ELECTROCHEMISTRY

electrons) are required. Hence, 3 x 2.00 =6.00 F are required to produce 53.96 g of Al.

(c) 1F = 96500 C per mole e^-

hence 6.00F = 6.00 x 96500 C = 5.790×10^5 C

(d) 1C = 1 amp-s (OR Q = It)

$\therefore$ t = Q/I = 5.790×10^5C/10A = 57900 s = 16.08 h

(e) 5.790×10^5 C are required to produce 53.96g Al

2 min = 2 x 60 = 120s

$$Q = It \therefore I = Q/t = \frac{5.790 \times 10^5\ C}{120\ s}\ (A)$$

I = 4,825 A

In general, electrolysis of aqueous solutions containing any metal ion that is a weaker oxidizing agent than H^+ (or H_3O^+) (like alkali metal and alkaline earth cations, Al^{3+}, Mn^{2+}, Zn^{2+}, Cr^{3+}, Fe^{2+}, CO^{2+}, Ni^{2+}, Sn^{2+}, Pb^{2+}, Fe^{3+}) will produce $H_2(g)$ at the cathode. In other words, no reducing agent stronger than H_2 is liberated during electrolysis of aqueous solutions.

QUESTIONS

6.1 Which of the following redox reactions will be spontaneous?

(a) $H_2(g) + Hg^{2+}(aq) \rightarrow 2H^+(aq) + Hg(l)$ E^o = 0851 V

(b) $Zn(s) + 2Tl^+(aq) \rightarrow Zn^{2+}(aq) + 2Tl(s)$ E^0 = 0.427 V

(c) $2Al(s) + 3Ni^{2+}(aq) \rightarrow 2Al^{3+}(aq) + 3Ni(s)$ E^0 = 1.43 V

(d) $2Fe^{2+}(aq) + I_2(aq) \rightarrow 2Fe^{3+}(aq) + 2I^-(aq)$ E^o = -0.235 V

(e) $Fe(s) + Cr^{3+}(aq) \rightarrow Fe^{3+}(aq) + Cr(s)$ E^o = -0.70 V

(f) $6H^+(aq) + 2Sc(s) \rightarrow 3H_2(g) + 2Sc^{3+}$ E^o = 2.08 V

6.2 Given the following data:

$Ni^{2+} + 2e^- \rightarrow Ni(s)$ E^o = -0.23 V

$Zn^{2+} + 2e^- \rightarrow Zn(s)$ E^o = -0.76 V

(a) Determine the standard cell potential (for a spontaneous reaction)

(b) Write the spontaneous cell reaction

(c) Write the cell diagram

6.3 Given the following data:

$2H^+ + 2e^- \rightarrow H_2$ $E^o = 0.00$ V

$Cu^{2+} + 2e^- \rightarrow Cu(s)$ $E^o = 0.34$ V

$HNO_3 + 3H^+ + 3e^- \rightarrow NO + 2H_2O$ $E^o = 0.96$ V

Explain why copper metal does not dissolve in a typical strong acid like HCl, but will dissolve in 1.0M HNO_3.

6.4 The standard cell potential for the following reaction is 1.105V:

$Zn(s)/Zn^{2+}$ (1.0M)// Cu^{2+} (1.0M)/Cu(s)

(a) Write equations for the anode, cathode and overall cell reactions

(b) Calculate $E^o_{Cu^{2+}/Cu}$, given thn $E^o_{Zn^{2+}/Zn}$ $E^o_{Cu^{2+}/Cu}$ = -0.763 V

6.5 Will Mn reduce Mg^{2+} ions to Mg when all concentrations are 1.0M?

6.6 Will $Cr_2O_7^{2-}$ oxidize Fe^{2+} ions to Fe^{3+} ions in acidic solution and under standard state conditions?

6.7 Which of the following reactions would occur spontaneously as written, when all substances are in their standard states?

(a) $2MnO_4^- + 16H^+ + 10Br^-_{(aq)} \rightarrow 5Br_2 + 2Mn^{2+}(aq) + 8H_2O$

(b) $ClO^-(aq) + NO_2^-(aq) \rightarrow Cl^-(aq) + NO_3^-(aq)$

(c) $Pb(s) + Zn^{2+}(aq) \rightarrow Pb^{2+}(aq) + Zn(s)$

(d) $Cl_2(g) + 2Br^-(aq) \rightarrow Br_2(aq) + 2Cl^-(aq)$

6.8 Calculate E° for the following reactions and predict whether the reactions should occur spontaneously as written when run under standard conditions:

(a) $2CrO_4^{2-}(aq) + 3Ni(s) + 8H_2O(l) \rightarrow 2Cr(OH)_3(s) + 3Ni(OH)_2(s) + 4OH^-(aq)$

(b) $Ca(s) + 2H_2O(l) \rightarrow Ca^{2+}(aq) + 2OH^-(aq) + H_2(g)$

(c) $2Fe^{2+}(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + H_2(g)$

6.9 (a) Will I_2 oxidize Fe^{2+} to Fe^{3+} in acid solution?

(b) Will I_2 oxidize H_2SO_3 to SO_4^{2-} in acid solution?

$E^o_{H_2O|H_2} = -0.828V$

$E^o_{Fe^{2+}|Fe^{3+}} = -0.770V$

$E^o_{I_2|I^-} = 0.535V$

$E^o_{Ca|Ca^{2+}} = -2.76V$

$E^o_{Fe^{3+}|Fe^{2+}} = 0.77V$

$E^o_{CrO_4^{2-}|Cr(OH)_3} = -0.12V$

$E^o_{Ni|Ni^{2+}} = 0.72V$

(c) Will Sn^{4+} oxidize H_2O_2 to O_2 in acid solution?

