Chapter 2

1. The equation for the reaction is

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

ΔG^o (kcal/mole): –56.69 –54.64

For the overall reaction, $\Delta G^o = -54.64 - (-56.69) = 2.05$ kcal/mole

2. The equation for the reaction is

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

ΔG^o (kcal/mole): –95.51 0 –89.0

For the overall reaction, $\Delta G^o = -89.0 + 0 - (-95.51) = 6.51$ kcal/mole

From Eq. (2.12):

$K = \exp(-\Delta G^o/RT) = \exp[-(6\,510 \text{ cal/mole})/(1.987\,2 \text{ cal/°/mole})/(298.2°)]$

$= 1.69 \times 10^{-5}$

3. Reaction 14 in Table 1.3:

$Fe^{3+} + e^- = Fe^{2+}$ $\Delta G^o = -17.78$, $\tfrac{1}{2}Cl_2 + e^- = Cl^-$ $\Delta G^o = -31.39$

Combining the two reactions:

$Fe^{2+} = Fe^{3+} + e^-$ 17.78

$\underline{\tfrac{1}{2}Cl_2 + e^- = Cl^-}$ $\underline{-31.39}$

$Fe^{2+} + \tfrac{1}{2}Cl_2 = Cl^- + Fe^{3+}$ –13.61

From Eq. (2.12):

$$K = \exp\left(-\frac{\Delta G°}{RT}\right) = \exp\left[-\frac{-13\,610 \text{ cal/mole}}{(1.987\,2 \text{ cal/°/mole})(298.2°)}\right]$$

$= 9.43 \times 10^{9}$

The products on the right-hand side are strongly favored.

4. F.E. of formation of ClO_4^-

$$\tfrac{1}{8}ClO_4^- + H^+ + e^- = \tfrac{1}{2}Cl^- + \tfrac{1}{2}H_2O \qquad \Delta G^o = -31.6 \text{ kcal/mole}$$

H^+: $\Delta G^o = 0$

H_2O: $\Delta G^o = -56.69$ kcal/mole

Cl^-: $\Delta G^o = -31.35$ kcal/mole

e^-: $\Delta G^o = 0$

$$-31.6 = (1/2)(-56.69) + (1/2)(-31.35) - [0 + 0 + (1/8)(\Delta G^o\ ClO_4^-)]$$

$$\Delta G^o\ ClO_4^- = -8(-31.6 + 44.0) = -99.2 \text{ kcal/mole}$$

5. Ratio of K at 20 and 80°C

$T_1 = 20 + 273.2 = 293.2°K$, $T_2 = 80 + 273.2 = 353.2°K$

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$

Ca^{2+}: $\Delta H^o = -129.77$ kcal/mole

CO_3^{2-}: $\Delta H^o = -161.63$ kcal/mole

$CaCO_3$: $\Delta H^o = -288.45$ kcal/mole

for the reaction, $\Delta H^o = -288.45 - (-161.63 - 129.77) = 2.95$ kcal/mole

R = 1.987 2 cal/°-mole

$$\ln \frac{K_{T_1}}{K_{T_2}} = \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\frac{K_{T_1}}{K_{T_2}} = \exp\left[\frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right] = \exp\left[\frac{2.95\ \text{kcal/mole}}{1.987\,2\ \text{cal/°/mole}}\left(\frac{1\,000\ \text{cal}}{\text{kcal}}\right)\left(\frac{1}{353.2°} - \frac{1}{293.2°}\right)\right]$$

$$= 0.423$$

$$\frac{K_{80}}{K_{20}} = \frac{1}{0.423} = 2.36$$

6. In the nomograph, the temperature scale represents the equilibrium constant as a function of temperature. The equilibrium constant does not monotonically change since values of it above 52°C have values that are equal to those below 52°C. Since a TDS of 0 results in activity coefficients of 1, projecting from TDS = 0 to the temperature line merely confirms the former statement.

   The equilibrium constant does not follow the van't Hoff equation which predicts a monotonic variation in the equilibrium constant as a function of temperature.

7. The semi-permeable membrane selectively allows ions to migrate from one cell to the other. Ions that are being oxidized or deduced are not allowed to migrate through the membrane. The semi-permeable membrane allows the internal circuit to be completed and forces electrons through the external circuit allowing the potential of the reaction to be measured.

