

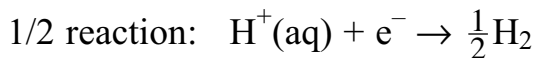
Chem 338

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 $P_{\text{H}_2} = 1.45$ bar in HBr(aq) :



$$Q = \frac{\sqrt{a(\text{H}_2)}}{a(\text{H}^+)} = \frac{\sqrt{P_{\text{H}_2}}}{[\text{H}^+]}$$

$$\text{Nernst eqn: } E = E^\circ - \frac{RT}{\nu F} \ln Q$$

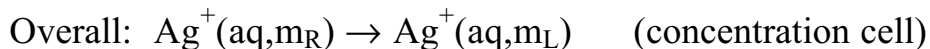
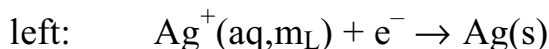
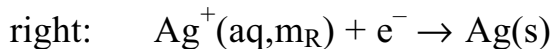
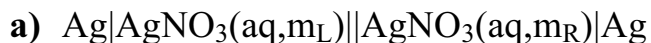
For the change in potential in going from 0.005 M to 0.025 M in H^+ :

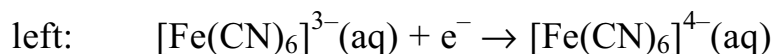
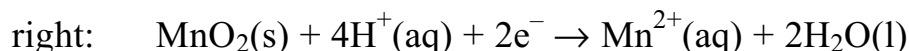
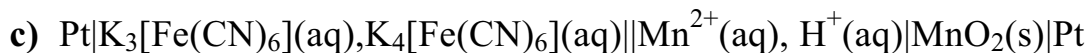
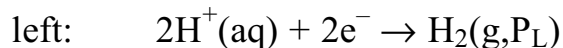
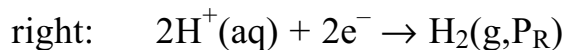
$$\Delta E = -\frac{RT}{\nu F} \ln Q_2 - \left(-\frac{RT}{\nu F} \ln Q_1 \right)$$

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

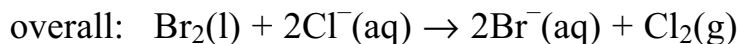
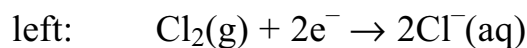
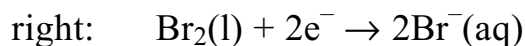
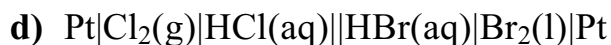
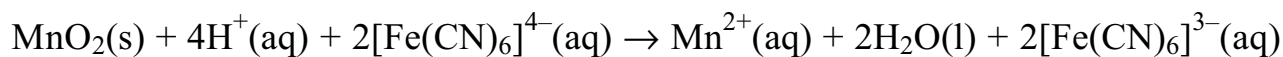
$$\begin{aligned} \Delta E &= \frac{RT}{\nu F} \ln \frac{Q_1}{Q_2} = \frac{RT}{F} \ln \frac{\frac{\sqrt{1.45}}{0.005}}{\frac{\sqrt{1.45}}{0.025}} = \frac{(8.3145)(298)}{96,485} \ln \frac{0.025}{0.005} \\ &= +41 \text{ mV} \end{aligned}$$

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





Overall:



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

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

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

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

d)
$$E = E^\circ - \frac{RT}{(2)F} \ln \frac{[\text{Br}^-]^2 P_{\text{Cl}_2}}{[\text{Cl}^-]^2}$$

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

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

b) As in part a), $E^\circ = 0 \text{ V}$

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

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

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

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) $[\text{AgNO}_3(\text{aq})]$ is increased in the left-hand compartment

then $[\text{Ag}^+(\text{aq}), \text{L}]$ will increase, which will increase Q , which will increase $\ln Q$.

