

# **Electrolytes and Electrolysis**

- (b) Sugar solution does not form ion; hence does not conduct 1. electricity in solution.
- 3 (c) Strong electrolytes are almost completely ionised in polar solvent. 7.

(b) The reduction potential of Mg is less than that of water  $(E^{o} = -0.83V)$ . Hence their ions in the aqueous solution

cannot be reduced instead water will be reduced  $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ .

8.

(b) Water is reduced at the cathode and oxidized at the anode 9. instead of  $Na^+$  and  $SO_4^{2-}$ .

Cathode: 
$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Anode : 
$$H_2 O \to 2H^+ + \frac{1}{2}O_2 + 2e^-$$
.

- 10. (a) In electrolysis process oxidation occurs at anode and reduction occurs at cathode.
- Because in it covalent bonding is present. 11. (a)
- 12. According to Faraday's law. (c) (d)
- Impure metal made anode while pure metal made cathode. 13. In electrolytic cell, cathode acts as source of electrons. 14. (d)
- (c)  $AgNO_3$  is an electrolyte. 15.
- At cathode:  $2H^+ + 2e \rightarrow H_2$ , 17. (a)

At anode : 
$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e$$

- In between dilute  $H_2SO_4$  and platinum electrode  $O_2$  gas 18. (c) evolve at anode.
- When polar solvent added in to solid electrolyte than it is 19. (c) ionised
- In fused NaCl chloride ions are oxidized at anode and it is 20. (a) called oxidation.

w = zit, Q = it.21. (a)

- $2H^+ + 2e^- \rightarrow H_{2(g)}$  at cathode. (b) 22.
- $Na^+_{+1} + e^- \rightarrow Na$ , means oxidation number is decreased so 23. (b) the reaction is reduction.
- (d) Degree of dissociation of weak electrolyte increases on 24. increasing temperature.
- Since discharge potential of water is greater than that of 25. (b) sodium so water is reduced at cathode instead of Na<sup>+</sup>

Cathode: 
$$H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH$$
  
Anode:  $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ .

Because it does not have ions. 26. (b)

**27.** (b) 
$$NaCl \Rightarrow Na^+ + Cl^-$$

28. Cathode:  $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$ (a)

Anode : 
$$H_2 O \to 2H^+ + \frac{1}{2}O_2 + 2e^-$$
.

(c) Electrolysis use for electroplating and electrorefining. 29.

- The degree of ionization depend upon the nature of the solute 32. (d) the size of the solute molecules and the concentration of the solution.
- $C_{12} \boldsymbol{H}_{22} \boldsymbol{O}_{11}$  is an non-electrolyte. 33. (c)
- On electrolysis molten ionic hydride liberate  $\,{\cal H}_2\,$  at the anode. 34. (b)
- During electrolysis cation discharged at cathode and anion 35. (b)discharged at anode.
- Calcium is produces when molten anhydrous calcium chloride 36. (a) is electrolysed.
- All metals conducts heat and electricity. (d) 37.
- $2Al + dil H_2 SO_4 \rightarrow Al_2 SO_4 + H_2 \uparrow.$ 38. (c)
- 39. (d) Generally fussed potassium chloride flow the electric conductivity.
- 41. (a) The substances whose aqueous solutions allow the passage of electric current and are chemically decomposed, are termed electrolytes. Electrolytic substances are classified as strong or weak according to how readily they dissociate into conducting ions. Acetic acid is a weak electrolyte. Glucose, ethanol and urea are non-electrolytes.

# Faraday's law of electrolysis

(c) 
$$Ag^+ + e^- \rightarrow Ag$$
;  $E_{Ag} = \frac{Atomic Mass}{1} = 108$   
Number of faraday  $= \frac{W_{Ag}}{E_{Ag}} = \frac{108}{108} = 1$ .

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(a) 
$$W_{Ag} = \frac{E_{Ag} \times Q}{96500} = \frac{108 \times 9.65}{96500}$$
  
= 1.08 × 10<sup>-2</sup> gm = 10.8 mg

**3.** (b) 
$$Fe^{2+} + 2e^- \rightarrow Fe$$
;  $E_{Fe} = \frac{56}{2} = 28$ 

$$W_{Fe} = E_{Fe} \times \text{Number of faraday} = 28 \times 3 = 84 \text{ gm}.$$

(c) 
$$W_{Ag} = \frac{E_{Ag} \times Q}{96500} = \frac{107.87 \times 965}{96500} = 1.0787 \ gm$$

(c) 
$$Al^{3+} + 3e^- \rightarrow Al$$
  
 $E_{Al} = \frac{27}{3} = 9$ 

$$W_{Al} = E_{Al} \times \text{No.of faradays} = 9 \times 5 = 45 \ gm$$
.

6. Cu voltameter or Cu or Ag coulometer are used to detect the (c) amount deposited on an electrode during passage of know charge through solution.

(b) 
$$\frac{\text{Weight of } Cu}{\text{Weight of } H_2} = \frac{\text{Eq. weight of } Cu}{\text{Eq. weight of } H}$$
$$\frac{\text{Weight of } Cu}{0.50} = \frac{63.6/2}{1}$$
Weight of  $Cu = 15.9 \text{ gm.}$ 

(c) 
$$Cu^{2+} + 2e^- \rightarrow Cu$$
  
2 Faradays will deposit = 1 g atom of  $Cu = 63.5 g$ .

(a) At cathode; 
$$Al^{3+} + 3e^- \rightarrow Al$$
  
 $E_{Al} = \frac{27}{3} = 9$   
 $W_{Al} = E_{Al} \times \text{No.of faradays} = 9 \times 0.1 = 0.9 \text{ gm}$ 

4. (b) 
$$W = zit; W = \frac{32.69 \times 5 \times 60 \times 40}{96500} = 4.065 \, gm$$
.

**15.** (b) 
$$m = Z \times 4 \times 120$$
;  $M = Z \times 6 \times 40$ 

**530 Electrochemistry**  

$$\frac{M}{m} = \frac{6 \times 40}{6 \times 120} = \frac{1}{2}; \quad M = m/2.$$
**16.** (c)  $W_{metal} = \frac{E \times I \times i}{96500} = \frac{E \times 3 \times 50 \times 60}{96500}$   
 $E = \frac{96500 \times w}{3 \times 50 \times 60} = \frac{96500 \times 1.8}{96500}$   
 $E = \frac{96500 \times w}{3 \times 50 \times 60} = \frac{96500 \times 1.8}{96500} = 19.3.$ 
**17.** (a)  $A1 \rightarrow A1^{3+} + 3e^{-}$ .  
The charged obtained is  $3 \times 96500C$ .
**18.** (a) Wt.of  $Ag$  deposited  $= Eq.wt.of Ag = 108 gm$   
Wt.of  $Ni$  deposited  $= Eq.wt.of Cr = 17.3 gm$ .
**19.** (d) One Faraday = 1 gm of equivalent of  $Cu$ .
**20.** (c)  $W = Zit; Z = \frac{E}{96500}$ .
**21.** (d) During electrolysis of  $CuSO_4 + Cu^{2+}$  gets discharged at cathode and  $OH^-$  at anode. Thus solution becomes acidic due to excess of  $H^+$  and  $SO_4^{-1}$  or  $H_2SO_4$ .
**23.** (b) 1 mole of electrons = 1 furaday  
 $Mg^{++} + 2e^- \rightarrow Mg;$  2 moles of electrons = 2 furaday .
**24.** (d)  $Cu^{++} + 2e^- \rightarrow Cu$   
 $E_{Cu} = \frac{63.54}{2} = 31.77$   
Amount of electricity required to deposit .6354 gm of  $Cu$   
 $= \frac{96500 \times 0.6354}{9500 \times 1.577} = 1930 Coulombs$ .
**25.** (a) The amount deposited is directly proportional to current intensity, electrochemical equivalent of ions and the time for electrolysis and is independent of the temperature.
**27.** (a)  $W = ZQ$ ;  $W = Zit$ .
**28.** (d)  $Ca^{++} + 2e^- \rightarrow Ca$   
 $E_{Ca} = \frac{40}{2} = 20$   
 $W_{Ca} = E_{Ca} \times No$  of faradays  $= 20 \times 0.04 = 0.8 gm$ .
**29.** (c)  $E_{metal} = \frac{Weight of metal  $= \frac{177}{59.5} = \pm 3$ 
**30.** (a) Quantity of electricity passed  $= \frac{2}{1000} \times 60 = 1.5$   
 $2F = 2 \times 96500C$  deposit  $Ca = 1mole$   
 $\therefore 15 C will deposit  $Ca = \frac{1}{2 \times 96500} \times 1.5 mole$   
 $= \frac{1}{2 \times 96500} \times 1.5 \times 6.023 \times 10^{23}$  atom  $= 4.68 \times 10^{18}$ .
**31.** (b) Equivalent of  $Cl$  deposit  $Ca = 1$$$ 

