Part 2. The Hydrosphere

Chapter 10.
Distribution of Species in Aquatic Systems

Chapter 10. Distribution of species in aquatic systems

10.1 Single-variable diagrams: Phosphate species

- Single variable diagram: a plot of some measure of species conc. Vs. a particular variable like pH, redox status, or conc. of important complexing ligand. E.g.

$$H_3PO_4 \leftrightarrow H_2PO_4^{-} \leftrightarrow HPO_4^{2-} \leftrightarrow PO_4^{3-} \qquad (10.1)$$

$$K_{a1} = \frac{[H_2PO_4^{-}][H_3O^{+}]}{[H_3PO_4]} \qquad (10.2)$$

$$\alpha_{H_3PO_4} = \frac{[H_3PO_4]}{[H_3PO_4]+[H_2PO_4^{-}]+[HPO_4^{2-}]+[PO_4^{3-}]} \qquad (10.3)$$

$$\alpha_{H_2PO_4^{-}} = \frac{[H_2PO_4^{-}]}{C_p} \qquad (10.4)$$

$$\alpha_{HPO_4^{2-}} = \frac{[HPO_4^{2-}]}{C_p} \qquad (10.5)$$

$$\alpha_{PO_4^{3-}} = \frac{[PO_4^{3-}]}{C_p} \qquad (10.6)$$

Chapter 10. Distribution of species in aquatic systems

10.1 Single-variable diagrams: Phosphate species

- Conc. of individual phosphate species:

Table 10.1 Acid dissociation constants for phosphoric acid		
	K_a	pK_a
First dissociation	7.1×10^{-3}	2.15
Second dissociation	6.3×10^{-8}	7.20
Third dissociation	4.2×10^{-13}	12.38

$$[H_2PO_4^-] = \frac{K_{a1} \times [H_3PO_4]}{[H_3O^+]} \quad (10.7)$$

$$[HPO_4^{2-}] = \frac{K_{a1} \times K_{a2} \times [H_3PO_4]}{[H_3O^+]^2} \quad (10.8)$$

$$[PO_4^{3-}] = \frac{K_{a1} \times K_{a2} \times K_{a3} \times [H_3PO_4]}{[H_3O^+]^3} \quad (10.9)$$

$$C_p = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

$$= [H_3PO_4](1 + \frac{K_{a1}}{[H_3O^+]} + \frac{K_{a1} \times K_{a2}}{[H_3O^+]^2} + \frac{K_{a1} \times K_{a2} \times K_{a3}}{[H_3O^+]^3}) \quad (10.10)$$

From eqn 10.3

$$\alpha_{H_3PO_4} = \frac{[H_3PO_4]}{[H_3PO_4](1 + K_{a1}/[H_3O^+] + K_{a1} \times K_{a2}/[H_3O^+]^2 + K_{a1} \times K_{a2} \times K_{a3}/[H_3O^+]^3)} \quad (10.11)$$

We then multiply the top and bottom of the right-hand side of the equation by $[H_3O^+]^3$:

$$\alpha_{H_3PO_4} = \frac{[H_3O^+]^3}{[H_3O^+]^3 + [H_3O^+]^2 \times K_{a1} + [H_3O^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.12)$$

Using similar calculations, we find that

$$\alpha_{H_2PO_4^-} = \frac{[H_3O^+]^2 \times K_{a1}}{[H_3O^+]^3 + [H_3O^+]^2 \times K_{a1} + [H_3O^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.13)$$

$$\alpha_{HPO_4^{2-}} = \frac{[H_3O^+] \times K_{a1} \times K_{a2}}{[H_3O^+]^3 + [H_3O^+]^2 \times K_{a1} + [H_3O^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.14)$$

$$\alpha_{PO_4^{3-}} = \frac{[H_3O^+] \times K_{a1} \times K_{a2} \times K_{a3}}{[H_3O^+]^3 + [H_3O^+]^2 \times K_{a1} + [H_3O^+] \times K_{a1} \times K_{a2} + K_{a1} \times K_{a2} \times K_{a3}} \quad (10.15)$$

Chapter 10. Distribution of species in aquatic systems

10.1 Single-variable diagrams: Phosphate species

- Distribution of phosphate species in open water

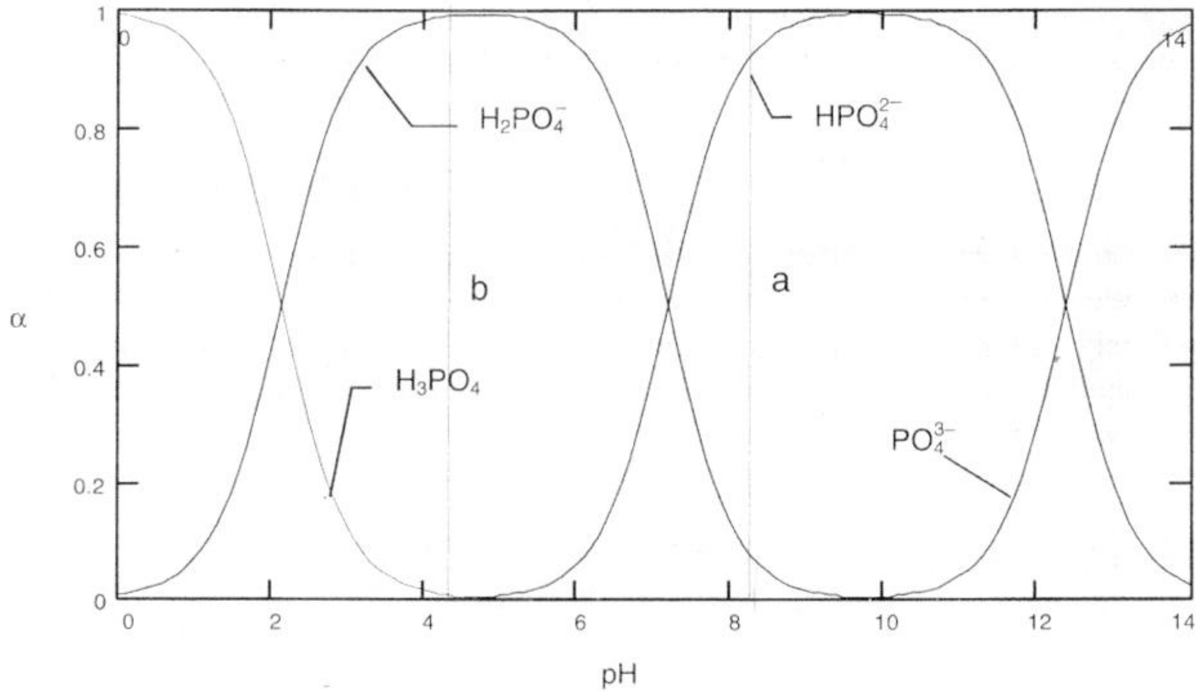

Fig. 10.1 Distribution of phosphorus species expressed as the fraction, α, as a function of aqueous solution pH.

