18
Chapter
ELECTROCHEMISTRY

A SINGLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

1. During the passage of electricity through the solution of an electrolyte, current is carried by
(a) cations only
(b) anions only
(c) both cations and anions, fractions of current carried being equal
(d) both cations and anions, usually fractions carried being different

2. When electric current is passed through a cell having an electrolytic solution, the cations move towards the cathode and anions towards the anode. If anode is pulled out from the solution
(a) the cations and anions will move towards the cathode
(b) the cations will continue to move towards cathode and anions will stop moving
(c) both the cations and anions will stop moving
(d) the cations and anions will start moving randomly.

3. Which of the following statements is correct for an electrolytic solution upon dilution
(a) conductivity increases
(b) conductance decreases
(c) molar conductance decreases but equivalent conductance increases
(d) molar conductance increases while equivalent conductance decreases.

4. Molar conductance of KCl increases slowly with decrease in concentration because of
(a) increase in degree of ionisation
(b) increase in total number of current carrying species
(c) weakening of interionic attractions and increase in ionic mobilities
(d) increase in hydration of ions.

5. Which of the following is correct for the solution of C_2H_5COOH upon dilution regarding current carrying species ?
(a) The number in 1 cm^3 as well as in total volume increases
(b) The number in 1 cm^3 decreases whereas that in the total volume remains constant
(c) The number in 1 cm^3 decreases but that in the total volume increases
(d) The number in 1 cm^3 as well as in total volume decreases.

6. The cell constant of a conductivity cell with electrodes 0.5 cm × 0.5 cm and separation of 0.5 cm, is :
(a) $0.5\ cm^{-1}$ (b) $2.0\ cm^{-1}$
(c) 2.0 cm (d) $2.0\ cm^2$

7. Absolute ionic mobility is the speed of the ion under the electric field of
(a) 10 *V* across a distance of 5 cm
(b) 5 *V* across a distance of 10 cm
(c) 5 *V* across a distance of 5 cm
(d) none of these

8. Which has the maximum conductivity in their 0.1 *M* solution ?
(a) $[Co(NH_3)_3Cl_3]$ (b) $[Co(NH_3)_4Cl_2]Cl$
(c) $[Co(NH_3)_5Cl]Cl_2$ (d) $[Co(NH_3)_6]Cl_3$

9. Which of the following statements is correct for a strong electrolyte :
(a) λ_m increases linearly with $C^{1/2}$
(b) λ_m increases linearly with C^2
(c) λ_m decreases linearly with C^2
(d) λ_m decreases linearly with $C^{1/2}$

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	

10. The relationship $\lambda_m = \lambda_m^o - B\sqrt{C}$ will not hold good for the electrolyte?

(a) HCl (b) KCl
(c) $BaCl_2$ (d) HCN

11. Which is correct regarding the plot of λ_m *versus* $\sqrt{C}$ for an electrolyte ?

(a) Linear with positive slope for KCl
(b) Linear with positive slope for CH_3COOH
(c) Non-linear for NaCl
(d) Linear with negative slope for NaCl

12. Dimension of ionic mobility is :

(a) $m\,V^{-1}\,s^{-1}$ (b) $m^2\,V^{-2}\,s^{-1}$
(c) $m^2\,V^{-1}\,s^{-1}$ (d) $m^{-2}\,V\,s^{-1}$

13. Which of the following compounds has smallest molar conductance as molarity → 0

(a) HCl (b) LiCl
(c) NaCl (d) KCl

14. Conductance of 0.1 M KCl (conductivity = x $ohm^{-1}\,cm^{-1}$) filled in a conductivity cell is y ohm^{-1}. If the conductance of 0.1 M NaOH filled in the same cell is z ohm^{-1}, molar conductance of NaOH will be :

(a) $0.1\frac{xz}{y}$ (b) $10\frac{xz}{y}$

(c) $10^3\frac{xz}{y}$ (d) $10^4\frac{xz}{y}$

15. $\overset{o}{\lambda}_m$ value can not be determined by extrapolating the plot between λ_m *versus* $(\text{molarity})^{1/2}$ for the compound

(a) KCl (b) Na_2SO_4
(c) $NaNO_3$ (d) NH_4OH

16. Molar conductances of $BaCl_2$, H_2SO_4 and HCl at infinite dilutions are x_1, x_2 and x_3 respectively. Equivalent conductance of $BaSO_4$ at infinite dilution will be :

(a) $(x_1 + x_2 - x_3)/2$ (b) $x_1 + x_2 - 2x_3$
(c) $(x_1 - x_2 - x_3)/2$ (d) $(x_1 + x_2 - 2x_3)/2$

17. At 298 K, the conductivity of a saturated solution of AgCl in water is $2.6 \times 10^{-6}\ S\,cm^{-1}$. Its solubility product at 298 K (given :

$\lambda^{\infty}(Ag^+) = 63.0\ S\ cm^2 mol^{-1}$,

$\lambda^{\infty}(Cl^-) = 67.0\ S\ cm^2 mol^{-1}$)

(a) $2.0 \times 10^{-5}\,M^2$ (b) $4.0 \times 10^{-10}\,M^2$
(c) $4.0 \times 10^{-16}\,M^2$ (d) $2 \times 10^{-8}\,M^2$

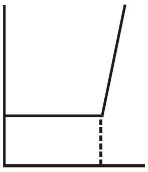
18. Specific conductance of 0.1 M CH_3COOH at 25ºC is $3.9 \times 10^{-4}\ ohm^{-1}\ cm^{-1}$. If $\lambda^{\infty}(H_3O^+)$ and $\lambda^{\infty}(CH_3COO^-)$ at 25ºC are 349.0 and 41.0 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively, degree of ionization of CH_3COOH at the given concentration is :

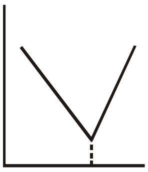
(a) 2.0% (b) 1.0%
(c) 4.0% (d) 5.0%

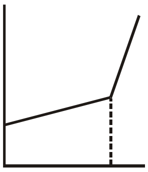
19. During conductometric titration of 0.1 M HCl with 1.0 M KOH, which is the correct observation.

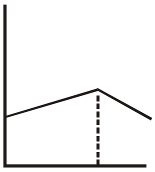
(a) Resistance of the solution decreases upto equivalence point and then increases
(b) Resistance increases upto equivalence point and then decreases
(c) Conductance increases upto equivalence point and then decreases
(d) Conductance decreases upto equivalence point and then becomes almost constant.

20. Variation of conductance (Y-axis) during the course of titration of NH_4OH with HCl (titrant) will be represented by

(a) 

(b) 

(c) 

(d) 

MARK YOUR RESPONSE	10. ⓐⓑⓒⓓ	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ
	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ
	20. ⓐⓑⓒⓓ				

21. Which of the following represents increasing order of ionic conductance ?

(a) $F^- < Cl^- < Br < I^-$ (b) $I^- < Br^- < Cl^- < F^-$

(c) $F^- < Cl^- < I^- < Br^-$ (d) $F^- < I^- < Cl^- < Br^-$

22. Specific conductance of 0.1 *M* HA is 3.75×10^{-4} ohm^{-1} cm^{-1}. If $\lambda^{\infty}(\text{HA}) = 250 \text{ ohm}^{-1}\text{cm}^2\text{ mol}^{-1}$, the dissociation constant K_a of HA is :

(a) 1.0×10^{-5} (b) 2.25×10^{-4}

(c) 2.25×10^{-5} (d) 2.25×10^{-13}

23. Equivalent conductance at infinite dilution is related to ionic mobilities by (*F* = Faraday = 96500 *C*)

(a) $\lambda^{\infty}F = U_+ + U_-$ (b) $\lambda^{\infty} = F(U_+ + U_-)$

(c) $\lambda^{\infty} = (U_+ + U_-)$ (d) $\lambda^{\infty} = F^2(U_+ + U_-)$

24. The equation which includes both Kohlrausch law and Ostawald's dilution law is :

(a) $K_a = \dfrac{C\,\lambda_m^2}{\lambda_m^o(\lambda_m^o - \lambda_m)}$ (b) $\lambda_m^o = \nu_+\lambda_+ + \nu_-\lambda_-$

(c) $\lambda_m = \lambda_m^o - B\sqrt{C}$ (d) $\lambda_e^o = F(u_+ + u_-)$

25. In an electrolytic cell, electrons move

(a) towards anode (b) away from the anode

(c) away from the cathode

(d) towards anode and cathode

26. A 1.0 *M* with respect to each of metal halides AX_3, BX_2, CX_3 and DX_2 is electrolysed using platinum electrodes. If $E^o_{A^{3+}/A} = 1.50V$, $E^o_{B^{2+}/B} = 0.34V$, $E^o_{C^{3+}/C} = -0.74V$, $E^o_{D^{2+}/D} = -2.37V$, the correct sequence in which the various metals are deposited at the cathode, is :

(a) *A, B, C, D* (b) *D, C, B, A*

(c) *A, B, C* (d) *C, B, A*

27. Given that $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$, $E^o = -1.36V$; $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2\text{e}^-$, $E^o = -1.23V$. On electrolysing 1 *M* NaCl solution with inert electrodes, which of the following is correct regarding liberation of electrolytic products ?