$$W_{Cl_2} = \frac{E_{Cl_2} \times I \times t}{96500} = \frac{35.5 \times 2 \times 30 \times 60}{96500} = 1.32 \ gm \,.$$

(b) It is Faraday's law. 34.

36.

48.

57.

gm of Cu

(b) Equivalent wt. of  $O_2$  = Equivalent wt. of Cu35.

(d)  $O_2\% = 20\%$ Metal% = 80% =  $\frac{80}{20} \times 8 = 32 g \text{ of metal}$ .  $827 \times 10^{3}$ 

**37.** (b) 
$$V = \frac{827 \times 10}{4 \times 96500} = 2.14 V.$$

- (b)  $Ag^+ \xrightarrow{+e^-} Ag$ , 96500 *C* will liberate silver =108 gm. 38. 9650*C* will liberate silver = 10.8 *gm.*
- One mole of monovalent metal ion means charge of (a) 39. N electron i.e. 96500 C or 1 Faraday.
- 42. (a) 1 Faraday involves charge of 1 *mole* electrons.

**43.** (a) Coulomb = ampere (A) 
$$\times$$
 second (S).

44. (b) 
$$E = -\frac{13.6}{n^2}$$
 for  $He^+ n = 1$   
 $E = -\frac{13.6}{1^2} = -13.6 \text{ eV}$ .

(c)  $w \propto E$  if *i* and *t* are constant. 45.

**47.** (d) Charge (Coulombs) pass per second 
$$= 10^{-6}$$
 number of electrons passed per second  $10^{-6}$ 

$$= \frac{10}{1.602 \times 10^{-19}} = 6.24 \times 10^{12} .$$
(d) At cathode;

$$Fe^{2+} + 2e^- \rightarrow Fe \; ; \; Fe^{3+} + 3e^- \rightarrow Fe$$

$$(E_{Fe})_1 = \frac{\text{Atomic.weight}}{2}; \; (E_{Fe})_2 = \frac{\text{Atomic.weight}}{3}$$
Ratio of weight of *Fe* liberated
$$A \text{ tomic weight} \quad A \text{ tomic weight}$$

 $=\frac{\text{Atomic weight}}{3}:\frac{\text{Atomic weight}}{2}=3:2.$ 3

- (b) 31.75 g copper gets deposited at cathode on passing 96500 49. coulomb charge. We know that 31.75 gm of Cu is equal to 0.5 mole of Cu deposited at cathode on passing 1F of current.
- (b) For deposition of one equivalent silver required charged is 52. 96500 C.

**53.** (b) 
$$Cu^{++} + 2e^- \rightarrow Cu$$
;  $E_{Cu} = \frac{63.55}{2} = 31.75 \ gm \ Cu$ .

54. (a) 
$$Q = 2.5 \times 386 = 96500 C$$
  
 $2F(2 \times 96500C)$  deposited  $Cu = 63.5 g$   
 $\therefore$  Hence 965 C will deposited;  $Cu = 0.3175 gm$ .  
55. (c)  $\frac{\text{Wt.of } Cu}{W_{12}} = \frac{\text{Eq. wt.of } Cu}{1000}; \frac{\text{Wt. of } Cu}{1000} = \frac{63.5/2}{1000}$ 

5. (c) 
$$\frac{\text{wt.of } Cu}{\text{Wt.of } Ag} = \frac{\text{Eq. wt.of } Cu}{\text{Eq. wt.of } Ag}; \frac{\text{wt.of } Cu}{1.08} = \frac{65.572}{108}$$
  
Wt. of  $Cu = 0.3177 \ gm.$ 

**56.** (c) 
$$1 g$$
 atom of  $Al = 3$  equivalent of  $Al = 3$  faraday charge 3 *mole* electrons = 3 *N* electron.

(c) At cathode :  $Al^{3+} + 3e^- \rightarrow Al$  $E_{Al} = \frac{\text{Atomic mass}}{3}$ At cathode :  $Cu^{2+} + 2e^- \rightarrow Cu$  $E_{Cu} = \frac{\text{Atomic mass}}{2}$ 2 At cathode :  $Na^+ + e^- \rightarrow Na$  $E_{Na} = \frac{\text{Atomic mass}}{1}$ 

For the passage of 3 faraday;

mole atoms of *A1* deposited = 1  
mole atoms of *Cu* deposited 
$$=\frac{1 \times 3}{2} = 1.5$$
  
mole atoms of *Na* deposited  $= 1 \times 3 = 3$ 

**58.** (d) At cathode:  $Ag^+ + e^- \rightarrow Ag$ 

At Anode: 
$$2OH^- \to H_2O + \frac{1}{2}O_2 + 2e^-$$
  
 $E_{Ag} = \frac{108}{1} = 108; E_{O_2} = \frac{\frac{1}{2} \times 32}{2} = 8$ 

$$\frac{W_{Ag}}{E_{Ag}} = \frac{W_{O_2}}{E_{O_2}}; \ W_{Ag} = \frac{1.6 \times 108}{8} = 21.6 \ gm.$$

**59.** (d) *KI* is an electrolyte.

**60.** (d) Number of gm equivalent = Number of faraday pass 4 gm = 4 faraday.

**61.** (c) Eq. of 
$$AI = \frac{13.5}{27/3} = 1.5$$
.

Thus 1.5 Faraday is needed.

**63.** (b) Electricity required

= No. of gm equivalent  $\times$  96500 coulombs

 $= 0.5 \times 96500 = 48250$  C.

- (a) Equivalent weight of silver = 107.870 g.1 Faraday = 96500 coulomb.
- **67.** (a) Equivalent weight and atomic weight of *Na* metal are the same, so 1*g* atom of *Na* is deposited by one Faraday of current.

**68.** (a)  $Al \to Al^{3+} + 3e^{-}$ .

64.

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81.

- (c) : 1*F* obtained from 1 *g* equivalent
  - $\therefore$  2.5 *F* obtained from 2.5 *g* equivalent.
- 75. (c) Faraday constant depends upon the current passed.
  80. (b) In 5 gm CuO, 4 gm Cu and 1 gm O be present.
  - Element At Wt. Ratio Wt.  $Wt. / At. Wt. \neq x$ Cu 4/63.5=.0625 63.5 4 *gm* .0625 = 1 .0625 0 1/16 = .06251 *gm* 16 .0625 = 1 .0625

Emperical formula = *CuO* of oxide

In this oxide, oxidation no. of Cu = +2

Equivalent weight = 
$$\frac{\text{Molecular weight}}{\text{Oxidation no.}} = \frac{63.5}{2} \approx 31.75$$

but Equivalent weight should be an integeral no. = 32 (c) Given, Current = 241.25 *columb* 

1 coulomb current will deposite  $= 1.118 \times 10^{-3} gm Ag$ .

