Chem 338

Homework Set #9 solutions November 14, 2001

From Atkins: 9.7, 9.10a-d, 9.11a-d, 9.14a-d, 9.17a-d, 9.21a-c, 9.32a-c, 9.37, 9.39

9.7) For a standard hydrogen electrode with P_{H_2} = 1.45 bar in HBr(aq):

1/2 reaction: $H^+(aq) + e^- \rightarrow \frac{1}{2}H_2$

$$Q = \frac{\sqrt{a(H_2)}}{a(H^+)} = \frac{\sqrt{P_{H_2}}}{[H^+]}$$

Nernst eqn: $E = E^o - \dfrac{RT}{\nu F}\ln Q$

For the change in potential in going from 0.005 M to 0.025 M in H^+ :

$$\Delta E = -\frac{RT}{\nu F}\ln Q_2 - \left(-\frac{RT}{\nu F}\ln Q_1\right)$$

where Q_2 is Q at 0.025 M and Q_1 is for $[H^+]$ = 0.005 M (note that the E^o's cancelled out)

$$\Delta E = \frac{RT}{\nu F}\ln\frac{Q_1}{Q_2} = \frac{RT}{F}\ln\frac{\frac{\sqrt{1.45}}{0.005}}{\frac{\sqrt{1.45}}{0.025}} = \frac{(8.3145)(298)}{96{,}485}\ln\frac{0.025}{0.005}$$

$$= +41 \text{ mV}$$

9.10) Write the cell reactions and electrode 1/2 reactions for the following:

a) $Ag|AgNO_3(aq,m_L)||AgNO_3(aq,m_R)|Ag$

right: $Ag^+(aq,m_R) + e^- \rightarrow Ag(s)$

left: $Ag^+(aq,m_L) + e^- \rightarrow Ag(s)$

Overall: $Ag^+(aq,m_R) \rightarrow Ag^+(aq,m_L)$ (concentration cell)

b) $Pt|H_2(g,P_L)|HCl(aq)|H_2(g,P_R)|Pt$

right: $2H^+(aq) + 2e^- \rightarrow H_2(g,P_R)$

left: $2H^+(aq) + 2e^- \rightarrow H_2(g,P_L)$

Overall: $H_2(g,P_R) \rightarrow H_2(g,P_L)$

c) $Pt|K_3[Fe(CN)_6](aq),K_4[Fe(CN)_6](aq)||Mn^{2+}(aq), H^+(aq)|MnO_2(s)|Pt$

right: $MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$

left: $[Fe(CN)_6]^{3-}(aq) + e^- \rightarrow [Fe(CN)_6]^{4-}(aq)$

Overall:

$MnO_2(s) + 4H^+(aq) + 2[Fe(CN)_6]^{4-}(aq) \rightarrow Mn^{2+}(aq) + 2H_2O(l) + 2[Fe(CN)_6]^{3-}(aq)$

d) $Pt|Cl_2(g)|HCl(aq)||HBr(aq)|Br_2(l)|Pt$

right: $Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$

left: $Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$

overall: $Br_2(l) + 2Cl^-(aq) \rightarrow 2Br^-(aq) + Cl_2(g)$

9.11) Write the Nernst eqn. for the reactions in 6.5

a) $$E = E^o - \frac{RT}{(1)F}\ln\frac{[Ag^+,L]}{[Ag^+,R]}$$

b) $$E = E^o - \frac{RT}{(2)F}\ln\frac{P_L}{P_R}$$

c) $$E = E^o - \frac{RT}{(2)F}\ln\frac{[Mn^{2+}][Fe(CN)_6{}^{3-}]^2}{[H^+]^4[Fe(CN)_6{}^{4-}]^2}$$

d) $$E = E^o - \frac{RT}{(2)F}\ln\frac{[Br^-]^2 P_{Cl_2}}{[Cl^-]^2}$$

9.14) Use the standard potentials of the electrodes to calculate the standard potentials of the cells:

a) Since this is a concentation cell, no potential difference exists when the two electrodes have the same concentration (both are in their standard states), $E^o = 0$ V

b) As in part a), $E^o = 0$ V

Using table of std reduction potentials in Appendix 2 of the text:

c) $E^o = 1.23\text{ V} - 0.36\text{ V} = +0.87\text{ V}$ (cathode minus anode)

d) $E^o = 1.09\text{ V} - 1.36\text{ V} = -0.27\text{ V}$

9.17) State what you would expect to happen to the cell potential if the following changes were made to the cells of 6.5:

In each case, determine the change in the reaction quotient, Q, and then predict the change in E using the Nernst equation.

a) [$AgNO_3$(aq)] is increased in the <u>left-hand</u> compartment

then [Ag^+(aq),L] will increase, which will increase Q, which will increase lnQ. Since E^o is 0.0, E will increase in magnitude in the negative direction, or in other words, |E| will increase

b) P_{H_2} is increased in the <u>left-hand</u> side compartment

same as in part a) for the same reasons, |E| will increase

c) The pH of the <u>right-hand</u> compartment is decreased

therefore [H^+] <u>increases</u>, which makes Q decrease (H^+ appears in the denominator). Since E^o has a positive value, the decrease of lnQ will cause E to become larger.

d) The concentration of HCl is increased.

therefore [Cl^-] increases, which decreases Q. Depending on how small Q becomes, E will initially decrease in magnitude (–0.27 V → 0.0), but may eventually change sign and increase in magnitude in the positive direction. (natural log of a number less than 1 is a negative number)

9.21) Calculate the standard Gibbs free energies at 25ºC for the following from their standard reduction potentials

a) $Ca(s) + 2H_2O \rightarrow Ca(OH)_2(aq) + H_2(g)$

the 1/2 reactions are:

$2H_2O(l) + 2e^- \rightarrow H_2 + 2OH^-$ $\quad$ Eº = –0.83 V

$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$ $\quad$ Eº = –2.87 V

Eº(cell) = –0.83 – (–2.87) = +2.04 V

$\Delta G_r^o = -\nu F E^\circ$

$= -(2)(96485)(2.04) = -394 \times 10^3$ J/mol = –394 kJ/mol

b) $2Ca(s) + 4H_2O(l) \rightarrow 2Ca(OH)_2(aq) + 2H_2(g)$

the 1/2 reactions are the same as in part (a), but the number of moles of electrons transferred is now 4 instead of 2.