(a) Cathode : Na and H_2 (b) Cathode : Na, O_2

(c) Anode : O_2 (d) Anode : Cl_2

28. In electrolytic reduction of a nitroarene with 50% current efficiency, 20.50 g of the compound is reduced by 2 × 96500 *C* of electric charge. The molar mass of the compound is :

(a) 20.50 g (b) 10.25 g

(c) 123.00 g (d) 61.50 g

29. A lead storage battery containing 5.0 *L* of H_2SO_4 solution is operated for 9.65×10^5 s with a steady current of 100 *mA*. Assuming volume of the solution remaining constant, normality of H_2SO_4 will :

(a) increase by unity (b) increase by 0.20

(c) decrease by 0.40 (d) remain unchanged

30. Electrolysis is carried out in three cells : (A) – 1.0 *M* $CuSO_4$, Pt electrodes; (B) – 1.0 *M* $CuSO_4$, Copper electrodes; (C) – 1.0 *M* KCl, Pt electrodes. If volume of electrolytic solution is maintained constant in each of the cells, which is correct set of pH changes in (A), (B) and (C) cells respectively?

(a) increase in all the three

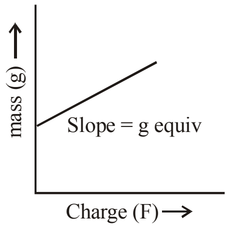
(b) decrease in all the three

(c) increase, constant, increase

(d) decrease, constant, increase

31. During electrolysis, the amount (g) of the liberated product is plotted against the electric charge (*F*) as x-axis. The correct graph is :

(a)



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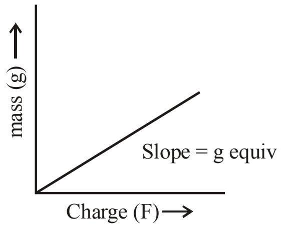
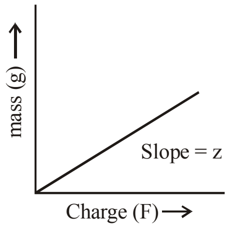


(c)



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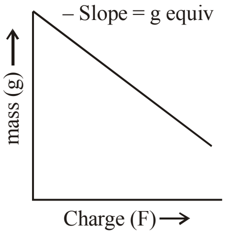


MARK YOUR RESPONSE	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	25. ⓐⓑⓒⓓ
	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ	30. ⓐⓑⓒⓓ
	31. ⓐⓑⓒⓓ				

32. Acidulated water is electrolysed by 1 *A* current for 16 minutes and 5 seconds using inert electrodes. The volume of gases liberated at STP will be :

(a) 224 ml (b) 112 ml
(c) 168 ml (d) 336 ml

33. On electrolysing K_2SO_4 solution using inert electrodes, 1.68 L (STP) of gases was obtained. How many moles of MnO_4^- could be reduced to Mn^{2+} by the same quantity of electricity?

(a) 0.10 (b) 0.20
(c) 0.15 (d) 0.02

34. What current strength would be required to produce hydrogen gas at the rate of 1.12 $cm^3 s^{-1}$ (STP) by the electrolysis of aqueous NaCl solution with 96.5% current efficiency ?

(a) 9.65 *A* (b) 9.31 *A*
(c) 10.00 *A* (d) 0.10 *A*

35. The pH of 0.5L of 1.0 *M* NaCl after electrolysis for 965 s using 5.0 *A* current (100% efficiency), is:

(a) 1.00 (b) 13.00
(c) 12.70 (d) 1.30

36. Electrolysis of NaCl solution with inert electrodes for certain period of time gave 600 cm^3 of 1.0 *M* NaOH in the electrolytic cell. During the same period 31.80 g of copper was deposited in a copper voltameter in series with the electrolytic cell. What is the percent current efficiency in the electrolytic cell? (At. wt. of Cu = 63.6)

(a) 40 (b) 50
(c) 60 (d) 25

37. Using electrolytic method, if cost of production of 1*L* of oxygen at STP is Rs. *x*, the cost of production of 10*L* of hydrogen at STP will be :

(a) 10*x* (b) *x*/16
(c) 10*x*/32 (d) 10*x*/2

38. The charge required for the oxidation of one mole of Mn_3O_4 to MnO_4^{2-} in alkaline medium is (assume 100% current efficiency):

(a) 10/3 *F* (b) 6*F*
(c) 10 *F* (d) 4*F*

39. 48250 *C* of electricity was required to deposit all the copper present in 0.5*L* of $CuSO_4$ solution using inert electrodes. The molarity of the solution was : (Assume volume constant)

(a) 0.25 *M* (b) 1.00 *M*
(c) 2.50 *M* (d) 0.50 *M*

40. 1.0 *L* each of a buffer containing 1 Mole NH_3 and 1 mole of NH_4^+ were placed in the cathodic and anodic half cells, and 965 *C* of electricity was passed. If anodic and cathodic half cell reactions involve oxidation and reduction of water only as :

$2H_2O \to 4H^+ + O_2 + 4e^-$;

$2H_2O + 2e^- \to H_2 + 2OH^-$, then pH of

(a) anodic solution will decrease
(b) cathodic solution will increase
(c) both the solutions will remain practically constant
(d) both the solutions will increase

41. The value of the reaction quotient, *Q*, for the cell

$Cr_{(s)} \mid Cr_{aq}^{3+}(0.1M) \parallel Cu_{aq}^{2+}(0.5M) \mid Cu_{(s)}$ is :

(a) 12.5 (b) 0.08
(c) 0.20 (d) 5.0

42. Which of the following is always true regarding the spontaneity of reaction occurring in a galvanic cell?

(a) $E_{cell}^o > 0, \Delta G^\circ < 0 \text{ and } Q > K_e$
(b) $E_{cell}^o > 0, \Delta G^\circ < 0 \text{ and } Q < K_e$
(c) $E_{cell}^o > 0, \Delta G^o > 0 \text{ and } Q > K_e$
(d) $E_{cell}^o > 0, \Delta G < 0 \text{ and } Q < K_e$

43. If $E^o_{Fe^{2+}/Fe} = x_1 V$ and $E^o_{Fe^{3+}/Fe^{2+}} = x_2 V$, then $E^o_{Fe^{3+}/Fe}$ will be

(a) $(2x_1 + x_2) V$ (b) $(3x_2 - x_1) V$
(c) $(2x_1 + x_2)/3\ V$ (d) $(x_1 + 2x_2)/3\ V$

44. Consider the following reactions :

$Cd_{(aq)}^{2+} + 2e^- \to Cd_{(s)}, E^\circ = -0.40\ V$

$Ag_{(aq)}^{+} + e^- \to Ag_{(s)}, E^\circ = 0.80\ V$

Which of the following statements is **not** correct for the galvanic cell involving the above reactions?

(a) E_{cell} increases when Cd^{2+} solution is diluted
(b) E_{cell} decreases when Ag^+ solution is diluted
(c) Twice as many electrons pass through the cadmium electrode as through silver electrode
(d) Molar concentration of the cation in the cathodic compartment changes faster than that of the cation in anodic compartment.