- $\therefore$  241.25 current will deposite =  $1.118 \times 10^{-3} \times 241.25$
- $= 0.27 \ gm$  silver.

 $2H_2O \rightleftharpoons 4H^+ + 2O^{2-}$ 

$$2O^{2^-} \to O_2 + 4e^-$$

$$4e^- + 4H^+ \rightarrow 2H_2$$

 $\therefore$  n = 4 so 4 Faraday charge will liberate

1 mole =  $22.4 \ dm^3$  oxygen

$$\therefore$$
 1 Faraday charge will liberate  $\frac{22.4}{4} = 5.6 \ dm^3 \ O_2$ .

83. (a)  $Na^+ + e^- \rightarrow Na$ Charge (in *F*) = moles of *e* used = moles of *Na* deposited  $= \frac{11.5}{23} gm = 0.5$  Faraday.

(c) Hydrolysis of water : 
$$2H_2O \Rightarrow 4H^+ + 4e^- + O_2$$

4 *F* charge will produce = 1 mole 
$$O_2 = 32 \text{ gm } O_2$$

F charge will produce 
$$=\frac{32}{4}=8 gm O_2$$
.

- 85. (c) In a galvanic cell, the electrons flow from anode to cathode through the external circuit. At anode (-ve pole) oxidation and at cathode (+ pole) reduction takes place.
- 86. (e) Number of equivalents of silver formed = Number of equivalents of copper formed.

In  $AgNO_3$ , Ag is in +1 oxidation state.

In  $CuSO_4$ , Cu is in +2 oxidation state.

Equivalent weight of 
$$Ag = \frac{108}{1} = 108$$

Equivalent weight of  $Cu = \frac{63.6}{2} = 31.8$ 

$$\frac{M_1}{M_2} = \frac{E_1}{E_2} ; \frac{10.79}{M_{Cu}} = \frac{108}{31.8}$$
$$M_{Cu} = \frac{10.79 \times 31.8}{108} = 3.2 \ gm \,.$$

(b) Laws of electrolysis were proposed by Faraday.

(a) Given, Current (*i*) = 25 mA = 0.025 A  
Time (*t*) = 60 sec  
Q = *i* t = 60 × 0.025 = 1.5 coulombs  
No. of electrons = 
$$\frac{1.5 \times 6.023 \times 10^{23}}{96500}$$
  
 $e^{-} = 9.36 \times 10^{18}$   
 $Ca \rightarrow Ca^{2+} + 2e^{-}$   
 $2e^{-}$  are required to deposite one *Ca* atom  
 $9.36 \times 10^{18} e^{-}$  will be used to deposite =  $\frac{9.36 \times 10^{18}}{2}$   
=  $4.68 \times 10^{18}$ .

**89.** (d)  $C_6H_5NO_2 + 6H^+ + 6e^- \rightarrow C_6H_5NH_2 + 2H_2O$ 1 mole = 123 gm nitrogen requires 6 mole electron  $e^-$ = 6 × 96500 coulomb charge

$$\therefore$$
 12.3 gm nitrobenzene will require  $=\frac{6 \times 96500 \times 12.3}{123}$ 

 $= 6 \times 9650 = 57900 C.$ 

**90.** (c) *Au* and *Ag* settle down below the anode as anode mud during the process of electrolytic refining of copper.

# **Conductor and Conductance**

(b) 
$$\lambda^{\infty} BaCl_2 = \frac{1}{2}\lambda^{\infty}Ba^{2+} + \lambda^{\infty}Cl^{-}$$
  
=  $\frac{127}{2} + 76 = 139.5 \ ohm^{-1} \ cm^{-1} \ eq^{-1}$ 

- **3.** (d) Dilution, temperature and nature of electrolyte affect the conductivity of solution.
  - (a) Generally strong electrolyte on dilution shows conductivity characters.

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5.

84.

**6.** (b) Molar conductivity = 
$$\frac{1000}{MX}$$
.

7. (b) 
$$C = \frac{K[A]A}{l}, K = \frac{C \times l}{[A]A} = \frac{Sm}{mol m^{-3} m^2} = Sm^2 mol^{-1}.$$

**9.** (b) Conductivity of a solution is directly proportional to the number of ions.

**11.** (a) 
$$NaCl \Rightarrow Na^+ + Cl^-$$
. So it conduct electricity

- $\label{eq:conductor} \textbf{12.} \qquad (b) \quad \text{Graphite is a good conductor of electricity.}$
- **15.** (b) Electrolytic conduction resistance decreases with increasing temperature.
- 16. (d) Because conductance is increase when the dissociation is more.
- 17. (b) Strong electrolyte ionize completely at all dilutions and the number of ions does not increase on dilution. A small increase in  $\wedge_m$  volume with dilution is due to the weakening of electrostatic attraction between the ions on dilution.
- 18. (d) In electrolytic conductors, a single stream of electrons flow from cathode to anode.
- (b) In solid state NaCl does not dissociate into ions so it does not conduct electricity.
- 20. (c) The ions are not free to move in solid state and held up in lattice due to strong coulombic forces of attraction.
- **21.** (b)  $C_2H_5OH$  being non electrolyte so does not ionize.

**22.** (a) Since molar conductance 
$$\propto \frac{1}{\text{Molarity}}$$

**23.** (c) Molar condcutivity  $=\frac{1}{\rho M}$ 

So its unit will be  $\Omega^{-1} cm^2 mol^{-1}$  .

**25.** (a) 
$$l/a = 0.5 \ cm^{-1}$$
,  $R = 50 \ ohm$ 

$$p = \frac{Ra}{l} = \frac{50}{0.5} = 100$$
$$\Lambda = k \times \frac{1000}{N} = \frac{1}{p} \times \frac{1000}{N} = \frac{1}{100} \times \frac{1000}{1}$$
$$10 \ ohm^{-1} \ cm^2 \ gm \ eq^{-1}$$

26. (b) 
$$\Lambda^{o}_{m(C_{6}H_{5}COOH)} = \Lambda^{o}_{(C_{6}H_{5}COO^{-})} + \Lambda^{o}_{(H^{+})}$$
  
= 42 + 288.42 = 330.42  
 $\alpha = \frac{\Lambda^{c}_{m}}{\Lambda^{o}_{m}} = \frac{12.8}{330.42} = 3.9\%$ 

**27.** (d) Conductance = 
$$\frac{1}{\text{resistance}} = \frac{1}{ohm} = ohm^{-1}$$
 or *mho*

### Cell constant and Electrochemical cells

- 1. (d) In the absence of electric field the ions in the solution move randomly due to thermal energy.
- 2. (d) Since  $E^o_{A/A^-}$  has large negative value, the tendency of A to be reduced to  $A^-$  is very small. In other words tendency of  $A^-$  to be oxidized to A is very large.
- 3. (d) Practically only 60-70% efficiency has been attained.

**4.** (b) 
$$K = \frac{1}{R} \times \text{Cell constant}$$

Cell constant =  $K \times R$ ; 0.012×55 = 0.66 cm<sup>-1</sup>.

Anode : 
$$Zn \rightarrow Zn^{++} + 2e^{-}$$

Cathode: 
$$2MnO_2 + Zn^{++} + 2e^- \rightarrow ZnMn_2O_4$$
.

- **6.** (a) Because the reduction potential of Cu is highest.
  - (c) Overall reaction  $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O(l)$ .
- **9.** (b) During charging of a lead storage battery, the reaction at the anode and cathode are

Anode:  $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$ 

Cathode:  $PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$ 

In both the reactions  $H_2SO_4$  is regenerated.

