numerous possible reactions can be predicted. Take special note that the Mn species are in considerable excess of the Fe species. Consider the situation in which a large amount of Mn metal is placed in the solution with Fe metal. Obviously nothing happens because the Fe is as far reduced as it can be. In other words, Fe is not an upper species on a rung above

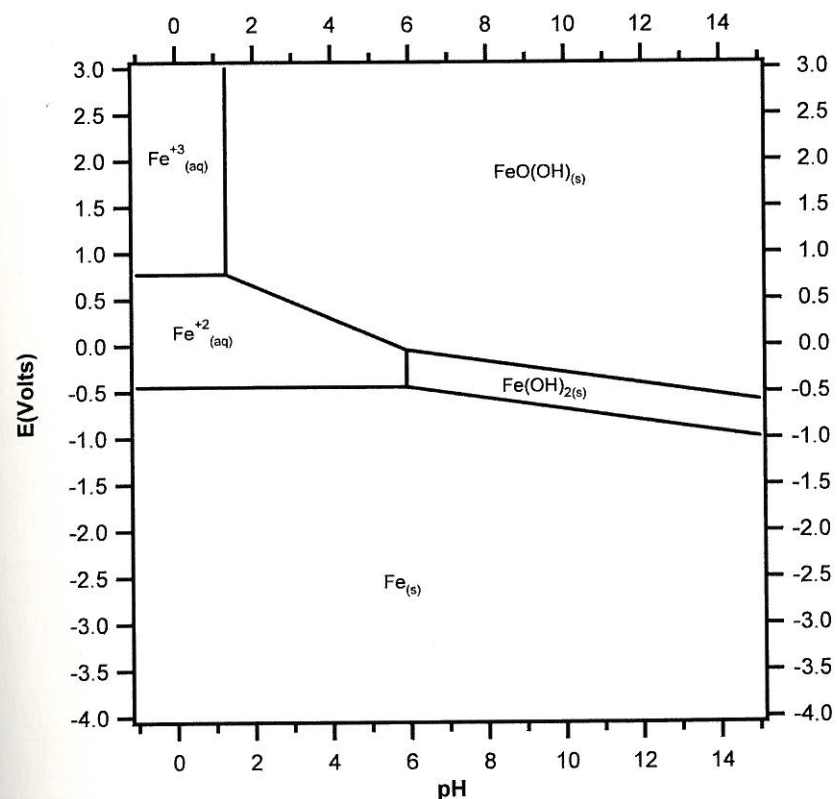


Figure 3.8 E-pH diagram for Fe species. Soluble species concentrations (except H⁺) = 10^{0.0} M. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH⁻.

the Mn. Next, consider Mn metal placed in a solution containing Fe²⁺. The Mn, being a lower species on a lower rung, will react with the Fe²⁺ to give the intermediate species Mn²⁺ and Fe, that is $\text{Mn} + \text{Fe}^{+2} \rightarrow \text{Fe} + \text{Mn}^{+2}$. Now notice that the next rung is the HOH \equiv H⁺/H₂ rung. This shows that Mn will react with H⁺ to give Mn²⁺ and H₂ (lower + upper \rightarrow intermediate species), or $\text{Mn} + 2\text{H}^+ \rightarrow \text{Mn}^{+2} + \text{H}_2$. In fact, Mn will react with any species on an upper rung above it: Fe²⁺, H⁺, Fe³⁺, O₂. Mn²⁺ will be produced and the Fe²⁺ would end up as Fe, except it in turn will react with H⁺ to produce Fe²⁺ and H₂. Hence in this system the final result of the reaction of excess Mn with a small amount of Fe²⁺ will be Mn²⁺, H₂, and Fe²⁺. By similar reasoning, the Fe³⁺ will end up as the same products.

Now consider starting with Mn²⁺ put into solution with various Fe species. In order to react Mn²⁺ must function as the lower species on a lower rung (a reductant) or as an upper species on an upper rung (an oxidant).