In sea water, dissociation const. of phosphoric acid

Chapter 10. Distribution of species in aquatic systems

10.1 Single-variable diagrams: Cadmium complexes with chloride

- Single variable diagram with logarithm scale: E.g. distribution of aq. cadmium chloro complexes as a function of chloride ion concentration.

$$Cd^{2+} + Cl^- \leftrightarrow CdCl^+ \qquad K_{f1} = \frac{[CdCl^+]}{[Cd^{2+}][Cl^-]} = 7.9\times 10 \tag{10.16}$$

$$CdCl^+ + Cl^- \leftrightarrow CdCl_2 \qquad K_{f2} = \frac{[CdCl_2]}{[CdCl^+][Cl^-]} = 4.0 \tag{10.17}$$

$$CdCl_2 + Cl^- \leftrightarrow CdCl_3^- \qquad K_{f3} = \frac{[CdCl_3^-]}{[CdCl_2][Cl^-]} = 2.0 \tag{10.18}$$

$$CdCl_3^- + Cl^- \leftrightarrow CdCl_4^{2-} \qquad K_{f4} = \frac{[CdCl_4^{2-}]}{[CdCl_3^-][Cl^-]} = 0.6 \tag{10.19}$$

The reactions may also be described using 'overall' steps and the overall stability constants are symbolized as β_f. It is readily seen that

$$\beta_{fn} = K_{f1}\times K_{f2}\times\cdots K_{fn} \tag{10.20}$$

$$Cd^{2+} + Cl^- \leftrightarrow CdCl^+ \qquad \beta_{f1} = K_{f1} = 7.9\times 10 \tag{10.21}$$

$$Cd^{2+} + 2Cl^- \leftrightarrow CdCl_2 \qquad \beta_{f2} = K_{f1}\times K_{f2} = 3.2\times 10^2 \tag{10.22}$$

$$Cd^{2+} + 3Cl^- \leftrightarrow CdCl_3^- \qquad \beta_{f3} = K_{f1}\times K_{f2}\times K_{f3} = 6.4\times 10^2 \tag{10.23}$$

$$Cd^{2+} + 4Cl^- \leftrightarrow CdCl_4^{2-} \qquad \beta_{f4} = K_{f1}\times K_{f2}\times K_{f3}\times K_{f4} = 3.8\times 10^2 \tag{10.24}$$

Chapter 10. Distribution of species in aquatic systems

10.1 Single-variable diagrams: Cadmium complexes with chloride

- Total conc. of cadmium in an aq. solution containing chloride

We can derive expression s for the concentrat ion of each of the five cadmium species in the following way. We begin by dividing eqn 10.25 by $[Cd^{2+}]$:

$$\frac{C_{Cd}}{[Cd^{2+}]} = 1 + \frac{[CdCl^{+}]}{[Cd^{2+}]} + \frac{[CdCl_2]}{[Cd^{2+}]} + \frac{[CdCl_3^{-}]}{[Cd^{2+}]} + \frac{[CdCl_4^{2-}]}{[Cd^{2+}]} \qquad (10.26)$$

Substituti ng the expression s for the β functions,

$$\frac{C_{Cd}}{[Cd^{2+}]} = 1 + \beta_{f1}[Cl^{-}]^{1} + \beta_{f2}[Cl^{-}]^{2} + \beta_{f3}[Cl^{-}]^{3} + \beta_{f4}[Cl^{-}]^{4} \qquad (10.27)$$

Rearrangin g eqn 10.27 :

$$[Cd^{2+}] = \frac{C_{Cd}}{1 + \beta_{f1}[Cl^{-}]^{1} + \beta_{f2}[Cl^{-}]^{2} + \beta_{f3}[Cl^{-}]^{3} + \beta_{f4}[Cl^{-}]^{4}} \qquad (10.28)$$

Similarly, the concentrat ions of other cadmium chloro species are given by

$$[CdCl^{+}] = \frac{\beta_{f1}[Cl^{-}]^{1} C_{Cd}}{1 + \beta_{f1}[Cl^{-}]^{1} + \beta_{f2}[Cl^{-}]^{2} + \beta_{f3}[Cl^{-}]^{3} + \beta_{f4}[Cl^{-}]^{4}} \qquad (10.29)$$

$$[CdCl_2] = \frac{\beta_{f2}[Cl^{-}]^{2} C_{Cd}}{1 + \beta_{f1}[Cl^{-}]^{1} + \beta_{f2}[Cl^{-}]^{2} + \beta_{f3}[Cl^{-}]^{3} + \beta_{f4}[Cl^{-}]^{4}} \qquad (10.30)$$

$$[CdCl_3^{-}] = \frac{\beta_{f3}[Cl^{-}]^{3} C_{Cd}}{1 + \beta_{f1}[Cl^{-}]^{1} + \beta_{f2}[Cl^{-}]^{2} + \beta_{f3}[Cl^{-}]^{3} + \beta_{f4}[Cl^{-}]^{4}} \qquad (10.31)$$

$$[CdCl_3^{2-}] = \frac{\beta_{f4}[Cl^{-}]^{4} C_{Cd}}{1 + \beta_{f1}[Cl^{-}]^{1} + \beta_{f2}[Cl^{-}]^{2} + \beta_{f3}[Cl^{-}]^{3} + \beta_{f4}[Cl^{-}]^{4}} \qquad (10.32)$$

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10.1 Single-variable diagrams: Cadmium complexes with chloride

- E.g. line b, surface water salinity=10 $\%_0$, $[Cl^{-1}]$=0.16 mol L^{-1}
- $[Cd^{2+}]$=0.04, $CdCl^+$=0.52, $CdCl_2$=0.33, $CdCl^{3-}$=0.10, $CdCl_4^{2-}$=0.01