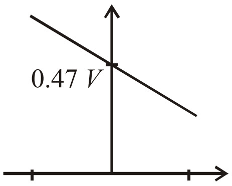
MARK YOUR RESPONSE	32. ⓐⓑⓒⓓ	33. ⓐⓑⓒⓓ	34. ⓐⓑⓒⓓ	35. ⓐⓑⓒⓓ	36. ⓐⓑⓒⓓ
	37. ⓐⓑⓒⓓ	38. ⓐⓑⓒⓓ	39. ⓐⓑⓒⓓ	40. ⓐⓑⓒⓓ	41. ⓐⓑⓒⓓ
	42. ⓐⓑⓒⓓ	43. ⓐⓑⓒⓓ	44. ⓐⓑⓒⓓ		

45. Consider the galvanic cell

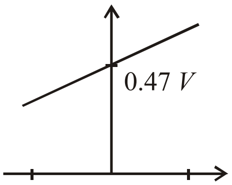
$$Pb_{(s)} \mid Pb^{2+}_{aq}(x_1 M) \parallel Cu^{2+}_{aq}(x_2 M) \mid Cu_{(s)}$$

$E^{o}_{cell} = 0.47V$

Which of the following graphs represents the variation of E_{cell} with $\log[Cu^{2+}]/[Pb^{2+}]$ (X-axis)



(a)



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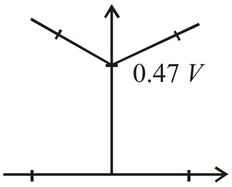

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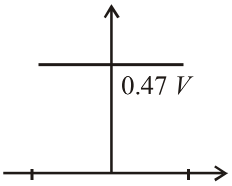


(d)

46. The electrode potential of hydrogen electrode set up in 1.0 M KCl and $P_{H_2} = 1$ atm will be :

(a) $-6.059\ V$ (b) $0.414\ V$
(c) $-0.414\ V$ (d) $-0.207\ V$

47. Which of the following cells has constant EMF during its working ?

(a) $Hg_{(l)}, Hg_2Cl_{2(s)} \parallel KCl_{(aq)} \parallel AgNO_{3(aq)} \mid Ag_{(s)}$

(b) $Pt(H_2) \mid HCl_{(aq)} \mid (Cl_2)\ Pt$

(c) $Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

(d) $Fe \mid FeO_{(s)} \mid KOH_{(aq)} \mid NiO_{(s)}, Ni_2O_{3(s)} \mid Ni$

48. The EMF of the cell

$$Pt, Cl_{2(g)}(p_1 atm) \mid Cl^{-}_{(aq)}(1M) \mid Cl_{2(g)}(p_2 atm), Pt$$

will be positive when :

(a) $p_1 > p_2$ (b) $p_1 = p_2$
(c) $p_1 < p_2$ (d) none of these

49. What is the EMF of the galvanic cell (K_{sp} of AgCl $= 1.0 \times 10^{-10}$)

$$Ag, AgCl_{(s)} \mid 1M\ KCl_{(aq)} \parallel 1M\ AgNO_{3(aq)} \mid Ag$$

(a) zero (b) $-0.592\ V$
(c) $1.391\ V$ (d) $0.592\ V$

50. Given :

$A^{2+} + 2e^- \rightarrow A_{(s)}$ $E^o = 0.10\ V$

$B^+ + e^- \rightarrow B_{(s)}$ $E^o = -2.71\ V$

$X_{2(g)} + 2e^- \rightarrow 2X^-$ $E^o = 1.08\ V$

Which of the following statements is **not** true ?

(a) $X_{2(g)}$ will oxidize both A and B

(b) A^{2+} will oxidize B

(c) The reaction $2X^-(1.0M) + A^{2+}(1.0M) \rightarrow X_2(1\text{ atm}) + A_{(s)}$ will be spontaneous

(d) The oxidizing power of A^{2+}, B^+ and $X_{2(g)}$ is in the order : $B^+ < A^{2+} < X_2$

51. 3.80 g of metal M is deposited at the cathode by passing 0.2 F of electricity through the solution of metal chloride. The formula of the metal chloride :
(Atomic mass of $M = 57$)

(a) MCl (b) MCl_2
(c) MCl_3 (d) MCl_4

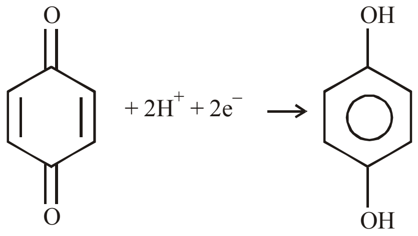
52. In acidic medium, MnO_2 is an oxidant as :

$$MnO_{2(s)} + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$$

If the pH of the solution is decreased by one unit, the electrode potential of the half cell Pt: MnO_2, Mn^{2+} will change by

(a) -0.118 V (b) 0.118 V
(c) 0.236 V (d) -0.236 V

53. The half cell potential for the quinhydrone electrode



set up at pH = 4 will be (quinhydrone = 1 : 1 molecular compound of quinone (Q) and hydroquinone (QH_2), $E^o = 0.699\ V$)

(a) $0.699\ V$ (b) $0.463\ V$
(c) $0.935\ V$ (d) $0.817\ V$

MARK YOUR RESPONSE	45. ⓐⓑⓒⓓ	46. ⓐⓑⓒⓓ	47. ⓐⓑⓒⓓ	48. ⓐⓑⓒⓓ	49. ⓐⓑⓒⓓ
	50. ⓐⓑⓒⓓ	51. ⓐⓑⓒⓓ	52. ⓐⓑⓒⓓ	53. ⓐⓑⓒⓓ	

54. Given that $E^{\circ}_{Cu^{2+}/Cu} = 0.34V$; $E^{\circ}_{Ag^{+}/Ag} = 0.80V$;

$E^{\circ}_{Mg^{2+}/Mg} = -2.37V$ and $E^{\circ}_{Al^{3+}/Al} = -1.66\ V$, in which of the following cells the standard free energy decrease is maximum:

(a) $Mg \mid Mg^{2+}(1M) \parallel Cu^{2+}(1M) \mid Cu$

(b) $Mg \mid Mg^{2+}(1M) \parallel Ag^{+}(1M) \mid Ag$

(c) $Ag \mid Ag^{+}(1M) \parallel Al^{3+}(1M) \mid Al$

(d) $Cu \mid Cu^{2+}(1M) \parallel Ag^{+}(1M) \mid Ag$

55. Given the cell reactions

$MX_{(s)} + e^{-} \rightarrow M_{(s)} + X^{-}_{(aq)}$; $E^{o} = 0.207\ V$

and $M^{+}_{(aq)} + e^{-} \rightarrow M_{(s)}$; $E^{o} = 0.799\ V$

The solubility of $MX_{(s)}$ at 298 K is :

(a) $1.0 \times 10^{-10}\ mol\,L^{-1}$ (b) $1.0 \times 10^{-9}\ mol\,L^{-1}$

(c) $1.0 \times 10^{-4}\ mol\,L^{-1}$ (d) $1.0 \times 10^{-5}\ mol\,L^{-1}$

56. Which of the following statements is **not** correct during the working of the cell :

$Cu_{(s)} \mid Cu^{2+}_{(aq)}(M_1) \parallel Cu^{2+}_{(aq)}(M_2) \mid Cu_{(s)}$

$M_1 < M_2$, M's being the molarities of $Cu^{2+}_{(aq)}$.

(a) E_{cell} decreases and falls ultimately to zero

(b) M_1 increases and M_2 decreases due to direct transfer of Cu^{2+} ions

(c) M_1 increases due to oxidation of $Cu_{(s)}$ and M_2 decreases due to reduction of Cu^{2+} ions

(d) $E^{\circ}_{cell} = 0.0V$

57. A concentration cell is a galvanic cell in which

(a) decrease in free energy in a spontaneous chemical process appears as electrical energy

(b) decrease in free energy in a spontaneous physical process appears as electrical energy

(c) decrease in free energy in a spontaneous physical or chemical process appears as electrical energy

(d) a non-spontaneous physical or chemical process produces electrical energy.

58. H_2 and D_2 gases at a pressure of 1 atm each at 25°C are in equilibrium with a solution containing H^+ and D^+ ions. If

$E^{\circ}_{D^{+}/D_2} = -0.003V$, calculate log $[D^{+}]/[H^{+}]$

(a) 5.0 (b) 0.50

(c) 0.05 (d) 0.005

59. Given that : $E^{\circ}_{Ag^{+}/Ag} = 0.80V$ and $[Ag^{+}] = 10^{-3}M$;

$E^{\circ}_{Hg_2^{2+}/Hg} = 0.785V$ and $[Hg_2^{2+}] = 10^{-1}M$

which is true for the cell reaction

$2Hg_{(l)} + 2Ag^{+}_{(aq)} \rightarrow 2Ag_{(s)} + Hg^{2+}_{2(aq)}$?