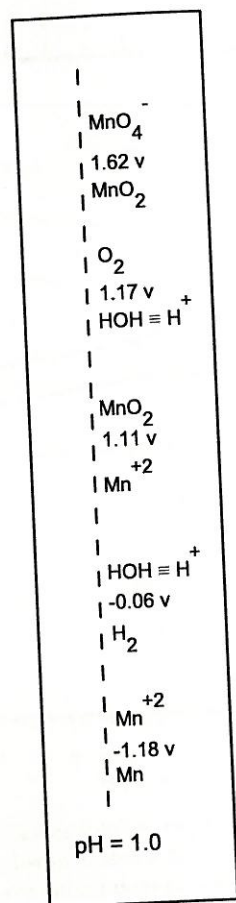


Figure 3.9 Combined electron ladder for Mn and H_2O at $\text{pH} = 1.0$. Soluble species concentrations (except H^+) = $10^{0.0}$ M.

If Mn^{+2} is placed with Fe^{+2} , there will be no reaction, because it is not the lower species with regard to Fe^{+2} . If Mn^{+2} is placed with Fe^{+3} , again there will be no reaction since the lower/lower-upper/upper relationship is not fulfilled. Further, take notice that Mn^{+2} does not react with $\text{HOH} \equiv \text{H}^+$ for the same reason. However, Mn^{+2} sits as the lower species on the $\text{MnO}_2/\text{Mn}^{+2}$ rung, which indicates that it can react with the upper species O_2 on the $\text{O}_2/\text{HOH} \equiv \text{H}^+$ rung as follows: $2\text{Mn}^{+2} + \text{O}_2 + 2\text{HOH} \rightarrow 2\text{MnO}_2 + 4\text{H}^+$. Thus, if the system is in air, O_2 would be available, and the process would occur.

Next, take a look at the situation in which MnO_2 is placed in solution with different Fe species. MnO_2 appears as the upper species on the $\text{MnO}_2/\text{Mn}^{+2}$ rung, therefore it is well to look at lower Fe and HOH species on rungs below.

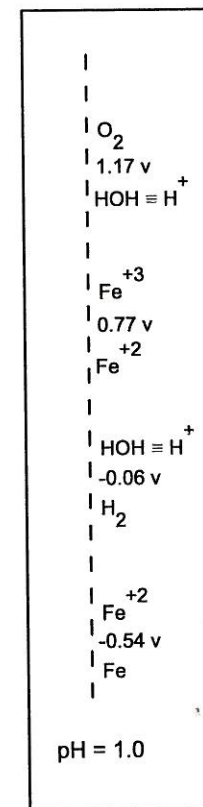
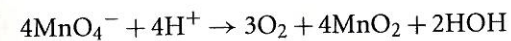


Figure 3.10 Combined electron ladder for Fe and H_2O at $\text{pH} = 1.0$. Soluble species concentrations (except H^+) = $10^{0.0}$ M.

It can be seen that MnO_2 will oxidize Fe^{+2} to Fe^{+3} , H_2 (if any is around) to H^+ , and Fe to Fe^{+2} , then on to Fe^{+3} . Appropriate equations may be written for these reactions, and voltages calculated by differences. MnO_2 appears as the lower species on the $\text{MnO}_4^-/\text{MnO}_2$ rung, which means that it will react with the upper species on any rung above it, and there is none.

As a final consideration in this system, look at MnO_4^- placed in solution with several Fe species. The anion MnO_4^- is the upper species on the upper rung of Figure 3.11. This implies that it has the potential to react with all lower species on rungs below it. These include $\text{HOH} \equiv \text{H}^+$, Fe^{+2} , H_2 (probably not present), and Fe. These reactions are described by the following equations, with the calculated E values appended:



$$E = 1.62 - 1.17 = 0.45 \text{ v}$$

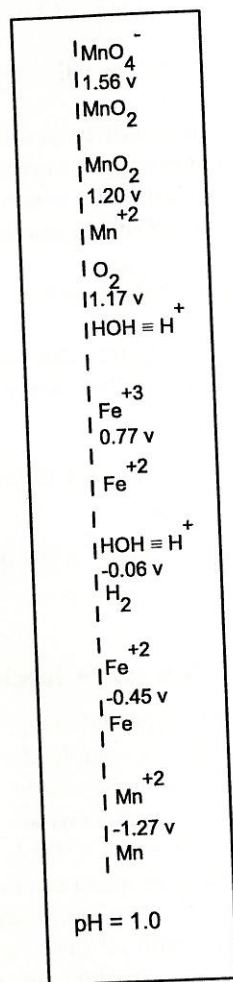
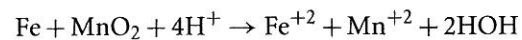
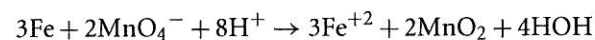


Figure 3.12 Combined electron ladder for Mn, Fe, and H₂O at pH = 1.0. Mn soluble species concentrations = 10^{-3.0} M. Fe soluble species concentrations = 10^{0.0} M.