8. E^o for

$Zn^{2+} + S^{2-}$ 🕓 ZnS

ΔG^o for ZnS: –47.40 kcal/mole; ΔG^o for Zn^{2+}: –35.18 kcal/mole; ΔG^o for S^{2-}: 20 kcal/mole

for the reaction:

$$\Delta G^o = -47.40 - (-35.18 + 20) = -32.2 \text{ kcal/mole}$$

F = 23 062 cal/V-eq; n is the no. of equivalents/ mole. n = 2

$$E^o = -\frac{\Delta G^o}{nF} = -\frac{-32.2\ \text{kcal/mole}}{(2\ \text{eq})(23\ 062\ \ \text{cal/V - eq})}\left(\frac{1\ 000\ \text{cal}}{\text{kcal}}\right) = 0.698\ \text{V}$$

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9. $MnO_4^- + 8H^+ + 5e^- = Mn^{2+} + 4H_2O$

From Table 1.3, $E^o = 1.491$ V, $[Mn^{2+}] = [MnO_4^-]$

The Nernst equation for this reaction is $E_{sys} = E^o - \frac{0.059}{5}\left(\frac{T}{298}\right) \log \frac{[Mn^{2+}]}{[MnO_4^-][H^+]^8}$

(a) pH = 5.0 and the temperature is 25°C.

$[H^+] = 10^{-pH} = 1.00 \times 10^{-5}$, T = 273 + 25 = 298°K

$$E_{sys} = 1.491 - \frac{0.059}{5}\left(\frac{298}{298}\right) \log \frac{1}{(1 \times 10^{-5})^8} = 1.019\ \text{V}$$

Below a system potential of 1.019 V, $[Mn^{2+}] > [MnO_4^-]$.

(b) pH = 4.5 and the temperature is 5°C.

$[H^+] = 10^{-pH} = 3.16 \times 10^{-5}$; T = 273 + 5 = 278°K

$$E_{sys} = 1.491 - \frac{0.059}{5}\left(\frac{278}{298}\right) \log \frac{1}{(3.16 \times 10^{-5})^8} = 1.095\ \text{V}$$

Below a system potential of 1.095 V, $[Mn^{2+}] > [MnO_4^-]$.

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10. (a) The half-reactions and standard potentials are:

$Cu^{2+} + 2e^- = Cu$	$E^o = 0.345$ V
$Zn^{2+} + 2e^- = Zn$	$E^o = -0.762$ V

Reversing the half-reaction for Zn and adding the two reactions:

$Cu^{2+} + 2e^- = Cu$	0.345
$Zn - 2e^- = Zn^{2+}$	0.762
$Cu^{2+} + Zn = Cu + Zn^{2+}$	1.107 V

The gram atomic weights of $CuSO_4$ and $ZnSO_4$ are 159.5 and 161.4 g, respectively. The initial concentrations are

$$[Cu^{2+}] = \frac{0.100\ \text{g/L}}{159.5\ \text{g/mole}} = 6.27 \times 10^{-4}\ \text{M}$$

$$[Zn^{2+}] = \frac{0.100\ \text{g/L}}{161.4\ \text{g/mole}} = 6.20 \times 10^{-4}\ \text{M}$$

From the overall reaction, if the concentration of Cu^{2+} that has reacted is defined as x M, the concentrations of Cu and Zn at any time are

$[Cu^{2+}] = 6.27 \times 10^{-4} - x$; $[Zn^{2+}] = 6.20 \times 10^{-4} + x$

At equilibrium the potentials of the two half-reactions are equal. The Nernst equations for each half-reaction are:

$$E_{Cu} = E^o_{Cu} - \frac{0.059}{2} \log \frac{[Cu(s)]}{[Cu^{2+}]} = 0.345 - \frac{0.059}{2} \log \frac{1}{6.27 \times 10^{-4} - x}$$

$$E_{Zn} = E^o_{Zn} - \frac{0.059}{2} \log \frac{[Zn(s)]}{[Zn^{2+}]} = -0.762 - \frac{0.059}{2} \log \frac{1}{6.20 \times 10^{-4} + x}$$