(a) The forward reaction is spontaneous

(b) The backward reaction is spontaneous

(c) $E_{cell} = 0.163\ V$

(d) $E_{cell} = 1.585\ V$

60. The equilibrium constant for the disproportionation reaction: $2Cu^{+}_{(aq)} \rightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$

at 25°C ($E^{o}_{Cu^{+}/Cu} = 0.52V$; $E^{o}_{Cu^{2+}/Cu^{+}} = 0.16V$) is :

(a) 1.2×10^{-6} (b) 6×10^{4}

(c) 6×10^{6} (d) 1.2×10^{6}

61. The electrical work done during the reaction at 298 K : $2Hg_{(l)} + Cl_{2(g)} \rightarrow Hg_2Cl_{2(s)}$, is:

given that $E^{\circ}_{Cl_2/Cl^{-}} = 1.36V$; $E^{\circ}_{Hg_2Cl_2/Hg,Cl^{-}}$

$= 0.27V$; $P_{Cl_2} = 1\,atm$,

(a) 210.37 kJ mol^{-1} (b) 105.185 kJ mol^{-1}

(c) 420.74 kJ mol^{-1} (d) 110.37 kJ mol^{-1}

62. Consider the cell : $X_{(s)} \mid X^{3+}_{(aq)} \parallel Y^{2+}_{(aq)} \mid Y_{(s)}$

If $E^{\circ}_{X^{3+}/X} = -1.66V$ and $E^{\circ}_{Y^{2+}/y} = 0.34V$, logarithm (to the base 10) of equilibrium constant of the net reaction in the above cell at 25°C, is :

(a) 67.56 (b) 101.35

(c) 202.70 (d) 168.92

MARK YOUR RESPONSE	54. ⓐⓑⓒⓓ	55. ⓐⓑⓒⓓ	56. ⓐⓑⓒⓓ	57. ⓐⓑⓒⓓ	58. ⓐⓑⓒⓓ
	59. ⓐⓑⓒⓓ	60. ⓐⓑⓒⓓ	61. ⓐⓑⓒⓓ	62. ⓐⓑⓒⓓ	

63. The electrode potential of the half cell :

$Pt,\ H_{2(g)}(2\text{ atm})\,|H_3O_{(aq)}(1M)$ is :

(a) $0.000\,mV$ (b) $8.90\,mV$
(c) $-8.90\,mV$ (d) $-17.8\,mV$

64. $\Delta G = \Delta H - T\Delta S$ and $\left[\dfrac{d(\Delta G)}{dT}\right]_p = -\Delta S$

The enthalpy of cell reaction, ΔH, is then given by

(a) $T\left[\dfrac{dE_{cell}}{dT}\right]_p - E_{cell}$

(b) $nF\left[T\left(\dfrac{dE_{cell}}{dT}\right)_p - E_{cell}\right]$

(c) $nF\left[E_{cell} - T\left(\dfrac{dE_{cell}}{dT}\right)_p\right]$

(d) $nFT\left(\dfrac{dE_{cell}}{dT}\right)_p$

65. $\Delta G = \Delta H - T\Delta S = \Delta H \quad T\left(\dfrac{d\Delta G}{dT}\right)_p$

The temperature coefficient of the EMF of the cell, $\left(\dfrac{dE_{cell}}{dT}\right)_p$ is :

(a) $-nFE_{cell}$ (b) $n\,F\,E_{cell}$
(c) $\dfrac{nF}{\Delta S}$ (d) $\dfrac{\Delta S}{nF}$

66. Given that $E_{K \quad /K} = -2.93V$; $E_{Fe^2 \quad /Fe} = -0.44V$;

$E_{Zn^2 \quad /Zn} = -0.76V$; $E_{Cu \ ^2/Cu} \quad 0.34V$

Based on this data, which of the following is the strongest reducing agent ?

(a) $Cu_{(s)}$ (b) $K_{(aq)}$
(c) $Zn^{2}_{(aq)}$ (d) $Fe_{(s)}$

67. Which of the following species is the strongest oxidizing agent ?

(a) $H_3O_{(aq)}$ (b) $Cu_{(s)}$
(c) $Cl^-_{(aq)}$ (d) $Zn_{(s)}$

68. A gas Y at 1 atm is passed through a solution containing a mixture of $1M\ X^-$ and $1\ M\ Z^-$. If the reduction potentials vary in the order $X > Y > Z$, then which of the following is correct ?

(a) both X^- and Z^- get oxidized
(b) Z^- is oxidized but not X^-
(c) Y is reduced but Z^- is not oxidized
(d) Y is reduced and X^- is oxidized

69. Given that $E_{Cl_2/Cl^-} \quad 1.36V$; $E_{I_2/I^-} \quad 0.54V$;

$E_{Fe^2 \quad /Fe} = -0.44V$, which of the following represents the correct sequence of reducing powers ?

(a) $Cl^- > I^- > Fe$ (b) $Fe > Cl^- > I^-$
(c) $Fe > I^- > Cl^-$ (d) $I^- > Fe > Cl^-$

70. A property which does not depend on the stoichiometry of the reaction in a cell, at a given temperature, is :

(a) ΔG
(b) ΔH
(c) electrical energy produced
(d) E_{cell}

71. EMF of an $H_2 - O_2$ fuel cell

(a) is independent of partial pressures of H_2 and O_2
(b) decreases on increasing P_{H_2} and P_{O_2}
(c) increases on increasing P_{H_2} and P_{O_2}
(d) varies with the concentration of OH^- ions in the cathodic and anodic compartments.

72. For the electrochemical cell, $M\,|\,M^+\,||\,X^-\,|\,X$,

($E_{M \quad /M} \quad 0.44V$ and $E_{X/X^-} \quad 0.33V$). From this data we can deduce that:

(a) $M + X \rightarrow M^+ \quad X^-$ is the spontaneous reaction
(b) $M^+ + X^- \rightarrow M \quad X$ is the spontaneous reaction
(c) $E^\circ_{cell} = 0.77\ V$
(d) $E^\circ_{cell} = -0.77\ V$

MARK YOUR RESPONSE	63. ⓐⓑⓒⓓ	64. ⓐⓑⓒⓓ	65. ⓐⓑⓒⓓ	66. ⓐⓑⓒⓓ	67. ⓐⓑⓒⓓ
	68. ⓐⓑⓒⓓ	69. ⓐⓑⓒⓓ	70. ⓐⓑⓒⓓ	71. ⓐⓑⓒⓓ	72. ⓐⓑⓒⓓ

73. The correct sequence of molar conductance of the following compounds

I. $K[Co(NH_3)_2(NO_2)_4]$

II. $[Cr(NH_3)_5(NO_2)]_3[Co(NO_2)_6]_2$

III. $[Cr(NH_3)_3(NO_2)_3]$

IV. $Mg[Cr(NH_3)(NO_2)_5]$

(a) $I < II < III < IV$ (b) $III < I < II < IV$

(c) $III < I < IV < II$ (d) $II < IV < I < III$

74. The density of a univalent metal X is 10.8 g cm^{-3}. Calculate the charge required to electroplate an area of 10^2 cm^2 of a metal to a thickness of 5×10^{-3} cm by electrolysing the solution of the metal nitrate with 96.5% current efficiency (At. wt. of $X = 108$)

(a) 4825 C (b) 9650 C

(c) 5000 C (d) 10,000 C

75. At certain temperature, the conductivity of pure water is $6.6 \times 10^{-8} ohm^{-1} cm^{-1}$. The ionic conductances of H^+ and OH^- ions at this temperature are 350 and 200 $ohm^{-1} cm^2 mol^{-1}$ respectively. The ionic product of water at this temperature is

(a) 1.01×10^{-14} (b) 1.2×10^{-14}

(c) 1.44×10^{-14} (d) 2.4×10^{-14}

76. Consider the cell : $Cu \mid Cu^{2+}(0.01M) \parallel Ag^+(0.1M) \mid Ag$. The e.m.f of the cell can be increased by

(a) exchanging the concentrations in the two half cells

(b) decreasing the concentrations to one tenth in each half cell

(c) making the concentrations 1.0 M of each side

(d) increasing the concentrations to ten times in each half cell

77. The e.m.f of the cell : Pt, H_2 (1 atm) | HA (0.01M) | | HCl (1.0 M) | H_2 (1 atm), Pt is 0.295 V. The dissociation constant of the acid HA is