11. (c) 
$$2NH_4Cl + Zn \rightarrow 2NH_3 + ZnCl_2 + H_2 \uparrow$$

- 13. (a) When platinum electrodes are dipped in dilute solution  $H_2SO_4$  than  $H_2$  is evolved at cathode.
- 14. (a) Electrode on which oxidation occurs is written on L.H.S. and the other on the R.H.S. as represented by

$$Zn | Zn^{2+} || Cu^{2+} | Cu.$$

7.

15.

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(d) 
$$Zn^{2+} + 2e^- \rightarrow Zn$$
. It shows reduction reaction.

- (c) In the electrolytic cell electrical energy change into chemical energy.
- 17. (c) In the cell  $Zn | Zn^{2+} || Cu^{2+} | Cu$  the negative electrode (anode) is Zn. In electrochemical cell representation anode is always written on left side while cathode on right side.
- (a) Galvanic cell converts the chemical energy into electrical energy.
- **19.** (b) Fuel-cells are used to provide power and drinking water to astronauts in space programme.

**21.** (b) 
$$E_{\text{cell}}^o = \frac{2.303 \ RT}{nF} \log K = \frac{0.0591}{n} \log K_c \ at \ 298K$$

**2.** (b) 
$$Cu^{2+} + 2e^{-} \rightarrow Cu$$
  
Reduction

**24.** (b) The cell in which *Cu* and *Zn* roads are dipped in its solutions called Daniel cell.

25. (c) 
$$K = C \times \text{Cell constant} = \frac{K}{C} = \frac{0.2}{0.04} = 5 \ cm^{-1}$$
.

**26.** (a) 
$$\frac{K}{C}$$
 = Cell Constant.

- 27. (c) Velocities of both  $K^+$  and  $NO_3^-$  are nearly the same in  $KNO_3$  so it is used to make salt-bridge.
- **28.** (a) In this reaction 4 electrons are needed for the reaction volume.
- **29.** (b) In electrochemical cell  $H_2$  release at anode and Cu is deposit at the cathode.
- **31.** (a) Anode has negative polarity.

**32.** (b) 
$$\wedge_m^o (CH_3 COOH) =$$

$$\wedge^{o} (CH_{3}COONa) + \wedge^{o} (HCl) - \wedge^{o} (NaCl)$$

- $=91+426.16-126.45=390.71 \ ohm^{-1}cm^{2}mol^{-1}$ .
- **36.** (b) At anode:  $Zn_{(s)} \to Zn^{2+} + 2e^{-}$ .

**38.** (d) 
$$PbSO_4 + 2H_2O \rightarrow 2PbO_2 + 4SO_4^{--} + 2e^{--}$$

- **39.** (b)  $MnO_2$  is used in dry batteries cell.
- **40.** (d)  $Pb + PbO_2 + 2H_2SO_4 \xrightarrow{\text{Discharge}} 2PbSO_4 + 2H_2O$ . Sulphuric acid is consumed on discharging.
- 42. (d) The metal placed below in electrochemical series does not react with that metal salt solution which metal is placed above in series.
- **43.** (c) In the electrochemical cell chemical energy changes into electrical energy.
- **44.** (a) In galvanic cell, the salt bridge used to complete the circuit.

- **45.** (d)  $Cu + FeSO_4 \rightarrow \text{No reaction Because } Cu \text{ has } E^o = 0.34$ volt and Fe has  $E^o = -0.44$  volt.
- **47.** (d) Calomel electrode as reference electrode is made by using  $Hg_2Cl_2$ .
- (b) In hydrogen-oxygen fuel cell following reactions take place to create potential difference between two electrodes.

$$2H_{2(g)} + 4OH \quad (aq) \rightarrow 4H_2O_{(l)} + 4e$$

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$$

Overall reaction =  $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ the net reaction is the same as burning (Combustion) of hydrogen to form water.

**49.** (c) 
$$Cl CH_2COONa + HCl \rightarrow ClCH_2COOH + NaCl \lambda_{ClCH_2COONa} + \lambda_{HCl} = \lambda_{ClCH_2COOH} + \lambda_{NaCl}$$
  
 $224 + 203 = \lambda_{ClCH_2COOH} + 38.2$ 

$$\lambda_{CICH_{2}COOH} = 427 - 38.2 = 388.8 \ ohm^{-1}cm^{2}gmeq^{-1}.$$

- 50. (c) In daniel cell copper rod acts as cathode so there cations move towards copper electrode and reduction take place on copper rod.
- **51.** (b) Elements with lower reduction potential act as anode. His placed above *Cu* in electrochemical series so it has lesser reduction potential and thus act as anode and *Cu* act as cathode.
- 52. (d) Fuel cells are more efficient as they are free from pollution and hence they run till the reactants are active. They have longer life than lead storage cells.
- **53.** (c) For gold plating, the used electrolyte is  $K[Au(CN)_2]$ .

55.

(c)

**54.** (a) Dil.  $H_2SO_4$  is used in lead in lead storage battery as electrolyte.

Cell constant = 
$$\frac{\text{Specific conductivity}}{\text{Observed conductors}}$$

$$= \frac{0.002765}{1/R} = 0.002765 \times 400 = 1.106.$$

57. (b)  $2AgCl_{+} + H_{-} \rightarrow 2HCl_{-} + 2Ag_{-}$ The activities of solids and liquids are takes as unity and at low concentrations, the activity of a solute is approximated to its molarity. Th cell reaction will be

$$Pt_{a} \mid H_{a}$$
, 1 bar  $\mid H_{a}$  1  $M \mid AgCl_{a}$  1  $M \mid Ag_{a}$ 

58. (a) 
$$E_{cell} = \frac{0.059}{n} \log \frac{1}{C} = -\frac{0.059}{2} \log \frac{1}{100}$$
  
=  $-\frac{0.059}{2}(-2) = 0.059V = 59mV$ . (increase)

59. (a) 
$$E_{cell} = -0.059 \log \frac{10^{-6}}{10^{-3}} = -0.059 \log 10^{-3}$$
  
=  $-0.059 \times (-3) = 0.177 V$ .

**60.** (c) The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons. *i.e.*, it is a measure of the relative tendency to undergo oxidation (loss of electrons) or reduction (gain of electrons).

 $M \rightarrow M^{n+} + ne^-$  (oxidation potential)

 $M^{n+} + ne^- \rightarrow M$  (reduction potential)

**61.** (a) On electrolysis of fused ionic hydride (LiH), hydrogen obtained at anode.  $MH + H_2O \rightarrow MOH + H_2 \uparrow$ 

## Electrode potential, Ecell, Nernst equation and ECS

1. (b) Reduction potential of hydrogen electrode,

$$E_H = \frac{-2.303 \,\text{RT}}{F} \log \frac{1}{[H^+]}$$
  
= -0.059 pH = -0.059 × 3 = -0.177 V

(a) 
$$E_{\text{cell}}^o = E_{\text{cathode}}^o - E_{\text{anode}}^o = 0.799 - (-0.763) = 1.562 \text{ V}$$

4. (b) Standard potential of Zinc < Copper.</li>
6. (c) A cation having highest reduction

b

2.

3.

7.

8.

9.

13.

(c) A cation having highest reduction potential will be reduced first and so on. However,  $Mg^{2+}$  in aqueous solution will not

e reduced 
$$\left( E_{Mg^{2^+}/Mg}^0 < E_{H_2O/\frac{1}{2}H_2+OH^-} \right)$$
. Instead water

would be reduced in preference.

(c) A is displace from D because D have a 
$$E^o = -0.402 V$$
.

(a) 
$$Z_{n_{(s)}}^{o} + 2Ag_{(aq)}^{+} \rightarrow Zn_{(aq)}^{2+} + 2Ag_{(s)}^{o}$$
  
Oxidation

In this reaction zinc act as a anode and Ag act as a cathode.