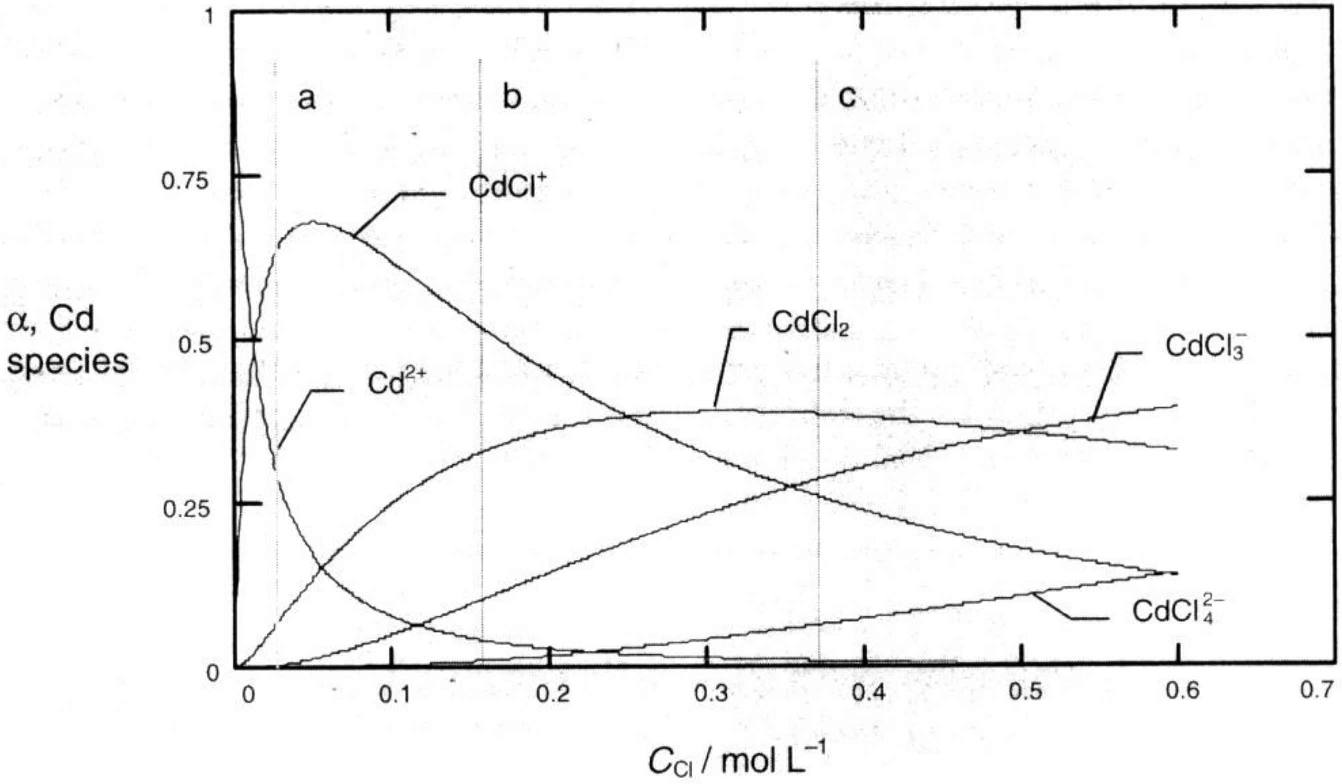

Fig. 10.2 Distribution of cadmium chloro complexes as a function of the concentration of chloride ion in water. The range of chloride concentrations is from zero to 0.56 mol L^{-1}; the latter value is the approximate concentration in sea water.

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: pE/pH diagrams (Pourbaix diagram)

- Concept of pE: pE =
- A large negative value of pE indicates a large value for the e- activity in solution, implying
- A large positive value of pE: low activity of e- in solution, implying
- pE values in water = -12~25

Consider the simple half reaction

$$Fe^{3+}(aq) + e^{-} \leftrightarrow Fe^{2+}(aq) \tag{10.34}$$

$$K_{eq} = \frac{a_{Fe^{2+}}}{a_{Fe^{3+}} \times a_{e^{-}}} \tag{10.35}$$

$$\frac{1}{a_{e^{-}}} = \frac{K_{eq} \times a_{Fe^{3+}}}{a_{Fe^{2+}}} \tag{10.36}$$

Using the definition of pE and taking logs of both sides of eqn 10.36, we have

$$pE = -\log a_{e^{-}} = \log K_{eq} + \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \tag{10.37}$$

Since

$$\Delta G^{\circ} = -2.303\,RT \log K_{eq} \tag{10.38}$$

$$= -nFE^{\circ} \tag{10.39}$$

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: pE/pH diagrams (Pourbaix diagram)

(n has the usual electrochemical meaning - i.e. the number of electrons transferred in the half reaction), at 298K (R = 8.314J K^{-1}mol^{-1} and F = 96 485Cmol^{-1}), we have

$$\log K_{eq} = \frac{nFE^\circ}{2.303RT} = \frac{nE^\circ}{0.0591} \quad (10.40)$$

In this case, n = 1, so

$$\log K_{eq} = \frac{E^\circ}{0.0591} \quad (10.41)$$

and

$$pE = \frac{E^\circ}{0.0591} + \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \quad (10.42)$$

Under standard conditions, $a_{Fe^{3+}} = a_{Fe^{2+}} = 1$:

$$\log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} = \quad (10.43)$$

and

$$\mathrm{pE} = \mathrm{pE}^\circ = \quad (10.44)$$

For non-standard conditions:

$$\mathrm{pE} = \mathrm{pE}^\circ + \quad (10.45)$$

When the standard pE° value and the actual activities (usually approximated by concentrations) of Fe^{3+} and Fe^{2+} are substituted into this equation, the pE of a particular environmental system can be calculated.

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10.2 Two-variable diagrams: pE/pH diagrams (Pourbaix diagram)

In the general case, for a reaction

$$aA + ne^- \leftrightarrow bB \qquad (10.46)$$

where A and B are the oxidized and reduced forms of a redox couple, the reaction quotient (Q) is defined as

$$Q = \frac{(a_B)^b}{(a_A)^a} \approx \frac{[B]^b}{[A]^a} \qquad (10.47)$$

The reaction quotient takes the form of an equilibrium constant, but uses activities (or, as an approximation, concentrations) that obtain under any conditions, not just those at equilibrium. The general form of eqn 10.45 is then

(10.48)

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: Methods of calculating pE^0

- Consider a half-reaction

$$Fe^{3+}(aq) + e^- \leftrightarrow Fe^{2+}(aq) \qquad E^0 = +0.771V \qquad (10.34)$$

- Therefore

$$pE^0 =$$

from eq (10.44)

- Second method, using eqs. (10.40) and (10.44)

A second method for calculatin g pE° makes use of the relations in eqns 10.40 and 10.44

$$\log K_{eq} = \frac{nE^\circ}{0.0591} = npE^\circ \qquad (10.49)$$

$$pE^\circ = \frac{\log K_{eq}}{n} \qquad (10.50)$$

This relation is applicable when an E° value is not available, but where the appropriat e equilibriu m constant is known.

In some cases, several reactions may be combined to produce an overall half reaction.

Consider t he half reaction for which no tabulated E° value is easily found :

$$Fe(OH)_3 + 3H_3O^+(aq) + e^- \leftrightarrow Fe^{2+}(aq) + 6H_2O \qquad (10.51)$$

The reaction is the sum of

$$Fe(OH)_3 \leftrightarrow Fe^{3+}(aq) + 3OH^-(aq) \qquad (10.51a)$$

$$Fe^{3+}(aq) + e^- \leftrightarrow Fe^{2+}(aq) \qquad (10.51b)$$

$$3H_3O^+(aq) + 3OH^-(aq) \leftrightarrow 6H_2O \qquad (10.51c)$$

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10.2 Two-variable diagrams: Methods of calculating pE^0

For reaction 10.51a, $K_a = K_{sp} = 9.1 \times 10^{-39}$ and $\log K_a = -38.0$. For reaction 10.51b, $pE_b^o = \log K_b = 0.771/0.0591$ and $\log K_b = +13.0$. For reaction 10.51c,

$$K_c = \frac{1}{(K_w)^3} = 10^{42}$$

and $\log K_c = +42.0$. For the original, overall reaction

$$\begin{aligned}\log K_m &= \log K_a + \log K_b + \log K_c \\ &= -38.0 + 13.0 + 42.0 \\ &= +17.0\end{aligned}$$