(a) 1.0×10^{-4} (b) 1.0×10^{-6}

(c) 1.0×10^{-8} (d) 1.0×10^{-5}

78. The galvanic cell : Pt, H_2 (1 atm) | buffer | | H^+ (1.0 M) | H_2 (1 atm) Pt, shows e.m.f to be 0.296 V at 25°C. The mole ratio of the salt to monobasic acid ($pK_a = 4.699$) in the buffer is

(a) 1 : 2 (b) 2 : 1

(c) 1 : 5 (d) 5 : 1

79. Electrode potential of the half cell $Hg_{(\ell)}$, $Hg_2Cl_{2(s)} \mid Cl^-_{(aq)}$ can be increased by

(a) increasing $[Cl^-]$ (b) decreasing $[Cl^-]$

(c) increasing $Hg_2Cl_{2(s)}$ (d) decreasing $Hg_{(\ell)}$

80. The oxidation potential of H-electrodes set up in buffer solution of a weak acid HX and its salt NaX in the mole ratios of $x : y$ and $y : x$ are E_1 and E_2 volts respectively at 25°C. The pK_a value of the acid at 25°C is

(a) $\dfrac{E_1 + E_2}{0.059}$ (b) $\dfrac{E_1 - E_2}{0.118}$

(c) $\dfrac{E_2 - E_1}{0.118}$ (d) $\dfrac{E_1 + E_2}{0.118}$

81. Two hydrogen electrodes (1 atm, 25°C) are set up in equimolar solutions of weak bases $(BOH)_1$ and $(BOH)_2$ having pK_b values 3 and 5. If the solutions are joined internally through a salt bridge, the cell potential will be

(a) 0.118 V (b) 0.0295 V

(c) 0.059 V (d) None of these

82. The reduction potential of

$Cl_{2(g)}(10\,atm) \mid Cl^-_{(aq)}(1.0 \times 10^{-3}M)$ at 298 K is

$\left(E^\circ_{Cl_2/Cl^-} = 1.36V\right)$

(a) 1.20 V (b) 1.48 V

(c) 1.50 V (d) 1.57 V

MARK YOUR RESPONSE					
	73. ⓐⓑⓒⓓ	74. ⓐⓑⓒⓓ	75. ⓐⓑⓒⓓ	76. ⓐⓑⓒⓓ	77. ⓐⓑⓒⓓ
	78. ⓐⓑⓒⓓ	79. ⓐⓑⓒⓓ	80. ⓐⓑⓒⓓ	81. ⓐⓑⓒⓓ	82. ⓐⓑⓒⓓ

83. A galvanic cell is made up of two hydrogen electrodes, one of which is the standard one. In which of the following solution should the other electrode be set up to give the maximum e.m.f?

(a) $0.1\,M\ CH_3COOH$ (b) $0.1\,M\,HCl$

(c) $0.1\,M\ H_2SO_4$ (d) $0.1\,M\ NH_4OH$

84. Consider the following cells ;

I. $Pt,\ Cl_2\ (1atm)\,|\,Cl^-(0.1\,M)\,|\,Cl_2\,(2\,atm), Pt$

II. $Pt,\ Cl_2\ (1atm)\ |Cl^-(0.1\ M)\,||\ Cl^-(0.2\ M)\,|\ Cl_2\ (1\ atm), Pt$

The half cells acting as cathodes will be

(a) *I* - Left, *II* - Right (b) Left in both cases

(c) Right in both cases (d) *I*-Right, *II*-Left

85. Calculate the e.m.f of the cell

$Pt,\ H_2\ (1\ atm)\,|\,BOH\,(1.0\,M)\,||\,HA\,(0.1\,M)\,|\ H_2\ (1\ atm), Pt$

K_a for HA = 4×10^{-5} and K_b for BOH = 2.5×10^{-5}

(a) $0.266\,V$ (b) $-0.532\ V$

(c) $0.532\,V$ (d) $-0.024\ V$

86. A cell ; $Cu\,|\,Cu^{2+}(1\,L\ of\ 1.0\,M)\,||\,Ag^{+}(1\,L\ \ of\ 1.0\,M)\,|\,Ag$ operates for 1000 s; a steady current of 9.65 *A* is withdrawn. Then

(a) $[Cu^{2+}] = 1.1\,M,\ [Ag^{+}]\ = 0.9\,M$

(b) $[Cu^{2+}] = 1.05M,\ [Ag^{+}] = 0.9\,M$

(c) $[Cu^{2+}] = 0.95\,M,\ [Ag^{+}]\ = 1.1\,M$

(d) $[Cu^{2+}] = 0.90\,M,\ [Ag^{+}] = 1.1\,M$

87. The velocities of Ba^{2+} and Cl^- ions in an electric field of 50 *V* across a distance of 10 cm are *x* and *y* cm s^{-1} respectively. The molar ionic conductance of $BaCl_2$ is

(a) $96500\,(x+y)$ (b) $2\times96500\,(x+y)$

(c) $19300\,(x+y)$ (d) $38600\,(x+y)$

88. Find the standard cell potential involving the cell reaction

$$In^{2+} + Cu^{2+} \longrightarrow In^{3+} + Cu^{+}\text{, at 298 K}$$

Given :

$E^\circ_{Cu^{2+}/Cu^{+}} = x_1\,V;\ E^\circ_{In^{3+}/In^{+}} = x_2\,V;\ E^\circ_{In^{2+}/In^{+}} = x_3\,V$

(a) $x_1 + x_3 - x_2$ (b) $(x_1 + x_3 - 2x_2)/3$

(c) $x_1 + x_3 - 2x_2$ (d) $x_1 + x_3 + 2x_2$

89. In Q.88, the standard free energy for the reaction is (Given ; $x_1 = 0.15\ V, x_2 = -\ 0.42\ V, x_3 = -0.40\ V$)

(a) 0.59 kJ (b) -0.59 kJ

(c) $+0.59\times96.5$ kJ (d) -0.59×96.5 kJ

90. Predict whether the following reactions are feasible?

I. $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$;

$E^\circ_{Sn^{4+}/Sn^{2+}} = 0.10\,V,\ \ E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\,V$

II. $2Cu^{2+} \longrightarrow Cu^{+} + Cu;\ E^\circ_{Cu^{+}/Cu} = 0.52V,$

$E^\circ_{Cu^{2+}/Cu^{+}} = 0.15V$

(a) I only (b) II only

(c) I and II (d) None of these

91. A galvanic cell is set up from electrodes *A* and *B*

Electrode *A* : $Cr_2O_7^{2-}/Cr^{3+},\ E^\circ_{red} = +\,1.33\ V$

Electrode *B* : $Fe^{3+}/Fe^{2+},\ \ \ E^\circ_{red} = 0.77\ V$

Which of the following statements is false ?

(a) Standard e.m.f of the cell is 0.56 *V*

(b) Current will flow from electrode *A* to *B* in the external circuit

(c) *A* will act as cathode and have positive polarity

(d) None

MARK YOUR RESPONSE	83. ⓐⓑⓒⓓ	84. ⓐⓑⓒⓓ	85. ⓐⓑⓒⓓ	86. ⓐⓑⓒⓓ	87. ⓐⓑⓒⓓ
	88. ⓐⓑⓒⓓ	89. ⓐⓑⓒⓓ	90. ⓐⓑⓒⓓ	91. ⓐⓑⓒⓓ	

92. Given : $2Br^- \rightarrow Br_2 + 2e^-$ $E^\circ = -1.09\,V$;

$I_2 + 2e^- \rightarrow 2I^-$ $E^\circ = 0.54\,V$

$Fe^{2+} + 2e \rightarrow Fe$ $E^\circ = -0.44\,V$

Which of the following reactions will not be spontaneous?

(a) $Fe + Br_2 \rightarrow FeBr_2$ (b) $Fe + I_2 \rightarrow FeI_2$

(c) $I_2 + 2Br^- \rightarrow 2I^- + Br_2$

(d) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

93. The characterististics of a reversible cell are :

(a) When the applied emf from external source is exactly equal to that of the cell, the chemical reaction going on in cell will stop

(b) If the applied emf is slightly more than the actual emf of the cell, the current will begin to flow in the opposite direction and the cell reaction is reversed

(c) If the applied emf is slighlty less than the actual emf of the cell, a current flows from the cell which is proportional to the chemical change occuring in the cell.

(d) All the above are correct.

94. At 25°C, the emf of the cell Pb | $PbCl_2$ (*s*) ; HCl (1 *M*) |AgCl(*s*) | Ag is 0.49 V and temperature coefficient $\left(\frac{\partial E}{\partial T}\right) = 1.84 \times 10^{-4}$ Volt/degree. The entropy change when one gram mole of silver is deposited is

[Given 1 Cal. = 4.2J].