(a) No doubt 
$$Be$$
 is placed above  $Mg$  in the second group of periodic table but it is below  $Mg$  in electrochemical series.

10. (b) Nernst's equation shows relation between E and  $E^{o}$ .

**11.** (a) 
$$E = E^o - \frac{RT}{nF} \ln \frac{1}{[M^{n+1}]}; E = E^o + \frac{RT}{nF} \ln [M^{n+1}]$$
  
 $E = E^o + \frac{2.303RT}{nF} \log [M^{n+1}]$   
Substituting the value of *R*, *T* (298*K*) and *F* we get  
0.0591

$$E = E^o + \frac{0.0571}{n} \log(M^{n+}).$$

12. (c) At 298 K standard electrode potential of *NHE* electrode is 0.00 V.

(a) Since, 
$$Ag^+$$
 ions are reduced to  $Ag$  and

 $E^o_{Ag^+/Ag} > E^o_{Cu^{++}/Cu}$  Cu is oxidized to  $Cu^{++}$ .

- 14. (d) The reducing power decreases as the reduction potential increase (becomes less negative).
- **15.** (c) Actually the equation is derived from Nerst equation assuming equilibrium condition in a cell reaction, when E = 0.
- 16. (a) More negative is the standard reduction potential, greater is the tendency to lose electrons and hence greater reactivity.
- 17. (a) Hg has greater reduction potential than that of  $H^+$  and hence cannot displace hydrogen from acid.
- **18.** (c) Brown layer is deposited on iron rod because Cu has greater reduction potential than that of  $Fe^{2+}$ .
- **19.** (b) Since  $E^{o}_{B^{2+}/A} < E^{o}_{B^{2+}/B}$ . A has greater tendency to be oxidized.

$$A + B^{2+} \to A^{2+} + B.$$

- **20.** (b) Since  $E_{Zn^{++}/Zn}^{o}$  is negative, so *Zn* has greater tendency to be oxidized than hydrogen. Hence it can act as reducing agent.
- **21.** (a) Standard electrode potential of Hydrogen is zero.
- 22. (b) According to electrochemical series.
- **23.** (a) The standard reduction potential of  $K^+$ ,  $Mg^{2+}$ ,  $Zn^{+2}$   $Cu^{2+}$  increase in this order.
- **24.** (c)  $E_{\text{cell}} = E_{Au^{3+}/Au}^o E_{Ni^{2+}/Ni}^o = 1.50 (-0.25) = 1.75 \text{ V}.$
- **25.** (a) Electromotive force is +*ve* if oxidation and reduction both takes place in a cell.
- **28.** (a) In galvanic cell anode always made up of negative electrode.

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$$E^o$$
 for the reaction  $= -\frac{\Delta G^o}{nF}$   
 $= -\frac{(-0.772 F)}{1 \times F} = +0.772 V.$ 

- **40.** (d) Reducing power *i.e.* the tendency to lose electrons increases as the reduction potential decreases.
- **41.** (b)  $Cu^{++}$  will be reduced and Fe will be oxidized.

$$\begin{array}{ll} Cu^{++}+Fe \rightarrow Cu+Fe^{++} \,. \\ \mbox{42.} & \mbox{(c)} & \mbox{Cell reaction is} \\ Cu_{(s)}+2Ag^+ \rightarrow Cu^{2+}+2Ag \\ \mbox{Two half cell reaction is} \\ Cu \rightarrow Cu^{2+}+2e^- & \mbox{Oxidation (anode)} \\ Ag^++e^- \rightarrow Ag & \mbox{Reduction (cathode)} \\ E_{Cell}=E_{ox}-E_{{\rm Re}\,d}=0.80-0.34=+0.46V \end{array}$$

**43.** (a) EMF = [s.r.p. of cathode–s.r.p of anode]

Where s.r.p. = Standard reduction potential If EMF is positive then the reaction is spontaneous For *e.g.* in Galvanic cell (a) EMF = 1.1 *volt* 

- (b) Cathode is made of copper
- (c) Anode is made of Zinc
- EMF = 0.34 (-0.76) = 1.1 volt.
- **6.** (d)  $H_2$  is anode because oxidation takes place. *Cu* is cathode because reduction is takes place.
- $(c) \quad E_{cell}^o = E_{cathode} E_{anode} .$
- (b) Standard hydrogen electrode have zero electrode potential.

$$\Delta G = -1 \times 96500 \times 1.02; \quad \Delta G = -98430.$$

i. (a) 
$$E = E^o - \frac{2.303 \ RT}{nF} \log \frac{[M]}{[M^{n+}]}$$

**6.** (a) Less is the reduction potential stronger is the reducing agent.

 (a) Reducing power, *i.e.* the tendency to lose electrons increases as the reduction potential decreases.

(a) 
$$OCl^{-} \to C^{-}, E^{o} = 0.94V$$
  
 $Cl^{-} \to \frac{1}{2}Cl_{2} + e^{-}E^{o} = -1.36V$ 

adding the two equations, we get

$$OCl^{-} \rightarrow \frac{1}{2}Cl_2, E^o = 0.94 - 1.36 = -0.42 V.$$

**60.** (a) It cannot evolved 
$$H_2$$
 from  $H_2S$ 

$$Hg + H_2 S \rightarrow \text{No reaction}$$
.

(b) 
$$E_{cell}^{o} = \frac{0.059}{n} \log K$$
  
 $\log K = \frac{1.10 \times 2}{0.059} = 37.2881 \text{ or } K = 10^{-37}.$ 

(d) 
$$E_{cell} = E_{cell}^o - \frac{\kappa_I}{nF} \ln \frac{c_2}{c_1}$$
 and  $\Delta G = -nFE_{cell}$ 

hence 
$$\Delta G$$
 is the function of  $\ln\left(\frac{C_2}{C_1}\right)$ 

6. (c) 
$$E = E^o - \frac{0.059}{n} \log \frac{[Zn^{++}]}{[Cu^{++}]} = 1.10 - \frac{0.059}{2} \log \frac{1}{0.1}$$
  
= 1.10 - 0.0295 log 10 = 1.07 volt.

67. (b) 
$$E_1 = E_o - \frac{0.0591}{2} \log \frac{0.01}{1} = E_o + \frac{0.0591}{2} \times 2$$
  
 $E_2 = E_o - \frac{0.0591}{2} \log \frac{100}{0.01} = E_o - \frac{0.0591}{2} \times 4$   
 $\therefore E_1 > E_2$ .  
Oxidation

**58.** (b) 
$$Fe^{+2} + Zn \rightarrow Zn^{2+} + Fe$$
  
Reduction  
 $EMF = E_{cathode} - E_{anode} = 0.44 - (0.76) = +0.32 V.$ 

- **69.** (a) *Fe* is more electropositive than copper. Hence  $Cu^{2+}$  can oxidise *Fe*.
- **70.** (b)  $E^o = 0$  because hydrogen have zero potential.
- **71.** (b) Cell potential of the cell is positive.
- **72.** (a,b) Because these comes after the *Fe* in electrochemical series.

73. (c) 
$$Fe^{2+} + \overline{Zn} \rightarrow Zn^{2+} + Fe$$

Reduction  

$$EMF = E_{cathode} - E_{anode} = -7.81 - (-7.62)$$
  
 $EMF = -0.19 V$ 

$$EMF = -0.19 V$$
.

74. (c)  $Cr^{3+} > Zn^{2+} > H > Fe^{3+}$ . Reducing nature decreasing order.