(d) Will H_2O reduce Cl_2 to Cl^- in acid solution?

Note that all reactions are run under standard conditions.

6.10 Calculate the *volume* of gas (at STP) that will collect at the cathode and anode when water is electrolyzed for 45.0 minutes with a 12.0-amp current.

6.11 With 10C of electric charge, how many grams of silver metal can be prepared? [Ar:Ag = 107.868].

6.12 Describe what happens during the electrolysis of the following aqueous solutions.

(a) NaCl; (b) Na_2SO_4; (c) NaI; (d) CaI_2 (e) $CuBr_2$

6.13 Consider the following cathode reaction

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

Calculate the initial concentration of the permanganate solution if passage of 0.600 – amp current for 10 minutes completely reduced all the permanganate present in 15.0mL of solution.

6.14 Use the Nernst equation to calcuiate the cell potential at 25°C for the following cells:

$E^0_{Zn/Zn^{2+}} = +0.763V$

(a) $Zn(s)/Zn^{2+}(0.100M)//Ag^+(0.010M)/Ag(s)$

(b) $Cu(s)/Cu^{2+}(0.075M)//Ag^+(0.015M)/Ag(s)$ $E^0_{Ag^+/Ag} = +0.800V$

6.15 Calculate the cell potential for a voltaic cell composed of a piece of chromium metal immersed in a 0.240M solution of Cr^{3+} and a piece of zinc in a solution of 0.0240M of Zn^{2+}. Which electrode is the cathode? $E^0_{Zn^{2+}/Zn} = -0.763$

$E^0_{Cr/Cr^{3+}} = +0.74$

6.16 For a cell composed of Cu/Cu^{2+} electrode and Fe/Fe^{2+} electrode, the overall cell potential is 0.80V when the concentration of Cu^{2+} solution is 0.0500 M. What is the concentration of the Fe^{2+} solution? $E^0_{Cu/Cu^{2+}} = -0.34$

$E^0_{Fe^{2+}/Fe} = -0.41$

6.17 Calculate the potential of the following cell when 99% of the zinc metal and Cu^{2+} ions have been consumed:

$Zn/Zn^{2+}(1.00 M)//Cu^{2+}(1.00 M)/Cu$

6.18 Write the Nernst equation and determine the cell potential for the following reaction at 25°C.

$Fe/Fe^{3+}(3.12M)//Al^{3+}(1.50M)/Al$

$E^{o}_{Fe|Fe^{3+}} = +0.036 V$

$E^{o}_{Al^{3+}/Al} = -1.706 V$

6.19 Ferrous ions are oxidised by silver ions according to the equation

$Fe^{2+}(aq) + Ag^{+}(aq) \rightleftharpoons Fe^{3+}(aq) + Ag(s)$

(a) Write a line notation for the cell

(b) Write the half-cell reactions (that is, equations for the anode and cathode reactions).

(c) Calculate the cell potential under standard –state conditions, and hence the standard free-energy change for the cell reaction, given that the equilibrium constant at 298 K is 7.810

($F = 96500 C\ mol^{-1}$; $R = 8.314\ J\ mol^{-1}K^{-1}$).

6.20 Calculate the equilibrium constant at 25°C for the following reactions.

(a) $Cu^{2+}(aq) + Zn(s) \rightleftharpoons Cu(s) + Zn^{2+}(aq)$

(b) $Cu(s) + Br_2(aq) \rightleftharpoons Cu^{2+}(aq) + 2Br^{-}(aq)$

(c) $Zn(s) + 2H^{+}(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$

(d) $MnO_4^{-}(aq) + 5Cl^{-} + 8H^{+} \rightleftharpoons Mn^{2+}(aq) + 5/2Cl_2(g) + 4H_2O(l)$

(e) $Cl_2(g) + 2Br^{-}(aq) \rightleftharpoons Br_2 + 2Cl^{-}(aq)$

(f) $Ag(s) + 2H^{+}(aq) \rightleftharpoons Ag^{+}(aq) + 1/2H_2(g)$

(g) $2Ag(s) + 2H^{+}(aq) \rightleftharpoons 2Ag^{+}(aq) + H_2(g)$

6.21 Calculate ΔG^{o} from the standard state cell potential, E^{o}_{cell}, determined in question 16.20(a).

6.22 Calculate ΔG^{o} for the following reaction at 25°C.

$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$

Will the reaction be spontaneous at this temperature?

6.23 Using the standard – state cell potentials given below, calculate the solubility products of (a) AgCl; (b) $Mg(OH)_2$; (c) $Cu(OH)_2$; (d) Hg_2Cl_2

(a) $AgCl + e^{-} \rightarrow Ag + Cl^{-}$ .... $E^{0} = 0.2223 V$

$Ag^{+} + e^{-} \rightarrow Ag$ .... $E^{0} = 0.7996 V$

(b) $Mg(OH)_2 + 2e^{-} \rightarrow Mg + 2OH^{-}$ .... $E^{o} = -2.69V$

$Mg^{2+} + 2e^{-} \rightarrow Mg$ .... $E^{o} = -2.375 V$

(c) $Cu(OH)_2 + 2e^{-} \rightarrow Cu + 2OH^{-}$ .... $E^{o} = -0.224 V$

$Cu^{2+} + 2e^{-} \rightarrow Cu(s)$ $E^{o} = +0.340 V$

$Cu \rightarrow Cu^{2+} + 2e^{-}$ $E^{o} = -0.340 V$

$Br_2 + 2e^{-} \rightarrow 2Br^{-}$ $E^{o} = 1.087 V$