Equating the above two equations:

$$0.345 - \frac{0.059}{2} \log \frac{1}{6.27 \times 10^{-4} - x} = -0.762 - \frac{0.059}{2} \log \frac{1}{6.20 \times 10^{-4} + x}$$

$$\frac{(1.107)2}{0.059} = 37.53 = \log \frac{6.20 \times 10^{-4} + x}{6.27 \times 10^{-4} - x}$$

$$10^{37.53} = 3.35 \times 10^{37} = \frac{6.20 \times 10^{-4} + x}{6.27 \times 10^{-4} - x}$$

$2.10 \times 10^{34} - 3.35 \times 10^{37}x = 6.20 \times 10^{-4} + x$

$$x = \frac{2.10 \times 10^{34}}{3.35 \times 10^{37}} = 6.27 \times 10^{-4}\,M$$

$[Cu^{2+}] = 6.27 \times 10^{-4} - 6.27 \times 10^{-4} = 0$. Effectively all of the available Cu^{2+} has reacted.

$[Zn^{2+}] = 6.20 \times 10^{-4} + 6.27 \times 10^{-4} = 1.25 \times 10^{-3}$ M

The half-reaction for Zn will be used to calculate E_{sys}.

$$E_{Zn} = -0.762 - \frac{0.059}{2} \log \frac{1}{1.25 \times 10^{-3}} = -0.848\ V$$

Note: This value can now be used to find the actual concentration of Cu^{2+} by applying the Nernst equation.

$$-0.848 = 0.345 - \frac{0.059}{2} \log \frac{1}{[Cu^{2+}]}$$

$\log [Cu^{2+}] = -40.4$, $[Cu^{2+}] = 10^{-40.4}$ confirming the result above.

(b) The initial potential difference is

$$E_{Cu} - E_{Zn} = E_C = E^o_{Cu} - E^o_{Zn} - \frac{0.059}{2} \log \frac{[Cu\ (s)][Zn^{2+}]}{[Cu^{2+}][Zn\ (s)]}$$

$$= 0.345 + 0.762 - \frac{0.059}{2} \log \frac{[6.20 \times 10^{-4}]}{[6.27 \times 10^{-4}]} = 1.107\ V$$

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11. $Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\ (s)$

ΔG^o (kcal/mole): −108.99 −37.594 −199.27

For the reaction: $\Delta G^o = -199.27 - [-108.99 + (2 \times -37.594)] = -15.09$ kcal/mole

$$K = \exp(-\Delta G^o/RT) = \exp -\left[\frac{(-15\,090 \text{ cal/mole})}{(1.987\,2 \text{ cal/°/mole})(298.2°)}\right]$$

$$= 1.15 \times 10^{11}$$

12. It is not possible to make an ORP measurement with the electrodes placed in solutions that are not in contact with a conductive medium. It is not possible for current to flow around a circuit in this case because the internal circuit is open.

13. E_{sys} is the ORP with respect to the hydrogen scale. The meter would read E_{sys} if the reference electrode had a potential of 0 which is the potential of the SHE. The potential with respect to the SHE is 0.26 V.

14. From Table 1.3 the half-reaction is

$$\tfrac{1}{8}NO_3^- + \tfrac{5}{4}H^+ + e^- = \tfrac{1}{8}NH_4^+ + \tfrac{3}{8}H_2O \qquad E^o = 0.880 \text{ V}$$

pH = 6.58, $[H^+] = 10^{-6.58} = 2.63 \times 10^{-7}$

The Nernst equation is

$$E_{sys} = E^o - \frac{0.059}{1} \log \frac{[NH_4^+]^{1/8}}{[NO_3^-]^{1/8}[H^+]^{5/4}}$$

$$[NH_4^+] = [NO_3^-]$$

$E_{sys} = 0.880 - 0.059 \log (2.63 \times 10^{-7})^{-1.25} = 0.395$ V

$E_{ref} = 0.24$ V

$E_{meter} = E_{sys} - E_{ref} = 0.395 \text{ V} - 0.24 \text{ V} = 0.155$ V

15. (a) Water with a higher concentration of ions promotes corrosion because the water has more current carrying ability. Effectively the resistance of the solution is reduced as the concentration of ions rises.

    (b) Glucose or any other non-ionized species in solution does not contribute to current carrying ability of the water. Therefore the rate of corrosion is independent of the concentration of these species.