(a) + 4.14 Cal | degree (b) + 1.44 Cal | degree

(c) − 4.14 Cal | degree (d) − 1.44 Cal | degree

95. The cell potential of the following concentration cell was found to be 0.029 V

$$Hg(\ell)\left|\begin{matrix}\frac{N}{20}\text{Mercurous nitrate}\\ \text{in}\frac{N}{10}\text{nitric acid}\end{matrix}\right|\left|\begin{matrix}\frac{N}{2}\text{Mercurous nitrate}\\ \text{in}\frac{N}{10}\text{nitric acid}\end{matrix}\right|Hg(\ell)$$

The valency of mercurous ion is

(a) +1 (b) +2

(c) either + 1or +2 (d) none of these

96. Select the correct statement

(a) (E) Efficiency of a fuel cell is given by the equation

$$E = \frac{\Delta G}{\Delta H} \times 100$$

(b) The efficiency (E) for H_2/O_2 fuel cell is 83%.

(c) The efficiency of H_2/O_2 fuel cell depends upon temperature at which it works

(d) All the above are correct

97. In anodising :

(a) The metal ion present in electrodyte gets reduced and a film of metal gets coated on the surface of metal cathode

(b) The anode metal gets oxidised to form a metal oxide coat

(c) both the above are correct

(d) none of the above is correct

98. For hydrogen-oxygen fuel cell, the cell reaction is

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(\ell)$$

If $\Delta G_f^\circ(H_2O) = -237.2\ \text{kJ mol}^{-1}$, then emf of this cell is

(a) +2.46 V (b) −2.46 V

(c) + 1.23 V (d) − 1.23 V

MARK YOUR RESPONSE	92. ⓐⓑⓒⓓ	93. ⓐⓑⓒⓓ	94. ⓐⓑⓒⓓ	95. ⓐⓑⓒⓓ	96. ⓐⓑⓒⓓ
	97. ⓐⓑⓒⓓ	98. ⓐⓑⓒⓓ			

B

COMPREHENSION TYPE

This section contains groups of questions. Each group is followed by some multiple choice questions based on a paragraph. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct.

PASSAGE-1

A fuel cell is the device to convert the energy of a fuel into electrical energy without the use of heat engine. Such conversions are possible because the combustion reactions are essentially redox reactions. Electrical energy can be obtained indefinitely from a fuel cell as along as the outside supply of fuel is maintained. The essential components of hydrogen-oxygen fuel cell are detailed in the figure below.

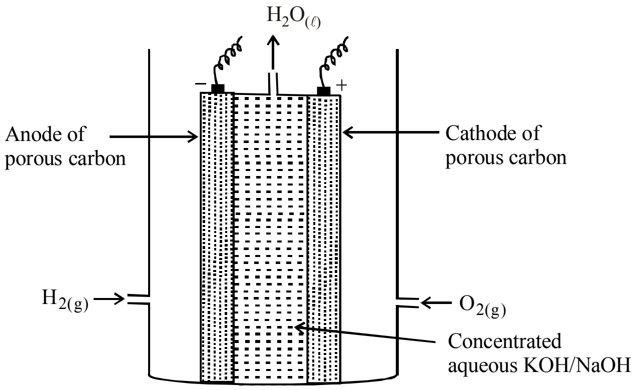


Figure - 1

It is seen from the figure that hydrogen and oxygen gases are supplied to the cell. Hydrogen molecules supplied at the anode undergo oxidation in presence of metal catalyst. The hydrogen ions migrate through the electrode while the electrons travel through the external circuit. At the cathode the electrons and hydrogen ions combine with O_2 molecules to form water. The following half reactions take place at anode and cathode.

Anode : $2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(\ell)} + 4e^-$

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

Overall reaction : $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$

The overall reaction has a value of $\Delta H^\circ = -285.8$ kJ mol^{-1} and $\Delta G^\circ = -237.39$ kJ mol^{-1} at 25°C.

1. If the cell voltage of hydrogen-oxygen fuel cell is 1.23V, and the potential for the half cell reaction is as indicated,

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}\ E^\circ = 0.40\text{ V}$$

what is E° for the half reaction

$$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$$

(a) 0.41V (b) 0.83 V
(c) −0.41 V (d) −0.83 V

2. Which of the following expressions gives ΔG° for the reaction in the fuel cell?

(a) $4 \times 96500 \times 1.23$ J
(b) $-4 \times 96500 \times 1.23$ J
(c) $-8.314 \times 298 \ln 1.23$ J
(d) $8.314 \times 298 \times \ln 286$ J

3. How many litres of gaseous H_2, when combined with excess O_2 in the fuel cell at 25° C and 1.00 atm, are needed to produce 23.7 kJ of work under ideal conditions?

(a) 2.5 L (b) 4.0 L
(c) 5.0 L (d) 7.0 L

4. Suppose the concentration of hydroxide ion in the cell is doubled. The cell voltage will be

(a) reduced by half
(b) increased by a factor of 2
(c) increased by a factor of 4
(d) unchanged

5. What is the approximate value of ΔS° for the fuel cell reaction at 25°C

(a) −1600 JK^{-1} (b) −160 JK^{-1}
(c) 160 JK^{-1} (d) 1600 JK^{-1}

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

6. The theoretical efficiency of the fuel cell is given by

(a) $\dfrac{(-2)(96500\ \text{C mol}^{-1})\times(1.23\text{V})\times 100}{-285.8\times 10^{3}\ \text{J mol}^{-1}}$

(b) $\dfrac{(2)(96500\ \text{C mol}^{-1})\times(1.23\text{V})\times 100}{-285.8\times 10^{3}\ \text{J mol}^{-1}}$

(c) $\dfrac{(-2)(96500\,\text{C mol}^{-1})\times 100}{-285.8\times 10^{3}\ \text{J mol}^{-1}}$

(d) $\dfrac{(-4)(96500\,\text{C mol}^{-1})(1.23\text{V})\times 100}{-285.8\times 10^{3}\ \text{J mol}^{-1}}$

PASSAGE-2

Experiment - 1 : One student was presented with a solution of KI and KCl of unknown concentration. In order to determine the concentration of each soluble salt, she titrated the solution with $AgNO_3$, using an electrode to measure the change in the electrode potential as $AgNO_3$ was added. The data she obtained is shown in Figure- 2

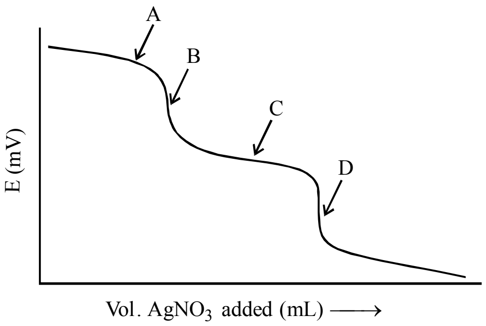


Fig. 2 Electron Potential for Addition of Tirant

Not knowing which endpoint belonged to KI and which to KCl, the student consulted a table of solubility constants, shown in Table- 2

Compound	**Ksp**
AgI	8.3×10^{-17}
AgBr	5.0×10^{-13}
AgCl	1.8×10^{-10}

Experiment – 2 : Another student performed a titration of a solution of KCl, but had no way of measuring the current in the solution. Consequently, he had no way of knowing if he had reached the endpoint. In order to determine concentration of KCl, he used a titration method known as the Volhard titration . First, he titrated the solution of KCl with $AgNO_3$ excess and filtered out the solid precipitate. He then titrated the solution with KSCN in the presence of Fe(III). The solution turned red when the endpoint was reached.