Using equation 10.50 ($n = 1$):

$$pE^o_{overall} = +17.0.$$

There is a third method for calculating pE^o values and this requires combining eqns 10.38 and 10.49:

$$\Delta G^o = -2.303\, RT\, n\, pE^o \qquad (10.52)$$

$$pE^o = \frac{-\Delta G^o}{2.303\, RT\, n} \qquad (10.53)$$

Consider the redox reaction

$$SO_4^{2-}(aq) + 10H_3O^+(aq) + 8e^- \rightleftharpoons H_2S\,(aq) + 14H_2O \qquad (10.54)$$

$$\Delta G^o = \Delta G_f^o\,(H_2S) + 14\Delta G_f^o\,(H_2O) - \Delta G_f^o\,(SO_4^{2-}) - 10\Delta G_f^o\,(H_3O^+) - 8\Delta G_f^o\,(e^-)$$

Using thermochemical tables and noting that ΔG_f^o for the aqueous electron is 0, and for the hydronium ion, ΔG_f^o has the same value as for water:

$$\begin{aligned}\Delta G^o &= -27.86 + 14 \times (-237.18) - 10 \times (-237.18) - (-744.60) \\ &= -231.98\ \text{kJ}\end{aligned}$$

$$\begin{aligned}pE^o &= \frac{-(-231.98)\ \text{kJ} \times 1000\ \text{J kJ}^{-1}}{2.303 \times 8.314\ \text{J mol}^{-1}\ \text{K}^{-1} \times 298.2\ \text{K} \times 8\ \text{mol}} \\ &= 5.08\end{aligned}$$

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: Chromium in tannery wastes

- Suppose the initial conc. of $[Cr^{3+}]$=26 mg L^{-1}, then dissolved oxygen in downstream oxidize to $Cr_2O_7^{2-}$, pH=6.5 ($a_{H3O^+}=10^{-6.5}$)

The relevant reaction for atmospheric O_2 in equilibrium with water (often called a well aerated system) is

$$O_2(g) + 4H_3O^+(aq) + 4e^- \leftrightarrow 6H_2O \qquad (10.55)$$

$$E^\circ = 1.23V$$

$$pE^\circ =$$

Using eqn 10.48:

$$pE = pE^\circ - \frac{1}{n}\log\frac{1}{P_{O_2}/P^\circ \times (a_{H_3O^+})^4}$$

$$= 20.8 - \frac{1}{4}\log\frac{1}{0.209 \times (10^{-6.5})^4}$$

$$= 14.1$$

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10.2 Two-variable diagrams: Chromium in tannery wastes

Note that in these calculations, the pressure is given as a ratio of P_{O_2}/P^o which is numerically identical to pressure in atmospheres. For oxygen, which makes up 20.9% of the atmosphere, $P_{O_2} = 21\,200$ Pa; $P^o = 101\,325$ Pa.

For the Cr system:

$$Cr_2O_7^{2-}\ (aq) + 14H_3O^+\ (aq) + 6e^- \rightleftharpoons 2Cr^{3+}\ (aq) + 17H_2O \qquad (10.56)$$

$$E^o = 1.36V \text{ and } pE^o = 23.0$$

$$pE = pE^o - \frac{1}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}](a_{H_3O^+})^{14}}$$

Since the chromium and oxygen systems are in equilibrium, pE is :

$$14.1 = 23.0 - \frac{1}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}](10^{-6.5})^{14}}$$

$$= 23.0 - \frac{1}{6}\log\frac{1}{(10^{-6.5})^{14}} - \frac{1}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}]}$$

$$= 7.8 - \frac{1}{6}\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}]}$$

$$\log\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}]} = -37.8$$

$$\frac{[Cr^{3+}]^2}{[Cr_2O_7^{2-}]} = 1.6 \times 10^{-38}$$

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: pE/pH diagrams

- In the diagram, areas define the regions where particular species are dominant
- P^0 =101325 Pa =1 atm: this is the min. pressure required for gas evolution from the aq. solution. I.e. when $P_{gas} > P^0$,
- E.g. gas evolution from acidic solution

$$2H_3O^+(aq) + 2e^- \leftrightarrow H_2(g) + 2H_2O \qquad (10.57)$$

Another type of condition is required for the situation where only soluble species are involved, or where there is a soluble species reacting to form one that is insoluble. Examples of these two cases are

$$Sn^{4+}(aq) + 2e^- \leftrightarrow Sn^{2+}(aq) \qquad (10.58)$$

and

$$MnO_2 + 4H_3O^+(aq) + 2e^- \leftrightarrow Mn^{2+}(aq) + 6H_2O \qquad (10.59)$$

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: pE/pH diagrams

- Consider aq. sulfur system where the species of interest are: SO_4^{2-} (aq), HSO_4^- (aq), S(s), HS^- (aq), and H_2S (aq)
- To consider first water itself,

$$2H_2O + 2e^- \leftrightarrow H_2(g) + 2OH^-(aq) \qquad (10.60)$$

For this reaction

$$E^\circ = -0.828V$$

$$pE^\circ = -14.0$$

Equation 10.48 for this reaction is written as

(10.61)

(note again that here and in subsequent calculatio ns, we will use concentrat ions rather than activities except for hydroxyl and hydronium ions).

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: pE/pH diagrams

For the boundary involving a gas, we choose the condition that

$$P_{H_2} = P^o = 101\,325\,\text{Pa}$$
$$pE = -14.0 - \log(a_{OH^-})$$
$$= -14.0 + pOH$$

Since

$$pH + pOH =$$

then

$$pE =$$

This line then defines the boundary for water stability with respect to reduction and is shown as the lower line on Fig. 10.4. Where the p*E* value is less than the pH value, water is unstable. It is possible also to calculate the same line by taking the reduction reaction to be

$$2H_3O^+\ (aq) + 2e^- \rightleftharpoons H_2\ (g) + 2H_2O \qquad (10.62)$$

Considering the other extreme, highly oxidizing conditions, water is unstable with respect to O_2 evolution and the reaction is written as

$$6H_2O \rightleftharpoons 4H_3O^+(aq) + O_2 + 4e^- \qquad (10.63)$$

For this reaction

$$E^o = 1.229\,V$$
$$pE^o = E^o/0.0591 = 20.80$$

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10.2 Two-variable diagrams: pE/pH diagrams