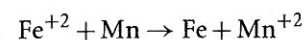
$$E = 1.20 - (-0.45) = 1.65 \text{ v}$$



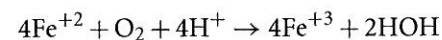
$$E = 1.56 - (-0.45) = 2.01 \text{ v}$$

The MnO₂ produced in the last reaction is subject to further reduction as will be pointed out below.

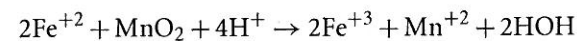
Next, excess Fe⁺² is to be introduced to a solution which might contain various Mn species. Fe⁺² functions as an upper species on the Fe⁺²/Fe rung and as the lower species on the Fe⁺³/Fe⁺² rung. Hence it can react with any lower species on a rung below it, or with any upper species on a rung above it. This indicates that Fe⁺² will react with Mn, and that Fe⁺² will react with O₂, MnO₂, and MnO₄⁻. Appropriate equations for these reactions are



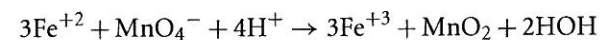
$$E = -0.45 - (-1.27) = 0.82 \text{ v}$$



$$E = 1.17 - 0.77 = 0.40 \text{ v}$$

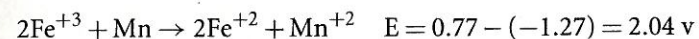


$$E = 1.20 - 0.77 = 0.43 \text{ v}$$



$$E = 1.56 - 0.77 = 0.79 \text{ v}$$

Now, consider the addition of an excess of Fe⁺³ to a solution which contains small concentrations of various Mn species. Fe⁺³ appears as only an upper species which indicates that it cannot be oxidized further, that is, it reacts with no species above it. However, being an upper species on the Fe⁺³/Fe⁺² rung, it can attack lower species on lower rungs, such as H₂ and Mn. H₂ is usually not present and thus no reaction occurs, but the attack on Mn is described by this equation:



It is well to realize that Fe⁺³ can also interact with Fe to give Fe⁺². This is recognized by noting that the Fe⁺³/Fe⁺² rung rests above the Fe⁺²/Fe rung.

5. Combining Redox Reactions

Consider the electron ladder in Figure 3.13. This ladder was abstracted from the E-pH diagrams of HOH and Cr with all soluble species at 10^{0.0} M and a

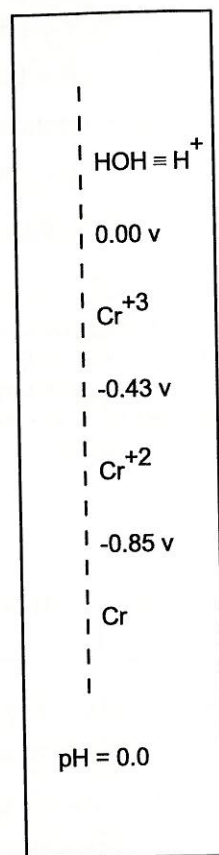
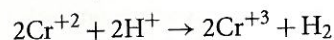


Figure 3.13 Combined electron ladder for Cr and H₂O at pH = 0.0. Soluble species concentrations (except H⁺) = 10^{0.0} M.

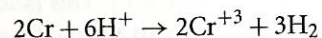
pH of 0.0. The interaction of Cr metal with H⁺ is described by this equation



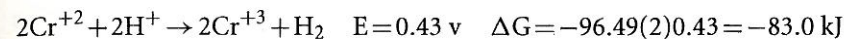
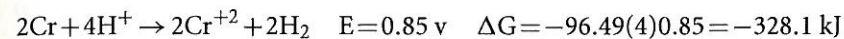
and the E value is obtained by subtracting the value on the lower rung from the value on the upper rung $0.00 - (-0.85) = 0.85$ v. Likewise, the interaction of Cr⁺² with H⁺ is described by



