Chemistry 360

CORRECTED WORKSHEET for Lecture 22

1 Write the cell reactions and electrode half-reactions for the following cells:

a. $Ag(s) \mid AgNO_3(aq, c_L) \parallel AgNO_3(aq, c_R) \mid Ag(s)$

Cell reaction $Ag^+ (c_R) \rightarrow Ag^+ (c_L)$

Reduction on the RHS

$Ag^+ (c_R) + e^- \rightarrow Ag(s)$ $E_{red} = +0.799$ V

Oxidation on LHS

$Ag(s) \rightarrow Ag^+ (c_L) + e^-$

b. $Pt(s) \mid H_2(g, p_L) \mid HCl(aq) \mid H_2 (g, p_R) \mid Pt(s)$

Cell reaction : $\frac{1}{2} H_2 (p_L) \rightarrow \frac{1}{2} H_2 (p_R)$

Reduction on RHS

$H^+ + e^- \rightarrow \frac{1}{2} H_2(p_R)$ $E_{red} = 0$ V

Oxidation

$\frac{1}{2} H_2 (p_L) \rightarrow H^+ + e^-$

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

Cell reaction

$MnO_2 + 4\ H^+ + 2\ Fe(CN)_6^{-4} \rightarrow Mn^{2+} + 2\ H_2O + 2\ Fe(CN)6_4^{-3}$

Reduction on RHS

$MnO_2\ (s) + 4\ H^+\ + 2\ e^- \rightarrow Mn^{2+}\ (m) + 2H_2O$ Ered = 1.23 V

Oxidation on LHS

$Fe(CN)_6^{-4} \rightarrow Fe(CN)_6^{-3} + e^-$ $E_{red} = 0.36$ V so ($E_{ox} = -0.36$ V)

2 Write the Nernst equations for the cells in problem 1

(a) The way the reaction was written, one electron was transferred. Therefore, n = 1. We look to the overall cell reaction to determine Q.

$E_{Cell} = E_{cell}^o$ - (RT/nF) ln Q

$= E_{cell}^o$ - (8.31 J mol^{-1}K^{-1} ·298K/96,485 coul mol^{-1}) · ln (c_L/c_R)

$= E_{cell}^o$ - (0.026 V)·ln (c_L/c_R)

(b) n = 1

$E_{cell} = E_{cell}^o$ - (0.026 V) · ln $(p_R/p_L)^{1/2}$

NOTE: It's equally valid to have n = 2 and use

$E_{cell} = E_{cell}^o$ - ½ ·(0.026V) ln (p_R/p_L)

(c) n = 2

$E_{cell} = E_{cell}^o$ - ½ (0.026 V)· ln {([Mn^{+2}]a_{H2O} [$Fe(CN)_6^{-3}$]^2)/(a_{MoO2}·[H^+]^4[$Fe(CN)_6^{-4}$]^2)}

where a_{H2O} is approximately 1, a_{MO2} is 1.

3 Use the standard potentials for the electrodes to calculate the standard potentials of the cells in problem 1.

The standard cell potentials are simply $E_{red, LHS}^{o} - E_{red, RHS}^{o}$

(a) E_{red}^{o} for $Ag^{+} + e^{-} \rightarrow Ag(s)$ is 0.7991 V
same reaction is happening on LHS, so E_{cell}^{o} = 0.7991 V – 0.7991 V = 0 V

(b) E_{cell}^{o} = 0V – 0 V = 0 V

(c) E_{cell}^{o} = 1.23 V – (0.36 V) = 0.87 V

4 The rate of formation of C in the reaction $2A + B \rightarrow 3C + 2D$ is 2.2 mol L^{-1} s^{-1}. State the rates of formation and consumption of A, B, and D.

$$rate = \frac{1}{3}\frac{d[C]}{dt} = \frac{1}{2}\frac{d[D]}{dt} = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{d[B]}{dt};$$
$$\frac{d[C]}{dt} = \frac{3}{2}\frac{d[D]}{dt} = -\frac{3}{2}\frac{d[A]}{dt} = -3\frac{d[B]}{dt}$$

So formation of D = (2/3)·2.2 mol L^{-1} s^{-1} = 1.5 mol $L^{-1}s^{-1}$
Rate of CONSUMPTION (negative of formation) of A is 1.5 mol $L^{-1}s^{-1}$
Rate of CONSUMPTION of B = (1/3)·2.2 mol $L^{-1}s^{-1}$ = 0.73 mol L^{-1} s^{-1}

5 The rate law for the reaction in 4 was reported as rate = k[A][B][C]. What are the units of k?

rate has units of mol L^{-1} s^{-1}, so k has units of mol $L^{-1}s^{-1}/(mol\ L^{-1})^3$ = $L^2mol^{-2}s^{-1}$

6 The rate of the reaction A + 3B $\rightarrow$ C + 2D was reported as 1 mol L^{-1} s^{-1}. State the rates of formation or consumption of the participants.

$$1\,mol\ L^{-1}s^{-1} = \frac{d[C]}{dt} = \frac{1}{2}\frac{d[D]}{dt} = -\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt}$$

$$\frac{d[A]}{dt} = -1 mol\ L^{-1}s^{-1}$$

$$\frac{d[B]}{dt} = -3 mol\ L^{-1}s^{-1}$$

$$\frac{d[C]}{dt} = 1 mol\ L^{-1}s^{-1}$$

$$\frac{d[D]}{dt} = 2 mol\ L^{-1}s^{-1}$$

Note that when we say "rate of consumption," of A, we're actually referring to $-$d[A]/dt, which (consistently with above) is + 1 mol L^{-1} s^{-1}.