

# ELECTROCHEMISTRY

## Electrochemistry

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

(c)  $1F = 96500 \text{ C per mole } e^-$   
hence  $6.00F = 6.00 \times 96500 \text{ C} = 5.790 \times 10^5 \text{ C}$

(d)  $1C = 1 \text{ amp-s (OR } Q = It)$   
 $\therefore t = Q/I = 5.790 \times 10^5 \text{ C} / 10A = 57900 \text{ s} = 16.08 \text{ h}$

(e)  $5.790 \times 10^5 \text{ C}$  are required to produce 53.96g Al  
 $2 \text{ min} = 2 \times 60 = 120 \text{ s}$

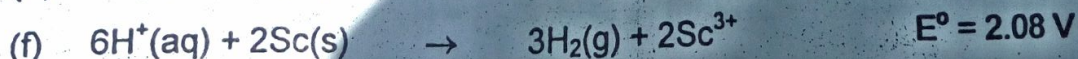
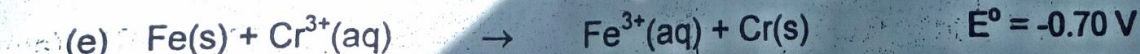
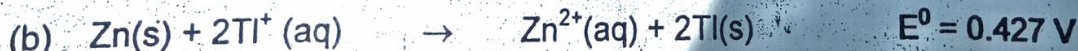
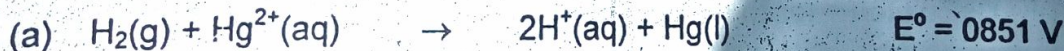
$$Q = It \therefore I = Q/t = \frac{5.790 \times 10^5 \text{ C}}{120 \text{ s}} \text{ (A)}$$

$$I = 4,825 \text{ A}$$

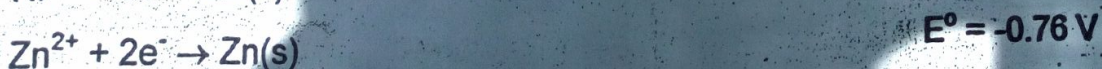
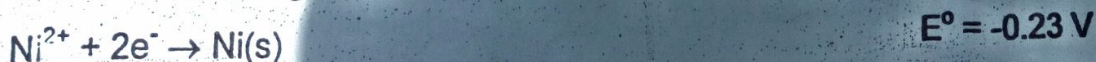
In general, electrolysis of aqueous solutions containing any metal ion that is a weaker oxidizing agent than  $H^+$  (or  $H_3O^+$ ) (like alkali metal and alkaline earth cations,  $Al^{3+}$ ,  $Mn^{2+}$ ,  $Zn^{2+}$ ,  $Cr^{3+}$ ,  $Fe^{2+}$ ,  $CO^{2+}$ ,  $Ni^{2+}$ ,  $Sn^{2+}$ ,  $Pb^{2+}$ ,  $Fe^{3+}$ ) 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?



6.2 Given the following data:



(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:
- $$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad E^\circ = 0.00 \text{ V}$$
- $$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)} \quad E^\circ = 0.34 \text{ V}$$
- $$\text{HNO}_3 + 3\text{H}^+ + 3\text{e}^- \rightarrow \text{NO} + 2\text{H}_2\text{O} \quad E^\circ = 0.96 \text{ V}$$

Explain why copper metal does not dissolve in a typical strong acid like HCl, but will dissolve in 1.0M  $\text{HNO}_3$ .

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



- (a) Write equations for the anode, cathode and overall cell reactions
- (b) Calculate  $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ , given that  $E^\circ_{\text{Zn}^{2+}/\text{Zn}} E^\circ_{\text{Cu}^{2+}/\text{Cu}} = -0.763 \text{ V}$
- 6.5 Will Mn reduce  $\text{Mg}^{2+}$  ions to Mg when all concentrations are 1.0M?
- 6.6 Will  $\text{Cr}_2\text{O}_7^{2-}$  oxidize  $\text{Fe}^{2+}$  ions to  $\text{Fe}^{3+}$  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)  $2\text{MnO}_4^- + 16\text{H}^+ + 10\text{Br}^- (\text{aq}) \rightarrow 5\text{Br}_2 + 2\text{Mn}^{2+} (\text{aq}) + 8\text{H}_2\text{O}$
- (b)  $\text{ClO}^- (\text{aq}) + \text{NO}_2^- (\text{aq}) \rightarrow \text{Cl}^- (\text{aq}) + \text{NO}_3^- (\text{aq})$
- (c)  $\text{Pb(s)} + \text{Zn}^{2+} (\text{aq}) \rightarrow \text{Pb}^{2+} (\text{aq}) + \text{Zn(s)}$
- (d)  $\text{Cl}_2(\text{g}) + 2\text{Br}^- (\text{aq}) \rightarrow \text{Br}_2(\text{aq}) + 2\text{Cl}^- (\text{aq})$
- 6.8 Calculate  $E^\circ$  for the following reactions and predict whether the reactions should occur spontaneously as written when run under standard conditions:
- (a)  $2\text{CrO}_4^{2-} (\text{aq}) + 3\text{Ni(s)} + 8\text{H}_2\text{O(l)} \rightarrow 2\text{Cr(OH)}_3(\text{s}) + 3\text{Ni(OH)}_2(\text{s}) + 4\text{OH}^- (\text{aq})$
- (b)  $\text{Ca(s)} + 2\text{H}_2\text{O(l)} \rightarrow \text{Ca}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) + \text{H}_2(\text{g})$
- (c)  $2\text{Fe}^{2+} (\text{aq}) + 2\text{H}^+ (\text{aq}) \rightarrow 2\text{Fe}^{3+} (\text{aq}) + \text{H}_2(\text{g})$
- 6.9 (a) Will  $\text{I}_2$  oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  in acid solution?
- (b) Will  $\text{I}_2$  oxidize  $\text{H}_2\text{SO}_3$  to  $\text{SO}_4^{2-}$  in acid solution?