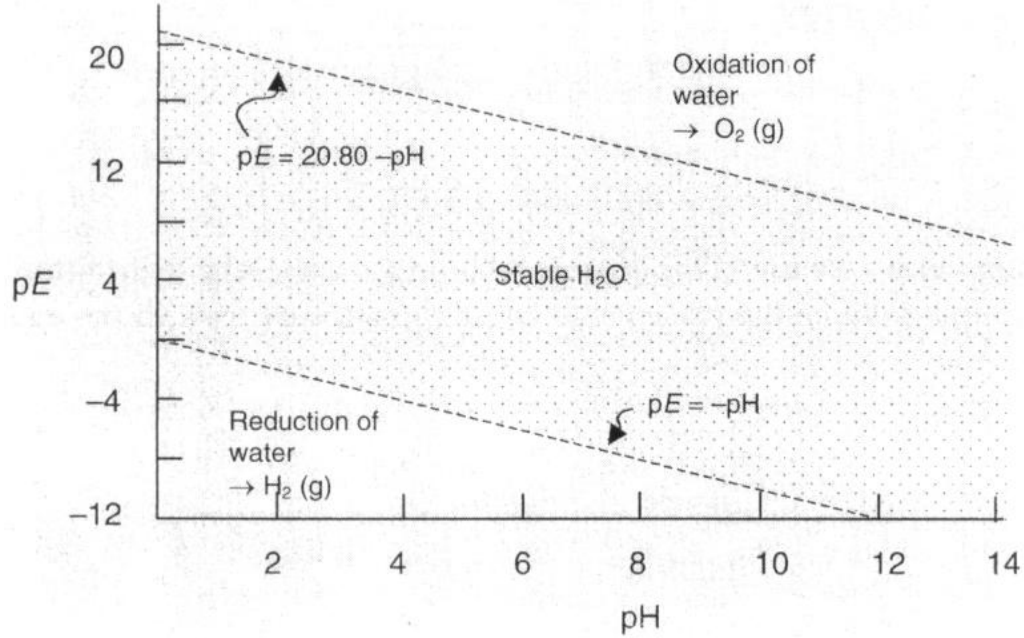


Fig. 10.4 Region of stability and stability boundaries for water on a pE/pH diagram.

$$pE = pE° - \frac{1}{4}\log(1/P_{O_2} \times (a_{H_3O^+})^4) \qquad (10.64)$$

Once again, the boundary condition requires that the pressure of the gas equal atmospheri c pressure.

$$P_{O_2} = P° = 101{,}325 Pa$$

$$pE = 20.80 - \log(1/a_{H_3O^+})$$

$$= 20.80 - pH$$

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: The sulfur system

The SO_4^{2-}/HSO_4^- boundary

The equation describing this boundary requires hydronium ion, but there is no oxidation or reduction involved:

$$SO_4^{2-}(aq) + H_3O^+(aq) \rightleftharpoons HSO_4^-(aq) + H_2O \quad (10.65)$$

To make things easier, we use H^+ as an abbreviation for H_3O^+, the hydronium ion, but of course the result would be the same if the latter species were used in the equations and calculations.

$$\Delta G^o = \Delta G_f^o\,(HSO_4^-) - \Delta G_f^o\,(SO_4^{2-}) - \Delta G_f^o\,(H^+)$$
$$= -755.99 - (-744.60) - 0$$
$$= -11.39\,\text{kJ} = -11\,390\,\text{J}$$

$$\log K = \frac{-\Delta G^o}{2.303\,RT}$$
$$= \frac{+11\,390}{2.303 \times 8.314 \times 298.2}$$
$$= 1.995$$

$$K = \frac{[HSO_4^-]}{[SO_4^{2-}]a_{H^+}}$$

At the boundary, $[HSO_4^-] = [SO_4^{2-}] = 10^{-2}$ M, and

$$K = \frac{1}{a_{H^+}}$$
$$\log K = \text{pH} = 1.995$$

Therefore, the boundary between HSO_4^- and SO_4^{2-} is a vertical line at pH 1.995. Below this value, HSO_4^- is the dominant form; above it SO_4^{2-} is most important. See line 'a' on Fig. 10.5.

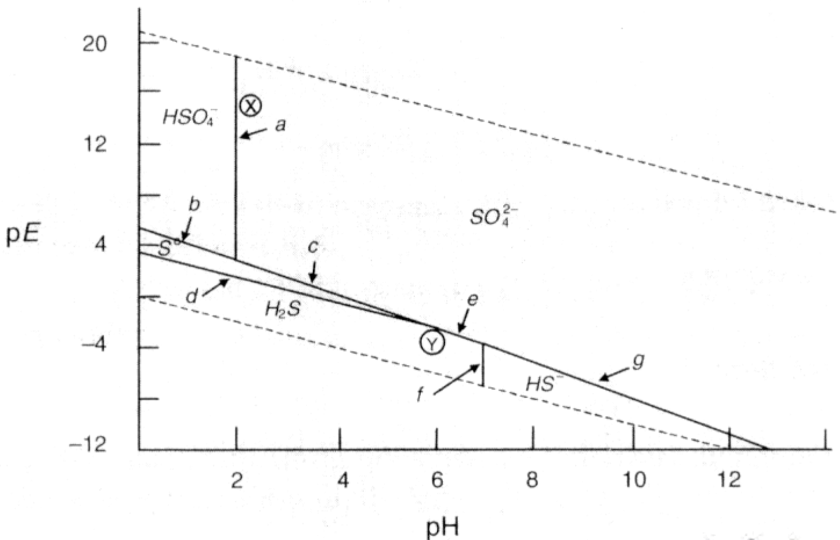


Fig. 10.5 The pE/pH for the aqueous sulfur system.

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: The sulfur system

The HSO_4^-/S^o boundary

$$HSO_4^- \text{ (aq)} + 7H^+ \text{ (aq)} + 6e^- \rightleftharpoons S^o \text{ (s)} + 4H_2O \quad (10.66)$$

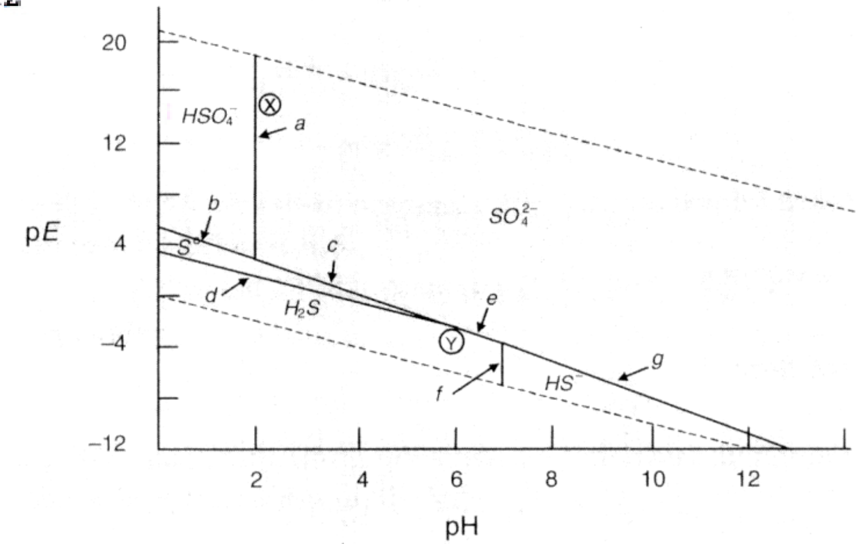
$$\begin{aligned}\Delta G^o &= \Delta G_f^o \text{ (S)} + 4\Delta G_f^o \text{ (}H_2O\text{)} - \Delta G_f^o \text{ (}HSO_4^-\text{)} - 7\Delta G_f^o \text{ (}H^+\text{)} - 6\Delta G_f^o \text{ (}e^-\text{)} \\ &= 0 + 4(-237.18) - (-755.99) - 0 - 0 \\ &= -192.73 \text{ kJ} = -192\,730 \text{ J}\end{aligned}$$