7. At what point in Figure 2 does the silver chloride begin to precipitate out of solution ?

(a) Point *A* (b) Point *B*

(c) Point *C* (d) Point *D*

8. In experiment 1, what is true regarding the quantities of I^- and Cl^- in solution at point *A* ?

(a) I^- is in large excess and Cl^- is unchanged from the start of the reaction

(b) Cl^- is in large excess and I^- is unchanged from the start of the reaction

(c) I^- is in small excess and Cl^- is unchanged from the start of the reaction

(d) Cl^- is in small excess and I^- is unchanged from the start of the reaction

9. How would figure-2 change if KBr were present in the mixture, in addition to KI and KCl ?

(a) A third endpoint would appear before point *A*

(b) A third endpoint would appear between point *B* and point *D*

(c) A third endpoint would appear after point *D*

(d) A third endpoint would appear, but its location cannot be determined from the information given

10. In Experiment 1, how can the concentration of the second precipitant be determined ?

(a) Calculate the number of moles of $AgNO_3$ added at point *D* and divide by the volume of the original solution

(b) Calculate the number of moles of $AgNO_3$ added at point *C* and divide by the volume of the original solution

(c) Calculate the number of moles of $AgNO_3$ added between point *B* and *D* and divide by the volume of the original solution

(d) Calculate the number of moles of $AgNO_3$ added between point *A* and *C* and divide by the volume of the original solution

MARK YOUR RESPONSE	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ

11. In the Volhard titration, what causes the red color?

(a) Formation of $FeSCN^{2+}$

(b) Formation of $Fe(NO_3)_3$

(c) Formation of AgSCN

(d) Formation of $FeCl_3$

12. The student performed a titration of KI with $AgNO_3$, and found that the endpoint of the titration was about 0.4% lower than in the titration of the mixture of KCl and KI. Which of the following best explains this observation?

(a) The mixture was saturated with other ions, so AgI precipitated more quickly than if no other ions were present.

(b) Small amount of AgCl began to precipitate, even though its solubility product had not yet been exceeded.

(c) Some Cl^- remained after the solubility product of AgCl had been exceeded, and AgCl continued to precipitate in small amount with KI

(d) The mixture was saturated with other ions, so $AgNO_3$ did not dissociate, preventing Ag^+ from association with.

PASSAGE-3

Billions of dollars are spent each year to replace or prevent the corrosion and subsequent destruction of government property such as ships, bridges, and metallic piping. Corrosion may result in decreased structural integrity and eventual ineffectuality. For example, a naval ship made from iron is highly susceptible to corrosion. One part of the hull acts as the anode, while another acts as the cathode, the iron hull itself connects the two parts, completing the circuit. Part of the metal hull begins oxidizing to Fe^{2+} in the presence of H_2O and O_2, the reduction reaction proceeds with an $E_{red} = 1.229V$. It is there that Fe^{2+} ions migrate from the anode and are further oxidized according to the Equation 1:

$$2Fe^{2+}_{(aq)} + \frac{1}{2}O_{2(g)} + (6+x)H_2O_{(l)} \longrightarrow Fe_2O_3.xH_2O + 4H_3O^+_{(aq)}$$

Equation – 1

The Fe_2O_3, or rust, formed is only a small part of the problem. Pitting, or loss of solid metal, weaken the structure of the hull and may lead to serious damage and destruction of the hull.

Using a sacrificial anode often successfully prevents corrosion. This metal, more easily oxidized than iron. Although the sacrificial anode eventually corrodes as well, the cost of replacing it is far less than that of replacing the iron hull.

Half Reation	Potential
$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$	$E° = 1.229\,V$
$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$	$E° = 0.771\,V$
$Cu^+ + e^- \rightleftharpoons Cu$	$E° = 0.521\,V$
$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^-$	$E° = 0.401\,V$
$Cu^{2+} + 2e^- \rightleftharpoons Cu$	$E° = 0.342\,V$
$Pb^{2+} + 2e^- \rightleftharpoons Pb$	$E° = -0.126\,V$
$Fe^{2+} + 2e^- \rightleftharpoons Fe$	$E° = -0.447\,V$
$Mn^{2+} + 2e^- \rightleftharpoons Mn$	$E° = -1.185\,V$
$Mg^{2+} + 2e^- \rightleftharpoons Mg$	$E° = -2.372\,V$

Table 3

13. Which of the following reactions may occur at the anode of the iron hull ?

(a) $Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-$

(b) $Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$

(c) $\frac{1}{2}O_{2(g)} + 2H_3O^+_{(aq)} + 2e^- \longrightarrow 3H_2O_{(l)}$

(d) $2H_2O_{(l)} \longrightarrow 2OH^-_{(aq)} + H_{2(g)} + 2e^-$

14. What is the standard voltage generated by the corrosion reaction on the iron hull of a ship ?

(a) $-1.676\,V$ (b) $-0.782\,V$

(c) $1.782\,V$ (d) $1.676\,V$

15. Which of the following materials can *not* serve as a sacrificial anode for lead?

(a) Copper (b) Iron

(c) Magnesium (d) Manganese

MARK YOUR RESPONSE	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ

16. An ammeter reading shows a current of 0.50 A running through the iron hull. How many grams of Fe (s) are lost in 1.0 hour?

(a) 261 mg (b) 521 mg

(c) 1041 mg (d) 2084 mg

17. A ship that has sunk to the bottom of the ocean may still exhibit corrosion. One difference in the corrosion reaction between a ship above water and one that has sunk of the bottom of the ocean may be that

(a) the oxidation reaction of the sunken ship does not include H_2O as a reactant

(b) the oxidation reaction of the sunken ship does not include O_2 as a reactant

(c) the reduction reaction of the sunken ship does not include H_2O as a reactant

(d) the reduction reaction of the sunken ship does not include O_2 as a reactant

18. If a solid iron bar were placed in pure water, the addition of which of the following solutes to water would most increase the amount of solid iron lost by corrosion ? (note all compounds listed have roughly the same solubility)

(a) PbF_2 (b) CuBr

(c) $PbSO_4$ (d) $AgIO_3$

PASSAGE-4

Below is a table showing some Standard State Reduction Potentials.

Half reaction	**E(V)**
$F_2 + 2e^- \rightarrow 2F^-$	2.87
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09
$Ag^+ + e^- \rightarrow Ag$	0.80
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Pb^{2+} + 2e^- \rightarrow Pb$	–0.13
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.25
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$Na^+ + e^- \rightarrow Na$	–2.71

19. What should happen when a piece of copper is placed in 1*M* HCl?

(a) The copper is dissolved by the acid

(b) The copper is dissolved by the acid with the release of hydrogen gas

(c) The copper bursts into greenish flames

(d) Nothing happens

20. What should happen when a piece of lead is placed in 1*M* HCl?

(a) The lead is dissolved by the acid

(b) The lead begins to dissolve with the release of hydrogen gas

(c) The lead bursts into flames

(d) Nothing happens

21. Suppose that the half-cell reaction $Ni^{2+} + 2e^- \rightarrow Ni$ is assigned to have a potential of 0.00 *V*. The standard reduction potential for the reduction of Br_2 would be?

(a) 1.34 *V* (b) 0.84*V*

(c) 1.09 *V* (d) 1.25 *V*

22. A voltaic cell is set up with F_2 / F^- as one half cell and Br_2 / Br^- as the other, what is the voltage of the cell at standard state?

(a) 3.96 *V* (b) 1.78 *V*

(c) 1.09 *V* (d) 2.87 *V*

23. NaCl is melted in a beaker and electrolysis carried out. What is the minimum potential difference required to separate sodium and chlorine?

(a) –4.07 *V* (b) –1.36 *V*

(c) 1.36 *V* (d) 4.07 *V*

24. If standard state oxidation potentials are used instead of standard state reduction potentials and the half reactions are listed in descending order, which one of the following would be true?

(a) the lead reaction would be above the silver reaction

(b) the fluorine reaction would be above the chlorine reaction

(c) the iron reaction would be above the nickel reaction

(d) the hydrogen reaction would be below the copper reaction

MARK YOUR RESPONSE	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ
	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ	24. ⓐⓑⓒⓓ	

PASSAGE-5

The solubility of AgCl (sparingly soluble salt) in water can be determined by setting up following cell.

$$\mathrm{Ag}\left|\begin{array}{l}\mathrm{AgCl},0.01M\ \mathrm{KCl}\\ \left[\mathrm{Ag}^+\right]=c\end{array}\right\|\begin{array}{l}0.01M\ \mathrm{AgNO_3}\\ \left[\mathrm{Ag}^+\right]=0.01\end{array}\left|\mathrm{Ag}\right.$$

To set up this cell one of the silver electrodes is placed in $0.01M$ solution of $AgNO_3$ and another silver electrode is placed in contact with $0.01M$ KCl solution. The electrodes are separated by means of a salt bridge of NH_4NO_3. A drop of $AgNO_3$ solution is added to KCl solution. The small amount of AgCl formed is sufficient to give a saturated solution of AgCl.

The above concentration cell is reversible with respect to Ag^+ ion and its EMF at 25°C is given by

$$E = 0.0591 \log \frac{0.01}{C}$$

Where C is the unknown concentration of silver ions given by silver chloride.