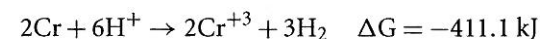
and the E is calculated to be $0.00 - (-0.43) = 0.43$ v. It can be seen that combining the two equations will lead to an equation describing the oxidation of Cr metal to Cr⁺³: $\text{Cr} \rightarrow \text{Cr}^{+2} \rightarrow \text{Cr}^{+3}$. This overall oxidation is given by the following equation:



Caution must be exercised with regard to calculating the E value of this overall oxidation reaction. Calculations which convert the E values for the $\text{Cr} \rightarrow \text{Cr}^{+2}$ and $\text{Cr}^{+2} \rightarrow \text{Cr}^{+3}$ equations into ΔG values are required. These conversions follow:



The equations are now added and the ΔG values are added to give the following:



This value of ΔG is now converted to the value of E, as follows: $E = -411.1 / -96.49(6) = 0.71$ v. ΔG values must be employed since the number of electrons in the final equation differs from those in the equations which are combined. This is because E values are potentials, whereas equations involve ΔG values which are energies.

6. The HOH E-pH Diagram Revisited

Thermodynamically, any species residing above the upper water line in an E-pH diagram should react to produce O₂, and any species below the lower water line should react to produce H₂ (See Figure 3.14). In a number of cases, these species do not react as predicted when they are investigated experimentally. There can be several reasons for this: (1) slow kinetics, (2) passivity, (3) reaction surface.

Experimentally, in some cases, the E^o for water decomposition to O₂ seems to be 1.48 ± 0.25 v or thereabouts rather than the 1.23 v that is predicted theoretically from free-energy considerations. Some reactions in the range of 1.23 to 1.73 v, and even above, go slowly enough that there is some pseudo-stability. This gives an added region of short-term, non-equilibrium stability in water solutions. For example, MnO₄⁻ can persist in water solution for several days. The E^o for the MnO₄⁻/MnO₂ transformation is 1.69 v. The persistence of the MnO₄⁻ is because the reaction $4\text{MnO}_4^- + 4\text{H}^+ \rightarrow 4\text{MnO}_2 + 2\text{HOH} + \text{O}_2$ is slow, not reaching thermodynamic equilibrium rapidly. It is observed that as the pH is increased, the reaction goes even more slowly. Other examples of this pseudo-stability are afforded by H₂O₂, BaO₂, RhO₂, and ClO₄⁻.

In practice, in some cases, the E^o for water decomposition into H₂ appears to be -0.25 ± 0.25 v or thereabouts rather than 0.00 v as is predicted thermodynamically. Examples are Yb⁺², Ti⁺³, V⁺², and Cr⁺². Often the reason is a slow reaction as treated above. The pseudo-stability of a solid species may often be attributed to one or both of two causes: (1) passivity or (2) reaction surface. Many metals, especially those which show high oxidation numbers, develop very strong, thin, refractory (non-reactive) oxide layers