$$pE^o = \frac{-\Delta G^o}{2.303\,nRT} = \frac{+192\,730}{2.303 \times 6 \times 8.314 \times 298.2} = 5.626$$

$$pE = pE^o - \frac{1}{6}\log\frac{1}{[HSO_4^-](a_{H^+})^7}$$

At the boundary, $[HSO_4^-] = 10^{-2}$ mol L^{-1}:

$$\begin{aligned}pE &= 5.626 - \frac{7}{6}\log\frac{1}{a_{H^+}} - \frac{1}{6}\log\frac{1}{10^{-2}} \\ &= 5.626 - \frac{7}{6}pH - 0.333 \\ &= 5.293 - 1.167\,pH\end{aligned}$$



This is line 'b' on Fig. 10.5; above it is the domain of HSO_4^-; below it is elemental sulfur, S^o.

Fig. 10.5 The pE/pH for the aqueous sulfur system.

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: The sulfur system

The SO_4^{2-}/S^o boundary

$$SO_4^{2-}\ (aq) + 8H^+\ (aq) + 6e^- \rightleftharpoons S^o\ (s) + 4H_2O \qquad (10.67)$$

$$\begin{aligned}\Delta G^o &= \Delta G_f^o\ (S) + 4\Delta G_f^o\ (H_2O) - \Delta G_f^o\ (SO_4^{2-}) - 8\Delta G_f^o\ (H^+) - 6\Delta G_f^o\ (e^-)\\ &= 0 + 4(-237.18) - (-744.60) - 0 - 0\\ &= -204.12\ \text{kJ} = -204\,120\ \text{J}\end{aligned}$$

$$\begin{aligned}pE^o &= \frac{\Delta G^o}{2.303\,nRT} = \frac{+204\,120}{2.303 \times 6 \times 8.314 \times 298.2}\\ &= 5.958\end{aligned}$$

$$pE = pE^o - \frac{1}{6}\log\frac{1}{[SO_4^{2-}](a_{H^+})^8}$$

At the boundary, $[SO_4^{2-}] = 10^{-2}\ \text{mol L}^{-1}$:

$$\begin{aligned}pE &= 5.958 - \frac{8}{6}\log\frac{1}{a_{H^+}} - \frac{1}{6}\log\frac{1}{10^{-2}}\\ &= 5.958 - \frac{8}{6}pH - 0.333\\ &= 5.625 - 1.333\ pH\end{aligned}$$

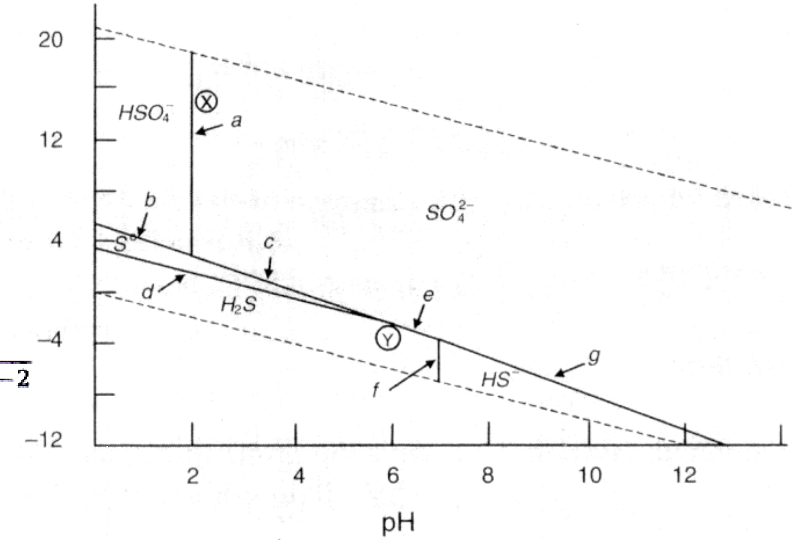


Fig. 10.5 The pE/pH for the aqueous sulfur system.

This is line ‘c’ on Fig. 10.5; above it is the domain of SO_4^{2-}, below it S^o.

10.2 Two-variable diagrams: The sulfur system

The S°/H_2S boundary

$$S\,(s) + 2H^+\,(aq) + 2e^- \rightleftharpoons H_2S\,(aq) \qquad (10.68)$$

$$\begin{aligned}\Delta G^o &= \Delta G_f^o\,(H_2S) - \Delta G_f^o\,(S) - 2\Delta G_f^o\,(H^+) - 2\Delta G_f^o\,(e^-)\\ &= -27.86 - 0 - 0 - 0\\ &= -27.86\,\text{kJ} = -27\,860\,\text{J}\end{aligned}$$

$$\begin{aligned}pE^o &= \frac{-\Delta G^o}{2.303\,nRT} = \frac{+27\,860}{2.303 \times 2 \times 8.314 \times 298.2}\\ &= 2.400\end{aligned}$$

$$pE = pE^o - \frac{1}{2}\log\frac{[H_2S]}{(a_{H^+})^2}$$

At the boundary, $[H_2S] = 10^{-2}$ mol L^{-1}:

$$\begin{aligned}pE &= 2.440 + 1 - pH\\ &= 3.440 - pH\end{aligned}$$

This is line 'd' on Fig. 10.5; above it is the domain of S°, below it H_2S.

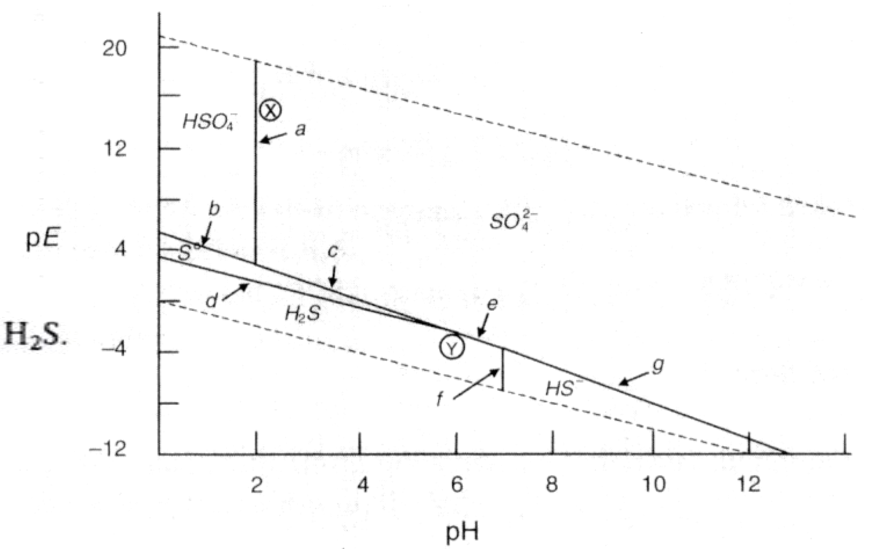


Fig. 10.5 The pE/pH for the aqueous sulfur system.