- **75.** (a) More is reduction potential, more is the power to get itself reduced or lesser is reducing power or greater is oxidising power.
- 76. (d)  $\Delta G = -nFE^{\circ}$   $\Delta G = -2.303RT\log K$ ;  $nFE^{\circ} = 2.303RT\log K$   $\log K = \frac{nFE^{\circ}}{2.303RT} = \frac{2 \times 96500 \times 0.295}{2.303 \times 8.314 \times 298}$  $\log K = 9.97 = K = 1 \times 10^{10}$ .
- **77.** (b) For the given cell  $M | M^+ || X^- | X$ , the cell reaction is derived as follows:

RHS: reduction  $X + e^- \rightarrow X^-$  .....(i) LHS: Oxidation  $M \rightarrow M^+ + e^-$  .....(ii) Add (i) and (ii)  $M + X \rightarrow M^+ + X^-$ The cell potential = -0.11 V

Since  $E_{cell}=-$  ve, the cell reaction derived above is not spontaneous. In fact, the reverse reaction will occur spontaneously.

**78.** (c) 
$$Z_{n+MgCl_2}^{0} \xrightarrow{+2} Z_nCl_2 + Mg$$
 No reaction  
Reduction  
This type of reaction does not easy because

This type of reaction does not occur because

$$Mg^{2+}E^o = -2.37V$$
 while  $Zn^{2+}E^o = -0.76V$ .

- **79.** (b) In neutral medium  $Mn^{+7}$  oxidation state change into +4 oxidation state, hence equivalent weight of  $KMnO_4 = \frac{M}{3}$ .
- **80.** (a) Increase in the concentration of  $Ag^+$  ion increase the voltage of the cell.

**81.** (a) 
$$E_{\text{cell}} = E_{\text{cell}}^o + \frac{0.059}{2} \log \frac{(Ag^+)}{(Sn^{2+})}$$

**82.** (b) The *K.E.* of proton is 1 *KeV.* 

**83.** (b) Anodic reaction :  $H_2(P_1) \rightarrow 2H^+$ 

Cathodic reaction : 
$$2H^+ \rightarrow H_2(P_2)$$

$$E_{cathode} = -\frac{RT}{2F} \ln \frac{P_2}{[H^+]^2} ; E_{anode} = -\frac{RT}{2F} \ln \frac{[H^+]^2}{P_1}$$

$$E_{inf} = E_{anode} + E_{cathode}$$
  
=  $-\frac{RT}{2F} \ln \frac{(H^+)^2}{P_1} - \frac{RT}{2F} \ln \frac{P_2}{(H^+)^2}$   
=  $-\frac{RT}{2F} \ln \frac{P_2}{P_1} = \frac{RT}{2F} \ln \frac{P_1}{P_2}.$ 

84. (c) 
$$\frac{1}{2}H_2 \to H^+(10^{-8}M) + e^-(\text{oxidation})$$
  
 $H^+(0.025M) + e^- \to \frac{1}{2}H_2(\text{reduction})$ 

Cell reaction is :

$$H^+(0.025\,M) \to H^+(10^{-8}\,M); E_{\text{cell}} = 0.38\,V.$$

- **85.** (a)  $E^o for Fe/Fe^{2+} = 0.44 \text{ V}$ .
- (c) (Reduction potential of cathode) (reduction potential of anode).
- **87.** (a) The correct decreasing electrode potential order is : K, Ba, Ca, Mg.

**89.** (c) 
$$E_{cell}^{o} = E_{cathode}^{o} - E_{anode}^{o}$$
  
= 0.34 - (-2.37) = +2.71 V.

95.

97. 98.

- **90.** (b) Because flourine is most powerful reducing agent than other halogens.
- 92. (c) Aluminium forms a protective oxide layer but iron does not.
- **93.** (d) The reduction potential of Zn is very higher than Cu.
- **94.** (a) The *pH* of 0.1 *M HCl* and 0.1 *M* acetic acid is not the same, because *HCl* is a strong acid so its *pH* is less and  $CH_3COOH$  is a weak acid, so its *pH* is more.

(d) The required reaction 
$$(Cu^{++} + Cu \rightarrow 2Cu^{+})$$
 can be  
obtained by using the following reactions.  
 $Cu^{++} + e^{-} \rightarrow Cu^{+}; E^{o}_{Cu^{++}/Cu^{+}} = 0.15 V$  .....(i)  
 $Cu^{++} + 2e^{-} \rightarrow Cu; E^{o}_{-u} = 0.34 V$  .....(ii)

Multiplying eq. (i) by 2 we get  

$$2Cu^{++} + 2e^- \rightarrow 2Cu^+$$
 .....(ii)

$$\Delta G_1 = -nFE = -2 \times F \times 0.15$$

$$Cu^{++} + 2e^{-} \rightarrow Cu \qquad \qquad \dots \text{(iv)}$$
$$\Delta G_{2} = -nFE = -2 \times F \times 0.34$$

$$Cu^{++} + Cu \rightarrow 2Cu^{+}$$

$$\Delta G_3 = -nFE = -1 \times F \times E^o$$

Also 
$$\Delta G_3 = \Delta G_1 - \Delta G_2$$

$$-1FE^{o} = (-2F \times 0.15) - (-2F \times 0.34)$$

 $E^{o} = -0.38$ 

- This is the value for the reaction
- $Cu^{++} + Cu \rightarrow 2Cu^{+}$
- But the given reaction is just reverse of it
- $\therefore E_{\text{cell}}$  for given reaction = + 0.38 V.
- (d) It connect two solutions and complete the circuit.
- (a) Greater the oxidation potential, greater is the reactivity.
- 99. (b) Electrochemical series compare the relative reactivity of metals.100. (d) Fuel cells are more efficient, free from pollution and they run till reactants are active.

102. (c) 
$$E^o = E^o_{Ae^{2+}/Ae} + E^o_{Cu/Cu^{2+}} = -0.34 + 0.80 = +0.46 V.$$

- **104.** (a) Lithium is the strongest reducing agent of the alkali metals.
- 105. (d) Potassium is more electropositive element, because it is the
- only alkali metal among the given elements. **106.** (b) Aluminium forms a self protecting film of oxide to prevent corrosion.

**107.** (a) 
$$Zn_{(s)} + 2H^+_{(aq)} \Rightarrow Zn_{(aq)}^{2+} + H_{2(g)}$$

$$E_{Cell} = E_{Cell}^{0} - \frac{.059}{2} \log \frac{[Zn^{2+}]}{[H^{+}]^{2}}$$

When  $H_2SO_4$  is added then  $[H^+]$  will increase therefore  $E_{Cell}$  will also increases and equilibrium will shift towards right.

**108.** (b) For 
$$M^+ + X^- \to M + X$$
  
 $E^0_{Cell} = E^0_{Cathode} + E^0_{Anode} = 0.44 - 0.33 = +0.11 V$ 

# scorer 536 Electrochemistry

Since  $E_{Cell}^0 = (+) 0.11 V$  is positive hence this reaction should be spontaneous.  $E_{Cell} = E_{Cell}^0 - \frac{0.0591}{\log K_c} \log K_c$ 

At 298 
$$K E_{Cell} = 0$$
  $O = 0.591 - \frac{0.0591}{n} \log K_c$   
 $\log K_c = \frac{0.591 \times 1}{0.0591} = 10$ ;  $K_c = \text{Antilog10} = 1 \times 10^{10}$ .

**110.** (a) 
$$\frac{1}{2}H_2 | H^+ | | Ag^+ | Ag|$$
  
 $E^0_{Cell} = E^0_{Cathode} - E^0_{Anode} = E^0_{Ag^+/Ag} - E^0_{H^+/\frac{1}{2}H_2}$ 

(a)

100

113.

(0.80) - (0.0) = 0.80 V.

**III.** (a) 
$$E_A = 2.23 V > E_B = 1.43 V$$
  
So *A* will act as cathode in galvanic cell. Hence  
 $E_{Cell}^0 = E_{Cathode} - E_{Anode} = E_A - E_B$   
 $= (2.23) - (-1.43) = 3.66 V$ .