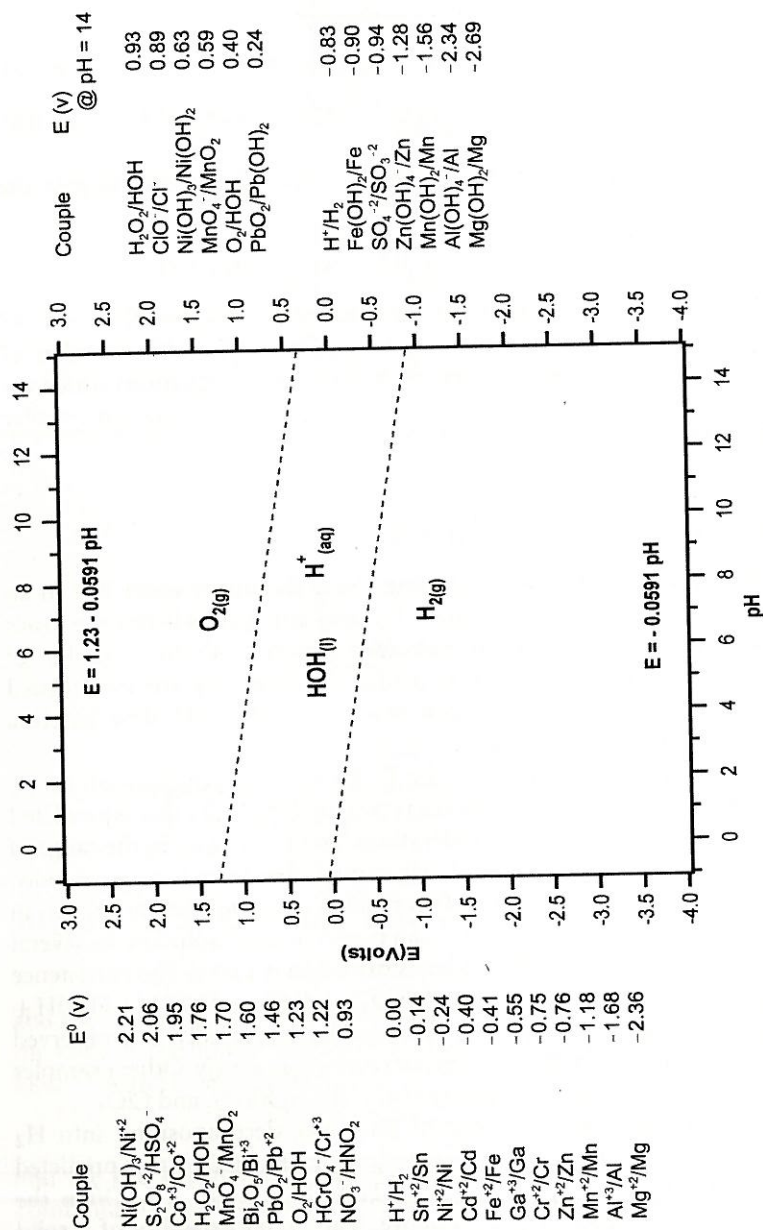


Figure 3.14 E-pH diagram for water system with commonly used oxidants and reductants. Soluble species and most solids are hydrated. No agents producing complexes or insoluble compounds are present other than HOH and OH^- .

when exposed to air or O_2 or HOH or oxidizing agents, particularly acids, such as HNO_3 . Examples are Al, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, and somewhat by Fe, Co, and Ni. These coatings often make the metals resistant to further attack by HOH and H^+ , and to other reactions. The degree of resistance can vary considerably depending upon the previous treatment of the metal. With regard to reaction surface, consider a cube of Zn 1.00 cm on a side. This chunk will dissolve slowly in acid, giving a portion of the Zn a relatively long-term existence. Should the same cube of Zn be powdered, the greatly increased surface area will shorten the existence of the metal.

Another important consideration with regard to reaction surface is illustrated by the behavior of oxides of higher-oxidation-number metals. Take for example, the oxide La_2O_3 . This oxide can be produced in several ways, but one of the most common methods is by the precipitation of $\text{La}(\text{OH})_3$ and then heating the precipitate to drive off the water. The rate and final temperature of this dehydration can strongly affect the reactivity of the oxide with acid. High temperatures and slow rates lead to an oxide which is resistant to dissolution by acids. This phenomenon is due to the character of the metal to oxide bridges in the compound, as well as the crystal structure. It is also to be noticed that different forms of compounds often show different standard free-energy values in addition to evidencing kinetic differences. Again, this is a crystal structure phenomenon. An example is afforded by the several forms of the oxide of Al. These are given here with the standard free energies in kJ/mole shown in parentheses: α -corundum (-1582.3), boehmite (-1588.2), diasporite (-1603.8), gibbsite (-1598.2), amorphous (-1532.0).

7. General Conclusions

In general then, reactions may be thermodynamically predicted by using the E-pH diagrams of the two elements involved. A pH is selected, and a vertical cut (an electron ladder) in both diagrams is made at that pH. Then a soluble-species concentration for each of the two elements is selected, and the rungs on the ladders (vertical cuts) are adjusted in E value by using the equations which describe the transformation lines on the E-pH diagrams. Following this, all rungs from both electron ladders, plus the HOH rungs, are combined into one electron ladder in decreasing order of E value. Then reactions can be predicted by combining lower species on lower rungs with upper species on upper rungs to give the intermediate species. The equations describing these reactions are readily balanced by consideration of the two half-reactions involved. Finally, attention is to be paid to the factors which might make the reactions go slowly. All of these considerations will lead to reactions which usually correlate with experimental observations.

Figure 3.14 displays commonly used oxidants and reductants along with their potentials. Accompanying the redox couples is the HOH E-pH diagram since it represents the medium to which they are referred.