16. The standard potentials for tin and iron are –0.136 and –0.44 V, respectively. Iron is the more active element and therefore it will corrode when these two metals are in contact.

17. The factors that influence the corrosion of a water distribution pipe laid underground are as follows.

    Pipe material: Some metals are more resistant to corrosion and alloys are more resistant than most metals. Some metals will corrode somewhat to form a protective metal oxide that acts as a barrier to further attack.

    Water composition: The oxygen content and concentration of other oxidants increases the rate of corrosion of metals. Dissolved solids content, particularly ionic species and pH influence the rate of corrosion. A high dissolved solids content increases the current carrying capacity of the water and enhances corrosion. Low pH can cause direct acid attack.

    Inhibitors in the water: The water may contain species that precipitate to form a protective barrier on the pipe.

Protective coating: A protective coating may be applied inside or outside of the pipe to provide a barrier against corrosive agents.

Backfill: Uniform backfill minimizes potential differences around the pipe.

Groundwater composition: The same water quality factors as discussed above apply to water in contact with pipe on its outside surface.

Cathodic protection: If cathodic protection is applied the pipe will be protected at the expense of a sacrificial anode or at a cost of electrical energy to raise its potential.

18. Microorganisms influence corrosion by changing environmental conditions. In particular, microbial activities change concentrations of substances such as oxygen, hydrogen ion (pH), and molecular hydrogen which are important factors in corrosion. Some products of microbial metabolism such as H_2SO_4 are strongly corrosive agents.

    The growth of colonies on surfaces causes concentration cells to form along the surface where concentrations of substances vary from point to point. Differences in concentration result in potential differences which causes corrosion.

    Some bacteria such as the iron-oxidizing bacteria directly attack structural materials.

19. Galvanic and electrolytic cathodic protection only protect the outside surface of a pipe against corrosion. The circuit consists of the soil solution, the pipe, and wire delivering electrons to the pipe. The pipe itself is a barrier to positive ions reaching the water inside the pipe. Electrons travelling to the inside of the pipe would cause a buildup of negative charge which is impossible.

20. A uniform backfill results in a constant electrochemical potential or pressure along the outer surface of the pipe or structure to be protected. Potential differences result in a flow of electrons and corrosion to occur.

21. The equivalent weights of Zn(II) and Mg(II) are 65.4/2 = 32.7 g and 24.3/2 = 12.2 g, respectively.

    Using Eq. (2.23),

$$m_{Mg} = \frac{it(\text{eq wt Mg})}{E_{Mg}F} \qquad m_{Zn} = \frac{it(\text{eq wt Zn})}{E_{Zn}F}$$

$E_{Mg} = 0.50$ and $E_{Zn} = 0.90$. Taking the ratio of the above 2 equations and noting that the current flow, i ,and time period, t, are equal:

$$\frac{m_{Mg}}{m_{Zn}} = \frac{(\text{eq wt Mg})E_{Zn}}{(\text{eq wt Zn})E_{Mg}} = \frac{12.2(0.90)}{32.7(0.50)} = 0.67$$

The mass of Mg required is 67% of the mass of Zn to provide the same degree of protection. The breakeven cost ratio is 1/0.67 = 1.49. If Mg is more than 149% of the cost of Zn then Zn is the more economical choice and vice-versa.

22. $l = 100$ m, $I = 17 \times 10^{-3}$ amp/m^2, o.d. = 0.315 m

    The surface area of the pipe is

$$A = \pi dl = \pi(100 \text{ m})(0.315 \text{ m}) = 99.0 \text{ m}^2$$

$$i = IA = (17 \times 10^{-3} \text{ amp/m}^2)(99.0 \text{ m}^2) = 1.69 \text{ amp}$$

t = 365 d, $E_{Zn} = 0.90$, the eq. wt. of Zn is 65.4/2 = 32.7 g, F = 96 493 coulombs/eq

$$m_{Zn} = \frac{it(\text{eq wt Zn})}{E_{Zn}F} = \frac{(1.69\text{ amp})(1\text{ coulomb/s/amp})(365\text{ d})(24\text{ h/d})(3\,600\text{ s/h})(32.7\text{ g/eq})}{(0.90)(96\,493\text{ coulombs/eq})}$$

$$= 20\,067\text{ g} = 20.1\text{ kg}$$