**112.** (b)  $E_{Cu}^0 > E_{Mg}^0$  hence *Cu* acts as cathode and *Mg* acts as anode.

$$E_{Cell}^{0} = E_{Cu}^{0} - E_{Mg}^{0} = (0.34) - (-2.37) = +2.71 V.$$

(b) In this cell *Co* is oxidised and it acts as anode and *Ce* acts as cathode.

$$E^{0}_{Cell} = E^{0}_{Cathode} - E^{0}_{Anode} = 1.89 = E^{0}_{Cell} - (-0.28)$$
$$E^{0}_{Cell} = 1.89 - 0.28 = 1.61 \text{ Volts.}$$

**114.** (b) Given: 
$$\Delta G = -21.20 \ kJ = 21200 J$$

: 
$$\Delta G = -nFE$$
  
 $E = \frac{21200}{1 \times 96500} = 0.2196 V = 0.22 V.$ 

**115.** (b)  $Ag|Ag^+(.1m)||Ag^+1M|Ag|$ 

$$E_{Cell} = \frac{2.303RT}{nF} \log \frac{c_1}{c_2} = \frac{0.059}{1} \log \frac{1}{0.1}$$
$$= 0.059 \log 10 = 0.059 \text{ Volt.}$$

**116.** (b) For this cell, reaction is: 
$$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$$

$$E = E^{0} - \frac{0.0591}{n} \log \frac{c_{1}}{c_{2}}; E^{0} = E + \frac{0.0591}{n} \log \frac{c_{1}}{c_{2}}$$
$$= 0.2905 + \frac{0.0591}{2} \log \frac{10^{-2}}{10^{-3}} = 0.32 V.$$
$$E^{0} = \frac{0.0591}{2} \log K_{c}; \log K_{c} = \frac{0.32 \times 2}{0.0591} = \frac{0.32}{0.0295}$$
$$\therefore K_{c} = \frac{0.32}{10^{0295}}.$$

II7. (d) Al displaces H from HCl but silver cannot it means Al is situated above the Ag in ECS, hence Al will acts as anode and Ag will act as cathode.

$$E_{Cell}^{0} = E_{Cathode}^{0} - E_{Anode}^{0} = E_{Ag^{+}/Ag}^{0} - E_{Al^{3+}/Al}^{0}$$
  
2.46 = 0.8 -  $E_{Al^{3+}/Al}^{0}$ ;  $E_{Al}^{0} = 0.8 - 2.46 = -1.66 V$ 

$$\begin{aligned} \text{118.} \quad (\text{a}) \quad & \text{For } Sn_{(s)} + 2Fe_{(aq)}^{3+} \to 2Fe_{(aq)}^{2+} + Sn_{(aq)}^{2+} \\ & E_{Cell}^0 = E_{Sn/Sn^{2+}}^0 + E_{Fe^{3+}/Fe^{2+}}^0 = (0.14) + (0.77) \\ & E_{Cell} = 0.91 \ Volts. \end{aligned}$$

(d) 
$$\Gamma$$
 get oxidised to  $I_2$  hence will form anode and  $Cr_2O_7^{2-}$  get  
reduced to  $Cr^{3+}$  hence will form cathode.  
 $E_{Cell}^0 = E_{Cathode}^0 - E_{Anode}^0$ ;  $E_{Cell}^0 = E_{Cr_2O_7^{-2}} - E_{I_2}^0$ 

 $0.79 = 1.33 - E_{I_2}^0; \ E_{I_2}^0 = 1.33 - 0.79; \ E_{I_2}^0 = 0.54 \ V.$ (b) According to nernst's equation

$$E_{Cell} = E_{Cell}^{0} - \frac{nRT}{F} \log \frac{c_1}{c_2}$$
  
For  $Zn_{(s)} + Cl_{2(1 atm)} \rightarrow Zn^{2+} + 2Cl^{-}$   
 $c_1 = [Zn^{2+}]$  and  $c_2 = [Cl^{-}]$ 

Hence to increase *E*,  $c_1$  should be decreased and  $c_2$  should be increased is  $[Zn^{2+}]$  should be decreased and *Cl* should be increased.

121. (c)

119.

120.

Reduction $E_0 M^{3+} / M^{2+}$	Cell reaction		$E_0 M^{2+} / M^{3+}$ (Oxidation)
– .41 V	Cr <sup>2+</sup>	Cr <sup>3+</sup>	+.41 V
+ 1.57 V	$Mn^{2+}$	$Mn^{3+}$	– 1.57 V
+ 0.77 V	$Fe^{2+}$	$Fe^{3+}$	– 0.77 V
+ 1.97 V	Co <sup>2+</sup>	Co <sup>3+</sup>	– 1.97 <i>V</i>

As Cr has maximum oxidation potential value, therefore its oxidation should be easiest.

122. (a)  $Fe(s) \longrightarrow Fe^{-} + 2e^{-}; \Delta G_1^o$ 

$$2H + 2e^{-} + \frac{1}{2}O \longrightarrow HO(I); \quad \Delta G_{2}^{o}$$

$$Fe(s) + 2H + \frac{1}{2}O \longrightarrow Fe + HO; \Delta G_{3}^{o}$$
Applying,  $\Delta G_{1}^{o} + \Delta G_{2}^{o} = \Delta G_{3}^{o}$ 

$$\Delta G_{3}^{o} = (-2F \times 0.44) + (-2F \times 1.23)$$

$$\Delta G_{3}^{o} = -(2 \times 96500 \times 0.44 + 2 \times 96500 \times 1.23)$$

$$\Delta G_{3}^{o} = -322310 J$$

$$\therefore \quad \Delta G_{3}^{o} = -322 \ kJ$$

128. (a)  $\Delta G^o = -2.303 RT \log K_{eq}$  or  $\Delta G^o = -nFE_{cell}^o$ 

129. (a) Any redox reaction would occur spontaneously if the free energy change  $(\Delta G)$  is negative.

 $\Delta G^o = nFE^o$ 

3.

4.

Where *n* is the number of electrons involved, *F* is the value of Faraday and  $E^o$  is the cell emf.  $\Delta G^o$  can be negative if  $E^o$  is positive.

#### Corrosion

**2.** (d) Rusting of iron is catalysed by  $[H^+]$ .

(d)  $HgCl_2$  has corrosive action. It is highly poisonous. It sublimes on heating. It is, therefore, known as corrosive sublimate.

(a) 
$$Fe \rightarrow Fe^{2+} + 2e$$
 (anode reaction)  
 $O_2 + 2H_2O + 4e \rightarrow 4OH^-$  (cathode reaction)  
The overall reaction is  
 $2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$ 

 $Fe(OH)_2$  may be dehydrated to iron oxide FeO, or further oxidised to  $Fe(OH)_3$  and then dehydrated to iron rust,  $Fe_2O_3$ .

### **Critical Thinking Questions**

1. (c) 
$$(126 \ scm^2) \wedge_{NaCl}^0 = \wedge_{Na^+}^0 + \wedge_{Cl^-}^0$$
 .....(1)  
 $(152 \ scm^2) \wedge_{KBr}^0 = \wedge_{K^+}^0 + \wedge_{Br^-}^0$  .....(2)  
 $(150 \ scm^2) \wedge_{KCl}^0 = \wedge_{K^+}^0 + \wedge_{Cl^-}^0$  .....(3)  
By equation (1)+(2) - (3)  
 $\because \wedge_{NaBr}^0 = \wedge_{Na^+}^0 + \wedge_{Br^-}^0$   
 $= 126 + 152 - 150 = 128 \ Scm^2 mol^{-1}$ 

**2.** (a) At cathode : 
$$2H^+_{(aq)} + 2e^- \rightarrow 2H$$

$$\frac{2H + \frac{1}{2}O_2 \rightarrow H_2O}{2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O}$$

**3.** (c)  $H_2$  undergoes oxidation and  $AgCl(Ag^+)$  undergoes reduction. Oxidation

4. (b) In this reaction 
$$Fe^{2+} + Zn \rightarrow Zn + Fe$$
  
Reduction  
 $EMF = E_{cathode} - E_{anode} = -0.41 - (-0.76)$   
 $EMF = \pm 0.35 V$ 

5. (c)  $NO_3^- + 4H^+ + 4e^- \rightarrow 2H_2O + NO$ . In this equation all the atoms are balanced. For balancing added  $3e^-$  to *L.H.S.* we have,  $NO_3^- + 4H^+ + 3e^- \rightarrow 2H_2O + NO$ .