Since E° 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 left-hand side compartment

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

c) The pH of the right-hand compartment is decreased

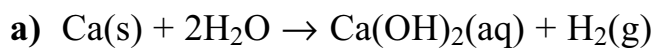
therefore $[\text{H}^+]$ increases, which makes Q decrease (H^+ appears in the

denominator). Since E° has a positive value, the decrease of $\ln Q$ will cause E to become larger.

d) The concentration of HCl is increased.

therefore $[\text{Cl}^-]$ increases, which decreases Q. Depending on how small Q becomes, E will initially decrease in magnitude ($-0.27 \text{ V} \rightarrow 0.0$), 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 25°C for the following from their standard reduction potentials



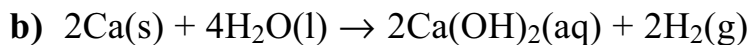
the 1/2 reactions are:



$$E^\circ(\text{cell}) = -0.83 - (-2.87) = +2.04 \text{ V}$$

$$\Delta G_r^\circ = -vFE^\circ$$

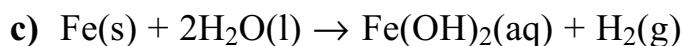
$$= -(2)(96485)(2.04) = -394 \times 10^3 \text{ J/mol} = -394 \text{ kJ/mol}$$



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.

$$\Delta G_r^\circ = -(4)(96485)(2.04) = -787 \times 10^3 \text{ J/mol} = -787 \text{ kJ/mol}$$

Note that this conflicts with the book's answer



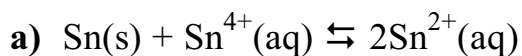
the 1/2 reactions are:



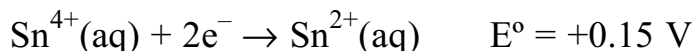
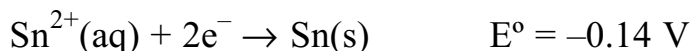
$$E^\circ(\text{cell}) = -0.83 - (-0.44) = -0.39 \text{ V}$$

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

9.32) Calculate equilibrium constants for the following



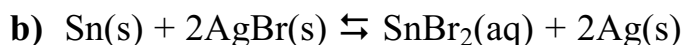
1/2 reactions:



$$\text{For the above overall reaction, } E^\circ(\text{cell}) = 0.15 - (-0.14) = +0.29 \text{ V}$$

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

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

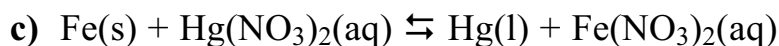


1/2 reactions:

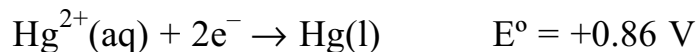
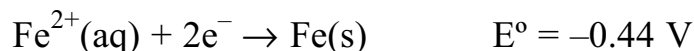


$$E^\circ(\text{cell}) = 0.0713 - (-0.14) = 0.2113 \text{ V}$$

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



1/2 reactions:

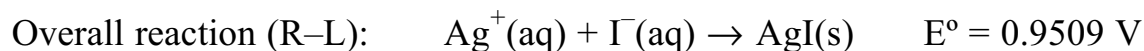
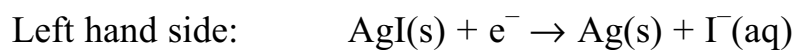


$$E^\circ(\text{cell}) = 0.86 - (-0.44) = 1.30 \text{ V}$$

9.37) Calculate the molar solubility and solubility constant of AgI for the cell

Ag|AgI(s)|AgI(aq)|Ag, which has an $E^\circ(\text{cell})$ at 25°C of +0.9509 V.

1/2 reactions:



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

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

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

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

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 $\Delta G_r = -nFE^\circ$ to calculate the zero-current potential of the cell.

a) The reaction is: $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$

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

the oxidation number of each H (there are 2) increases by 1 ($0 \rightarrow 1$) and the O decreases by 2 ($0 \rightarrow -2$), therefore $n=2$

$$E^\circ = -\frac{\Delta G_r^\circ}{nF} = -\frac{-237.13 \times 10^3}{(2)(96485)} = 1.23 \text{ V}$$

b) The reaction is: $\text{C}_6\text{H}_6(\text{l}) + \frac{15}{2}\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$

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

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

$$E^\circ = -\frac{\Delta G_r^\circ}{nF} = -\frac{-3201.85 \times 10^3}{(30)(96485)} = 1.11 \text{ V}$$