$$E^\circ_{\text{H}_2\text{O}/\text{H}_2} = -0.828 \text{ V}$$

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}^{3+}} = -0.770 \text{ V}$$

$$E^\circ_{\text{I}_2/\text{I}^-} = 0.535 \text{ V}$$

$$210 \quad E^\circ_{\text{Ca}/\text{Ca}^{2+}} = -2.76 \text{ V}$$

$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$$

$$E^\circ_{\text{CrO}_4^{2-}/\text{Cr(OH)}_3} = +0.12 \text{ V}$$

$$E^\circ_{\text{Ni}/\text{Ni}^{2+}} = -0.72 \text{ V}$$



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(c) Will  $\text{Sn}^{4+}$  oxidize  $\text{H}_2\text{O}_2$  to  $\text{O}_2$  in acid solution?

(d) Will  $\text{H}_2\text{O}$  reduce  $\text{Cl}_2$  to  $\text{Cl}^-$  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)  $\text{NaCl}$ ; (b)  $\text{Na}_2\text{SO}_4$ ; (c)  $\text{NaI}$ ; (d)  $\text{CaI}_2$  (e)  $\text{CuBr}_2$

6.13 Consider the following cathode reaction



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 calculate the cell potential at 25°C for the following cells:

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

(b)  $\text{Cu(s)}/\text{Cu}^{2+}(0.075\text{M})//\text{Ag}^+(0.015\text{M})/\text{Ag(s)}$

$$E^\circ_{\text{Zn}/\text{Zn}^{2+}} = +0.763\text{V}$$

$$E^\circ_{\text{Ag}^+/\text{Ag}} = +0.800\text{V}$$

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

$$E^\circ_{\text{Zn}^{2+}/\text{Zn}} = -0.763\text{V}$$

$$E^\circ_{\text{Cr}^{3+}/\text{Cr}} = +0.74\text{V}$$

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

$$E^\circ_{\text{Cu}/\text{Cu}^{2+}} = -0.34\text{V}$$

$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.41\text{V}$$

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



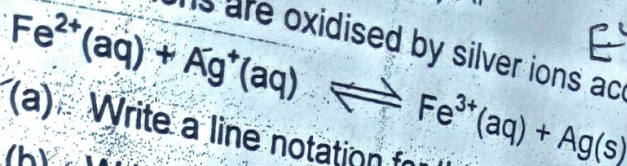
6.18 Write the Nernst equation and determine the cell potential for the following reaction at 25°C.



$$E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = +0.036 \text{ V}$$

$$E^\circ_{\text{Al}^{3+}/\text{Al}} = -1.706 \text{ V}$$

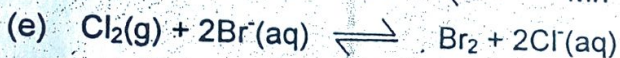
6.19 Fe/Fe<sup>3+</sup> (3.12M) // Al<sup>3+</sup> (1.50M) / Al  
 Ferrous ions are oxidised by silver ions according to the equation



(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<sup>-1</sup>; R = 8.314 J mol<sup>-1</sup> K<sup>-1</sup>).

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



6.21 Calculate  $\Delta G^\circ$  from the standard state cell potential,  $E^\circ_{\text{cell}}$ , determined in question 16.20(a).

6.22 Calculate  $\Delta G^\circ$  for the following reaction at 25°C.



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)<sub>2</sub>; (c) Cu(OH)<sub>2</sub>; (d) Hg<sub>2</sub>Cl<sub>2</sub>

