Assignment 5
CY102: Physical Chemistry
30.3.2004

1. Will the reaction 1/2Pb(s) + Ag^+ (a=1) = ½ Pb^{2+}(a=1) + Ag(s) be spontaneous? Given: $E^0(Ag^+/Ag)$ = 0.799 V; $E^0(Pb^{2+}/Pb)$ = -0.126V. **(Ans: Yes; E^0 cell = +0.925 V)**

Ans: Pb / Pb^{2+} // Ag^+ /Ag
a=1 a=1
E^0_{cell} = 0.799 – (-0.126) = 0.925V, spontaneous.

2. Write the cell reaction for the cell Sn/Sn^{2+}(0.1 M) // Fe^{3+}(0.3 M) / Fe and calculate the EMF of the cell. Given: $E^0(Sn^{2+}/Sn)$ = -0.136 V and $E^0(Fe^{3+}/Fe)$ = -0.0360V. **(Ans: 0.1193 V)**

Ans: 3 Sn + 2Fe^{3+} = 3 Sn^{2+} + 2Fe
(0.3m) (0.1m)
$E_{cell} = E^0_{cell} – 0.0591/6 \log [Sn^{2+}]^3/[Fe^{3+}]^2$
= 0.10 – 0.0591/6 log 0.1/9 = 0.1 + 0.0192 = 0.1192V.

3. For the cell SCE // $AgNO_3$ / Ag, the EMF of the cell was found to be 0.4 V. Calculate the Ag^+ concentration if E_{SCE} = 0.246 V and $E^0(Ag^+/Ag)$ = 0.799 V. **(Ans: 2.57 x 10^{-3}M)**

Ans: $E = E_{Ag^+/Ag} – E_{SCE}$ = 0.4 V.
$E_{Ag^+/Ag} = 0.4 + 0.246 = E^0_{Ag^+/Ag} + 0.0591 \log [Ag^+]$
0.646 – 0.799 = 0.0591 log [Ag^+]
log[Ag^+] = -2.5888
$\therefore [Ag^+] = 2.57 \times 10^{-3}$M.

4. Calculate ΔG, ΔH and ΔS for the cell Ag / AgCl / KCl (soln) / Hg_2Cl_2, Hg if the EMF if the EMF of the ell is 0.0445 V at 25^{0}C and the temperature coefficient is 3.38 x 10^{-4} V/degree.
(Ans: -4294 J, 5421 J, 32.6 JK^{-1})

Ans: Ag(s) + ½ Hg_2Cl_2(s) = AgCl(s) + Hg(l)
ΔG: -nFE = -1 x 96500 x 0.0445 = -4294.3J
$\Delta S = nF(\Delta E/\Delta T)_p = 1 \times 96500 \times 3.38 \times 10^{-4} = 32.6\ Jk^{-1}$
$\Delta H = \Delta G + T\Delta S$ = -4294.3 + 32.6 x 298 = 5420.5 J.

5. Calculate the equilibrium constant for the reaction that occurs in the cell Sn|Sn^{2+}(a=1) || Pb^{2+} (a=1) | Pb if E^0_{cell} is 0.014 V at 25^{0}C. **(Ans: 2.97)**

Ans: log K = $nE^0/0.0591$ = 2 x 0.014 / 0.0591 = 0.4738
K = 2.98

6. From the data provided, compute the standard half-cell potential for the reaction Fe^{3+} + 3e^- = Fe.

Half-cell reaction	**E^0/V at 298 K**
Fe^{3+} + e^- = Fe^{2+}	+0.77
Fe^{2+} + 2e^- = Fe	-0.44

(Ans: E^0 = -0.04 V)

Ans: $Fe^{3+} + 3e = Fe$, $E^0 = 1(0.77) + 2(-0.44)/3 = -0.037$ V.

7. The EMF of the cell SCE // HCl / quinhydrone (Pt) at 298K is + 0.25 V. Find the pH of the solution if E_{SCE} = 0.24 V and E^0 (Q, H_2Q) = 0.70 V at 298 K.

(Ans: 3.55)

Ans: $E_{cell} = E_{H2Q\,/\,Q} - E_{SCE}$

$= (E^0_{H2Q\,/\,Q} - 0.0591\ pH) - E_{SCE}$

$0.25 = (0.699 - 0.0591\ pH) - 0.24$

pH = 3.54.

8. ΔG and ΔH for the c ell Cd / $CdCl_2$ (aq) / AgCl (s) / Ag are –130.3 and –167.5 $kJmol^{-1}$ respectively at 300 K.

(Ans: 6.4 x 10^{-4} VK^{-1})

And: $Cd + 2\ AgCl = Cd^{2+} + 2\ Ag + 2Cl^-$

$\Delta G - \Delta H / T = -130.3 + 167.5 / 300 = 0.124\ kJ\ K^{-1} = -\Delta S$

$-\Delta S = -124\ JK^{-1} = 2 \times 96500 \times (\Delta E/\Delta T)_p$

$\therefore (\Delta E/\Delta T)_p = -6.42 \times 10^{-4}\ VK^{-1}$.

9. For the cell Ag / AgI / I^- // Ag^+ / Ag, E^0 (I^- / AgI / Ag) = 0.152 V. Find the solubility product of AgI.

(Ans: 1.95 x 10^{-17})

Ans: $Ag + I^- \rightarrow Ag\ I + e$

$Ag^+ + e \rightarrow Ag$

$Ag^+ + I^- \rightarrow Ag\ I$; $E^0 = 0.951$

$Ag\ I\ (s) \rightleftarrows Ag^+ + I^-$; $E^0 = -0.951$

$\log K_{sp} = 1 \times -0.951 / 0.0591 = -16.09$

$K_{sp} = 8.10 \times 10^{-17}$.

10. For the cell Al / Al^{3+} // Sn^{4+}, Sn^{2+} / Pt, the standard electrode potentials at 298K are $E^0(Al^{3+}/Al)$ = -1.66 V and $E^0(Sn^{4+}, Sn^{2+}/Pt)$ = +0.15 V. Calculate

(a) the cell EMF when the activities are all 0.1.
(b) the equilibrium constant. Comment on the magnitude of the equilibrium constant.

(Ans: (a) 1.83 V and (b) 10^{186})

Ans: (a) $2Al + 3\ Sn^{4+} \rightarrow 2Al^{3+} + 3\ Sn^{2+}$

$E = 1.81 - 0.0591 / 6 \quad \log 0.01 = 1.81 + 0.0197 = 1.83$ V.

(b) $\log K = 6(1.81) / 0.0591 = 183.76 \approx 184$

$\therefore K = 10^{184}$.

11. The solubility product of CuCl at 298 K is 2.29 x 10^{-7} and the standard reduction potential for the half-cell Cl^- (a=1) / CuCl(s) / Cu is 0.129 V. Calculate the standard electrode potential of the couple Cu^+ / Cu.

(Ans: 0.522 V)

Ans: $CuCl\ (s) = Cu^+ + Cl^-$; $K_{sp} = 2.29 \times 10^{-7}$

$E^0_{cell} = 0.0591 \log K_{sp} = -0.39$ V.

$-0.39 = 0.129 - E^{0}_{cu^{+}/cu}$

$\therefore E^{0}_{cu^{+}/cu} = 0.52$ V.

12. Write the working principles, half-cell reactions and the half-cell representations of the following reference electrodes:

(i) SHE
(ii) Saturated calomel
(iii) Quinhydrone
(iv) Silver-silver chloride
(v) Glass