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: The sulfur system

The SO_4^{2-}/H_2S boundary

$$SO_4^{2-}\ (aq) + 10H^+\ (aq) + 8e^- \rightleftharpoons H_2S\ (aq) + 4H_2O \qquad (10.69)$$

$$\Delta G^o = \Delta G_f^o\ (H_2S) + 4\Delta G_f^o\ (H_2O) - \Delta G_f^o\ (SO_4^{2-}) - 10\Delta G_f^o\ (H^+) - 8\Delta G_f^o\ (e^-)$$
$$= -27.86 + 4(-237.18) - (-744.60) - 0 - 0$$
$$= -231.98\ \text{kJ} = -231\,980\ \text{J}$$

$$pE^o = \frac{-\Delta G^o}{2.303\,nRT} = \frac{+231\,980}{2.303 \times 8 \times 8.314 \times 298.2}$$
$$= 5.079$$

$$pE = pE^o - \frac{1}{8}\log\frac{[H_2S]}{[SO_4^{2-}](a_{H^+})^{10}}$$

At the boundary, $[H_2S] = [SO_4^{2-}] = 10^{-2}\ \text{mol L}^{-1}$:

$$pE = 5.079 - \frac{10}{8}\log\frac{1}{a_{H^+}}$$
$$= 5.079 - 1.25\,pH$$

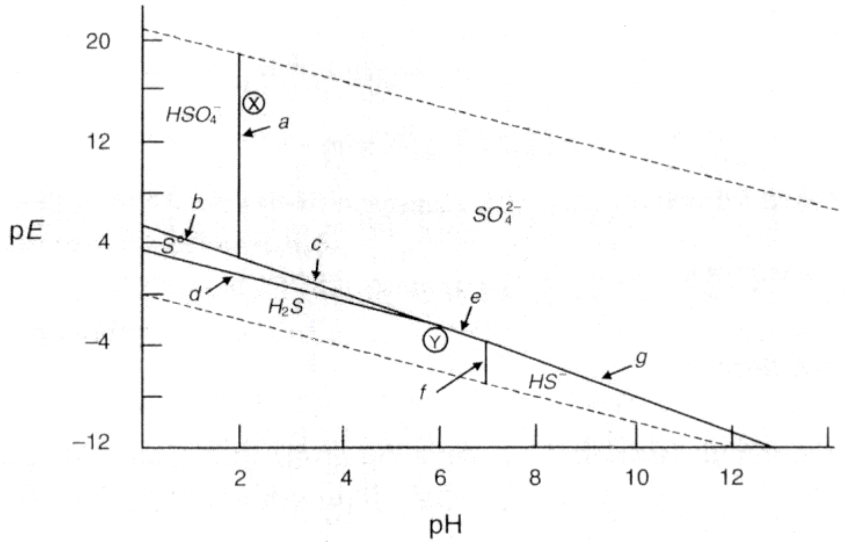


Fig. 10.5 The pE/pH for the aqueous sulfur system.

This is line 'e' on Fig. 10.5 (a very small segment, difficult to distinguish from line 'd'); above it is the domain of SO_4^{2-}, below it H_2S.

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: The sulfur system

The H_2S/HS^- boundary

$$H_2S\ (aq) \rightleftharpoons HS^-\ (aq) + H^+\ (aq) \qquad (10.70)$$

As for the HSO_4^-/SO_4^{2-} boundary, this is not a redox reaction and therefore the line will be vertical with the protonated species on the left.

$$\Delta G^o = \Delta G_f^o\ (HS^-) + \Delta G_f^o\ (H^+) - \Delta G_f^o\ (H_2S)$$
$$= 12.08 + 0 - (-27.86)$$
$$= 39.94\ kJ = 39\,940\ J$$

$$\log K = \frac{-\Delta G^o}{2.303\,RT} = \frac{-39\,940}{2.303 \times 8.314 \times 298.2}$$
$$= -6.995$$

$$K = \frac{[HS^-]a_{H^+}}{[H_2S]}$$

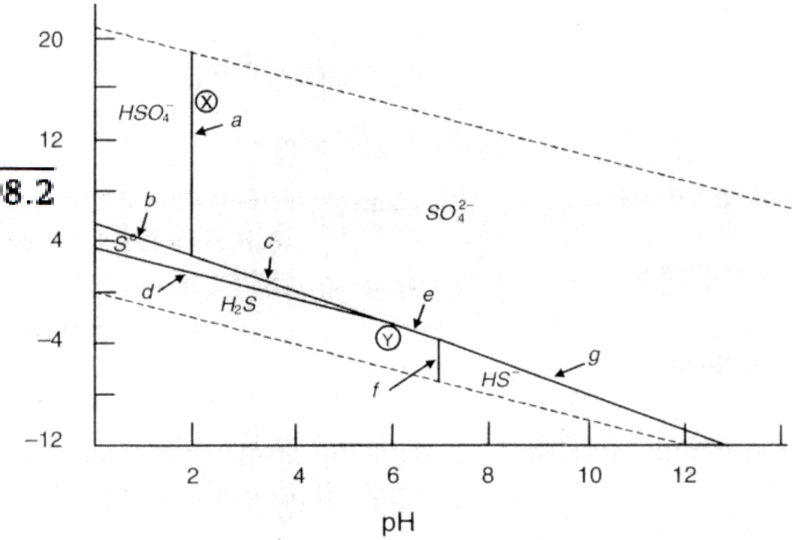


Fig. 10.5 The p*E*/pH for the aqueous sulfur system.

At the boundary, $[HS^-] = [H_2S] = 10^{-2}\ mol\ L^{-1}$:

$$K = a_{H^+}$$
$$\log K = \log[H^+] = -pH = -6.995$$
$$pH = 6.995$$

This is line 'f' on Fig. 10.5; to the left is the domain of H_2S and to the right HS^-.