6. (a) 
$$E_{cell} = E_{cell}^o - \frac{0.059}{2} \log \frac{(Zn^{++})}{(Cu^{++})}$$
  
=  $1.10 - \frac{0.059}{2} \log \frac{0.1}{0.1} = 1.10 V$ .

7. (a) The tendency to gain electron is in the order Z > Y > XThus  $Y + e \rightarrow Y^{-}$ ;  $X \rightarrow X^{+} + e$ .

8. (b) 
$$E_{OP} = E_{OP}^{o} - \frac{0.059}{1} \log \frac{[H^+]}{P_{H_2}}$$

$$\therefore [H^+] = 10^{-10}; P_{H_2} = 1 \text{ atm}; E_{OP} = 0.59 \text{ V}.$$

- 9. (a.c,d)Decomposition of  $H_2O_2$  is an example of exothermic reaction, negative catalysis and auto-oxidation.
- 10. (a) 27 gm of Al is obtained by passing a current of  $3 \times 96500 \ C$ .  $\therefore 1 \ gm$  of Al is obtained by passing a current of  $3 \times \frac{96500}{27} \ C$ .  $\therefore 5.12 \times 10 \ gm$  of Al is obtained by passing a current of  $3 \times \frac{96500}{27} \times 5.12 \times 1000$  $= 1.83 \times 10 \ C \times 3 = 5.49 \times 10 \ C$ .

**n.** (c) 
$$\Lambda^{\infty}_{HOAC} = \Lambda^{\infty}_{NaOAC} + \Lambda^{\infty}_{HCl} - \Lambda^{\infty}_{NaCl}$$
  
= 91.0 + 426.2 - 126.5 = 390.7

12. (d) 
$$\frac{\omega_1}{E_1} = \frac{\omega_2}{E_2}$$
;  $\frac{\omega_1}{3} = \frac{270}{93}$ ;  $\omega_1 = 90 \, kg$ .  
13. (c) Eq of Al = eq of H<sub>2</sub>

(c) Eq of 
$$Al = eq$$
 of  $H_2$   
$$\frac{4.5}{\frac{27}{3}} = eq \text{ of } H_2; \quad \frac{4.5}{9} = eq \text{ of } H_2$$
$$2H^+ + 2e^- \rightarrow H_2$$

eq. of  $H_2$  = Number of moles × n factor  $0.5 = n_{H_2} \times 2$ 

$$V_{H_2} = \frac{0.5}{2} \times 22.4$$
;  $V_{H_2} = 5.6 L$ 

(c) The reaction taking place at anode is  $2Cl \rightarrow Cl + 2e$   $1 \text{ mole} \quad 2 \times 96500 \text{ coulomb}$   $Q = i \cdot t = 1 \times 30 \times 60 = 1800 \text{ coulomb}.$ The amount of chlorine liberated by passing 1800 coulomb of electric charge  $= \frac{1 \times 1800 \times 71}{2 \times 96500} = 0.66 \text{ g}.$ 

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## **Assertion & Reason**

- (a) The nature of the cathode can affect the order of discharge of ions.
  (b) 1 mole of silver = 1g equivalent of silver
  1 mole of copper = 2g equivalent of copper
  We know from Faraday's law of electrolysis that "The weight of ion deposited on an electrode is directly proportional to the quantity of electricity passed".
- (d) Copper is present below hydrogen therefore hydrogen from HCl cannot be liberated by treating with copper. Hence assertion is false while reason is true.
- (d) Copper cannot liberate hydrogen from a dil. HCl solutions because it is situated below hydrogen in the reactivity series. Here both assertion and reason are false.
- (d) The formation of Zn is not possible by placing Cu plate in  $ZnSO_4$  solution because Zn is placed above Cu in electrochemical series. Therefore, both assertion and reason are false.
- (e) Electrical conductivity of copper decreases with increase in temperature because the metallic conductivity is due to the motion of electrons. On increasing temperature the motion of electron increases which hinder in conductance of current. Hence, here assertion is false but the reason is true.
- (a) Dry air is heavier than wet air because the density of dry air is more than water.
- (e) Copper is present below hydrogen therefore hydrogen from HCl cannot be liberated by treating with copper. Hence, assertion is false while reason is true.
- (a) K and Cs emit electrons on exposure to light hence, both are used in photoelectric cells. Here, assertion and reason are true and reason is a correct explanation.

(b) We know, 
$$R \propto \frac{l}{A}$$
 or  $R = \rho \left( \frac{l}{A} \right)$ , where proportionality

constant  $\rho$  is called resistivity. If l = 1m and  $A = 1m^2$ , then  $R = \rho$  *i.e.* Resistance = Resistivity.

- (a) According to Kohlrausch law, "Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte".
- (c) One Faraday deposite one gram equivalent of the substance.
- (b) Gold has higher reduction potential than the given metals. Hence  $AuCl_3$  will react with these metals.

#### UNIVERSAL SELF SCORER

# 538 Electrochemistry

17. (a)  $Zn(s) + Cu^{2+}(aq) \to Zn^{2+}(aq) + Cu(s)$ 

As the time passes, the concentration of  $Zn^{2+}$  keeps on increasing while the concentration of  $Cu^{2+}$  keeps on decreasing. At the same time voltage of the cell keeps on decreasing. When there is no change in concentration of  $Cu^{2+}$  and  $Zn^{2+}$  ions, voltmeter gives zero reading and this state is known as equilibrium.

- **18.** (e) A negative value of standard reduction potential means that oxidation takes place on this electrode with reference to *SHE*.
- (a) A standard cell is one whose *e.m.f.* almost does not change with temperature.
- 22. (d) Identification of cathode and anode is done by the use of ammeter/voltmeter. Higher is the value of reduction potentials greater would be its oxidising power.
- **23.** (b) If redox reaction is spontaneous,  $\Delta G$  is *-ve* and hence  $E^0$  is positive.  $-\Delta G^0 = nFE^0$  cell
- 24. (a) Zinc metal which has a more negative electrode potential than iron will provide electrons in preference of the iron, and therefore corrode first. Only when all the zinc has been oxidised does the iron start to rust.
- **25.** (a) Both assertion and reason are true and reason is the correct explanation of assertion.

Anode (oxidation) for eq.  $Zn \longrightarrow Zn^{2+} + 2e^-$ , so Excess of electrons and hence negatively charged while cathode is positively charged.

**26.** (a) Both assertion and reason are true and reason is the correct explanation of assertion.

$$E_{Au^{3+}/Au}^{0} - E_{Ni/Ni^{2+}}^{0} = 1.50 - (-0.25) = 1.75 V$$

- 27. (c) Assertion is true but reason is false. Ions of inert electrolytes are not involved in any electrochemical change until they react chemically with the electrolytes in the two half-cells.
- 28. (d) Both assertion and reason are false. Potential difference is the difference between the electrode potential of the two electrodes of the cell when cell is under operation while emf is the potential difference generated by a cell when there is zero electron flow.