$\Delta G_r^o = -(4)(96485)(2.04) = -787 \times 10^3$ J/mol = –787 kJ/mol

Note that this conflicts with the book's answer

c) $Fe(s) + 2H_2O(l) \rightarrow Fe(OH)_2(aq) + H_2(g)$

the 1/2 reactions are:

$2H_2O(l) + 2e^- \rightarrow H_2 + 2OH^-$ $\quad E^o = -0.83$ V

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $\quad E^o = -0.44$ V

$E^o(cell) = -0.83 - (-0.44) = -0.39$ V

$\Delta G_r^o = -(2)(96485)(-0.39) = 75.3 \times 10^3$ J/mol = 75 kJ/mol

9.32) Calculate equilibrium constants for the following

a) $Sn(s) + Sn^{4+}(aq) \leftrightarrows 2Sn^{2+}(aq)$

1/2 reactions:

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $\quad E^o = -0.14$ V

$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ $\quad E^o = +0.15$ V

For the above overall reaction, $E^o(cell) = 0.15 - (-0.14) = +0.29$ V

$$E^\circ = \frac{RT}{\nu F}\ln K, \quad \text{or} \quad K = e^{\frac{\nu F}{RT}E^\circ}$$

$$K = \exp\left[\frac{(2)(96485)}{(8.3145)(298)}(0.29)\right] = 6.44 \times 10^9$$

b) $Sn(s) + 2AgBr(s) \leftrightarrows SnBr_2(aq) + 2Ag(s)$

1/2 reactions:

$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$ $\quad E^o = -0.14$ V

$2AgBr(s) + 2e^- \rightarrow 2Ag(s) + 2Br^-(aq)$ $\quad E^o = +0.0713$ V

$E^o(cell) = 0.0713 - (-0.14) = 0.2113$ V

$$K = \exp\left[\frac{(2)(96485)}{(8.3145)(298)}(0.2113)\right] = 1.40 \times 10^7$$

c) $Fe(s) + Hg(NO_3)_2(aq) \leftrightarrows Hg(l) + Fe(NO_3)_2(aq)$

1/2 reactions:

$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $\qquad E^\circ = -0.44$ V

$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$ $\qquad E^\circ = +0.86$ V

E°(cell) = 0.86 – (–0.44) = 1.30 V

9.37) Calculate the molar solubility and solubility constant of AgI for the cell Ag|AgI(s)|AgI(aq)|Ag, which has an E°(cell) at 25°C of +0.9509 V.

1/2 reactions:

Right hand side: $Ag^+(aq) + e^- \rightarrow Ag(s)$

Left hand side: $AgI(s) + e^- \rightarrow Ag(s) + I^-(aq)$

Overall reaction (R–L): $Ag^+(aq) + I^-(aq) \rightarrow AgI(s)$ $\qquad E^\circ = 0.9509$ V

$$K = \exp\left[\frac{(1)(96485)}{(8.3145)(298)}(0.9509)\right] = 1.206 \times 10^{16}$$

But, $K_{sp} = 1/K$ (reverse reaction as written above), so $K_{sp} = 8.3 \text{ x } 10^{-17}$

Of course, you could also directly calculate the K_{sp} by reversing the overall cell reaction and appropriately changing the sign of E°.

As usual, $K_{sp} = [Ag^+][I^-] = S^2$

$$S = \sqrt{K_{sp}} = 9.10 \times 10^{-9} \text{ M}$$

9.39) A fuel cell develops an electric potential from the chemical reaction between reagents supplied from an outside source. What is the zero-current potential of a cell fuelled by (a) hydrogen and oxygen, (b) the complete oxidation of benzene at 1.0 bar and 298 K?

In each case, the strategy is to calculate ΔG_r using ΔG_f's , determine the number of electrons being transferred by assigning oxidation numbers, and then use $\Delta G_r = -n\mathrm{F}E^{\mathrm{o}}$ to calculate the zero-current potential of the cell.

a) The reaction is: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

$$\Delta G_r^o = -237.13 - (0) - 1/2(0) = -237.13 \text{ kJ/mol}$$

the oxidation number of each H (there are 2) increases by 1 (0 → 1) and the O decreases by 2 (0 → –2), therefore n=2

$$E^o = -\frac{\Delta G_r^o}{nF} = -\frac{-237.13\times10^3}{(2)(96485)} = 1.23 \text{ V}$$

b) The reaction is: $C_6H_6(l) + \frac{15}{2}O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l)$

$$\Delta G_r^o = 6(-394.36) + 3(-237.13) - (124.3) = -3201.85 \text{ kJ.mol}$$

in this reaction the oxidation number of each C goes from –1 to +4, and each O goes from 0 to –2. Therefore n=30 (6 x 5 and 15 x 2).

$$E^o = -\frac{\Delta G_r^o}{nF} = -\frac{-3201.85\times10^3}{(30)(96485)} = 1.11 \text{ V}$$