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: The sulfur system

The SO_4^{2-}/HS^- boundary

$$SO_4^{2-}\ (aq) + 9H^+\ (aq) + 8e^- \rightleftharpoons HS^-\ (aq) + 4H_2O \qquad (10.71)$$

$$\begin{aligned}\Delta G^\circ &= \Delta G_f^\circ\ (HS^-) + 4\Delta G_f^\circ\ (H_2O) - \Delta G_f^\circ\ (SO_4^{2-}) - 9\Delta G_f^\circ\ (H^+) - 8\Delta G_f^\circ\ (e^-)\\ &= 12.08 + 4(-237.18) - (-744.60) - 0 - 0\\ &= -192.04\ \text{kJ} = -192\,040\ \text{J}.\end{aligned}$$

$$\begin{aligned}pE^\circ &= \frac{-\Delta G^\circ}{2.303\,nRT} = \frac{+192\,040}{2.303 \times 8 \times 8.314 \times 298.2}\\ &= 4.204.\end{aligned}$$

$$pE = pE^\circ - \frac{1}{8}\log\frac{[HS^-]}{[SO_4^{2-}](a_{H^+})^9}$$

At the boundary, $[HS^-] = [SO_4^{2-}] = 10^{-2}\ \text{mol L}^{-1}$:

$$\begin{aligned}pE &= 4.202 - \frac{9}{8}\log\frac{1}{a_{H^+}}\\ &= 4.204 - 1.125\,pH\end{aligned}$$

This is line ‘g’ on Fig. 10.5; above it is the domain of SO_4^{2-}, below it HS^-.

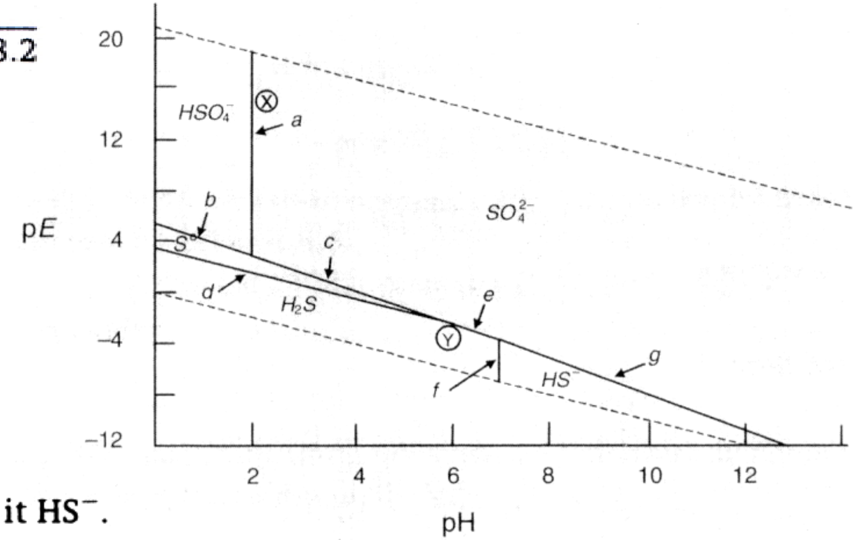


Fig. 10.5 The pE/pH for the aqueous sulfur system.

Chapter 10. Distribution of species in aquatic systems

10.2 Two-variable diagrams: The sulfur system

▪ Template of pE/pH diagram

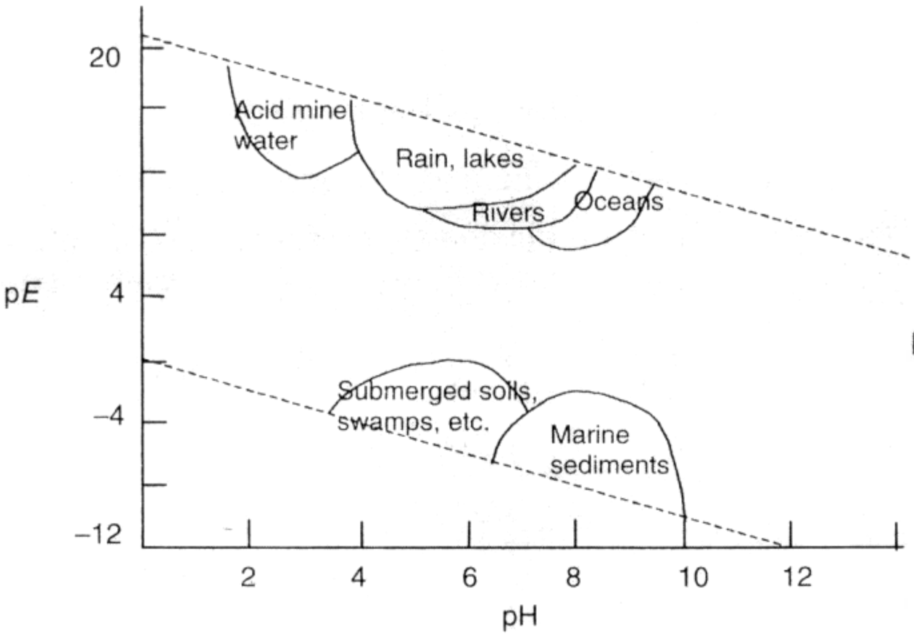


Fig. 10.6 Template for use with p*E*/pH plots. The indicated areas show typical p*E* and pH values for commonly encountered aqueous, soil, and sediment environments.

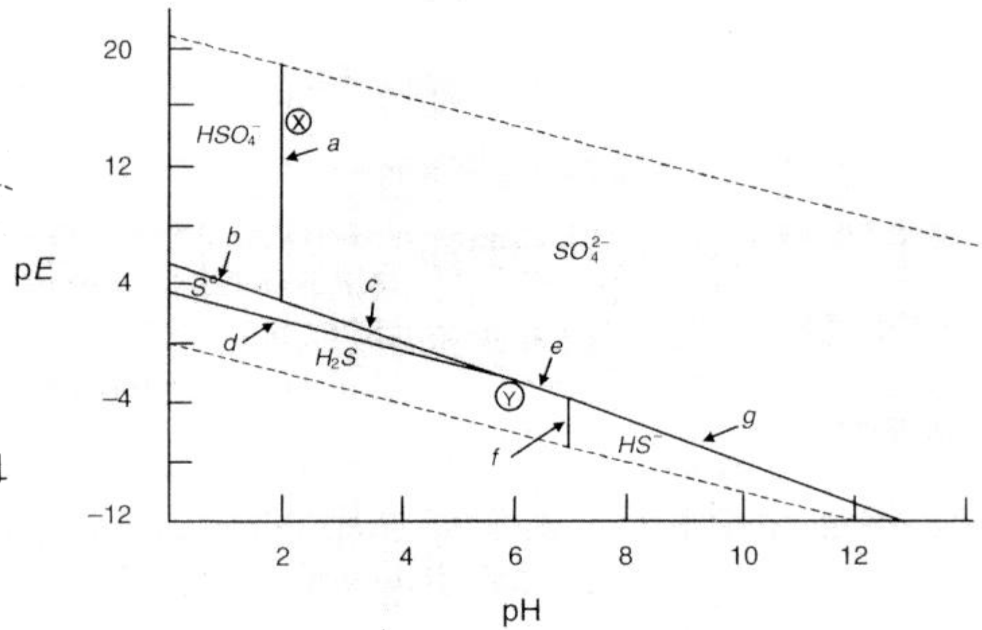


Fig. 10.5 The p*E*/pH for the aqueous sulfur system.