The solubility product, $K_{(AgCl)} = C \times 0.01$ and the solubility of AgCl (s) is given by

$$S = \sqrt{K_{AgCl}}$$

25. What is the solubility of AgCl if EMF of the following cell is 0.1182 V.?

Ag |Saturated AgCl solution (C_1) || $0.001M$ Ag $NO_3(C_2)$ |Ag

(a) 10^{-3} mole/litre (b) 10^{-4} mole/litre]

(c) 10^{-5} mole/litre (d) 10^{-6} mole/litre

26. What will be the EMF of the following concentration cell at 25° C?

Ag |0.001 M Ag NO_3 || 0.1 M Ag NO_3 | Ag

(Assume that the activities of Ag^+ in two solutions is equal to concentration)

(a) 0.01182 V (b) 0.1182 V

(c) 1.182 V (d) can't predict

27. What will be solubility product of AgCl if the EMF of the following cell is 0.45 V at 25°C

Ag |$0.1M$ Ag NO_3 || Saturated NH_4NO_3 |AgCl in $0.1M$ KCl |Ag

[In it $0.1M$ KCl is 85 % dissociated and $0.1M$ Ag NO_3 is 82 % dissociated]

(a) 1.7×10^{-10} (b) 2.0×10^{-10}

(c) 1.7×10^{-9} (d) 2.0×10^{-9}

PASSAGE-6

Consider a cell which operates revesibly at constant temperature and pressure. The electrical work done by the system per mole of reactant consumed (i.e electrical energy supplied by the cell) is nFE, where n is the number of electrons liberated at one electrode or valency of the metal, F is Faraday (i.e. 96500 coulombs) and E is the emf of the cell. At the same time free energy of the system decreases by an amount ΔG. Therefore

$$-\Delta G = nFE$$

Also $\Delta G = \Delta H + T\left\{\frac{\partial(\Delta G)}{\partial T}\right\}_P$ ... (Gibbs-Helmholtz equn.)

From the above two equations, we see

$$nFE = -\Delta H + nFT\left\{\frac{\partial E}{\partial T}\right\}_P$$

This equation gives heat of chemical reaction occurring within the cell as a function of EMF and temperature.

$\left\{\frac{\partial E}{\partial T}\right\}_P$ is known as temperature coefficient of the cell.

28. The voltage of the cell, Pb | Pb $SO_{4(S)}$, Na_2 $SO_4.10H_2O$ (Aq); $Hg_2SO_{4(s)}$|Hg is +0.9647 volt at 25°C and the temperature coefficient of the emf is + 0.000 174 volt per degree. The heat of the reaction at 25°C is

(a) 2370 Cal (b) – 42 100 Cal

(c) – 44470 Cal (d) none of these

29. At 25° the values of E for the reversible cells, Pb | $PbCl_2$(s) $KCl_{(aq)}$, AgCl (s) | Ag and Pb | Pb I_2 (s), $KI_{(aq)}$; Ag I (s) | Ag are 0.4902 V and 0.2111V, and the values of $\left(\frac{\partial E}{\partial T}\right)_p$ are – 0.000186 volt degree $^{-1}$and –0.000127 volt degree $^{-1}$ respectively. In both cases, the silver electrode is the positive pole of the cell. The ΔH in calories at 25°C for the reaction

$$PbI_2(s) + 2AgCl(s) + \rightleftharpoons PbCl_2(s) + 2AgI(s) \text{ is}$$

(a) – 25160 Cal (b) 11480 Cal

(c) – 13680 Cal (d) – 11480 Cal.

30. The EMF of Daniels's cell at 15°C is 1.0934 volt and temperature coeffficeint of emf is – 4.29×10^{-4} Volt/degree. The heat of reaction for the cell is

(a) – 56187 Cal (b) + 44702 Cal

(c) – 47402 Cal (d) + 56187 Cal

MARK YOUR RESPONSE	25. ⓐⓑⓒⓓ	26. ⓐⓑⓒⓓ	27. ⓐⓑⓒⓓ	28. ⓐⓑⓒⓓ	29. ⓐⓑⓒⓓ
	30. ⓐⓑⓒⓓ				

C

REASONING TYPE

In the following questions two Statement-1 (Assertion) and Statement-2 (Reason) are provided. Each question has 4 choices (a), (b), (c) and (d) for its answer, out of which ONLY ONE is correct. Mark your responses from the following options:

(a) Both Statement-1 and Statement-2 are true and Statement-2 is the correct explanation of Statement-1.
(b) Both Statement-1 and Statement-2 are true and Statement-2 is not the correct explanation of Statement-1.
(c) Statement-1 is true but Statement-2 is false.
(d) Statement-1 is false but Statement-2 is true.

1. Statement-1 : Specific conductance decreases with dilution whereas equivalent conductance increases.
Statement-2 : On dilution, number of ions per millilitre decreases but total number of ions increases considerably.

2. Statement-1 : When acidified zinc sulphate solution is electrolysed between zinc electrodes, it is zinc that is deposited at the cathode and hydrogen evolution does not take place.
Statement-2 : The electrode potential of zinc is more negative than hydrogen but the overvoltage for the hydrogen evolution on zinc is quite large.

3. Statement-1 : Conductivity of solutions of different electrolytes in the same solvent and at a given temperature is same.
Statement-2 : The conductivity depends on the charge and size of the ions in which they dissociate, the concentration of ions or ease with which the ions move under potential gradient.

4. Statement-1 : Sodium ions are discharged in preference to hydrogen ions at a mercury cathode.
Statement-2 : Na^+ is a strong reducing agent in comparison to H^+ ion.

5. Statement-1 : Conductivity of metals decreases with increase of temperature whereas that of electrolytic solution increases.
Statement-2 : Electrons in metals are very tightly held by the nucleus and are not free to move.

6. Statement-1 : An electrochemical cell can be set up only if the redox reaction is spontaneous.
Statement-2 : A reaction is spontaneous if free energy change is negative.

7. Statement-1 : If $\lambda^o_{Na^+}$ and $\lambda^o_{Cl^-}$ are molar limiting conductivity of sodium and chloride ions respectively, then the limiting molar conductivity for sodium chloride is given by the equation : $\Lambda^o_{NaCl} = \lambda^o_{Na^+} + \lambda^o_{Cl^-}$
Statement-2 : This is according to Kohlrausch law of independent migration of ions.

8. Statement-1 : During electrolysis of $CuSO_4(aq)$ using copper electrodes, copper is dissolved at anode and deposited at cathode.
Statement-2 : Oxidation takes place at anode and reduction at cathode.

9. Statement-1 : For a cell reaction $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$; at equilibrium, voltmeter gives zero reading.
Statement-2 : At the equilibrium, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions.

10. Statement-1 : In Daniel cell if concentrations of Cu^{2+} and Zn^{2+} ions are doubled, the EMF of the cell does not change.
Statement-2 : If the concentration of ions in contact with the metal is doubled, the electrode potential will be doubled.

11. Statement-1 : In a dry cell zinc acts as cathode and carbon rod as anode.
Statement-2 : A dry cell has a potential of nearly 1.5 V.

12. Statement-1 : $KCl/NaCl/NH_4Cl$ etc. cannot be used in the salt bridge of a cell containing silver.
Statement-2 : A salt bridge contains concentrated solution of an inert electrolyte like KCl, KNO_3, NH_4NO_3 etc. or solidified solution of such an electrolyte in agar-agar and gelatine.

13. Statement-1 : Production of electricity by thermal plants is a very efficient method.
Statement-2 : In thermal plants, the chemical energy (heat of combustion) of fossil fuels (coal, gas or oil) is used to produce electricity.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ
	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ		

14. **Statement -1** : $H_2 - O_2$ fuel cell gives a constant voltage throughout its life.

Statement -2 : In this fuel cell, H_2 reacts with OH^- ions yet the overall concentration of OH^- ions does not change.

15. **Statement -1** : Identification of cathode and anode is done by the use of a ammeter.

Statement -2 : Higher is the value of reduction potential, greater would be its reducing power.

16. **Statement -1** : The emf of a cell is expressed as cell constant

Statement -2 : Cell constant can be determined by using saturated KCl solution

17. **Statement -1** : For an electrolytic cell the value of E°_{cell} is negative

Statement -2 : For an electrolytic cell the value of ΔG° is possitive

18. **Statement -1** : When $1M\,CuSO_4$ (aq) solution is electrolysed using copper electrodes, copper is dissolved at anode and copper gets deposited at cathode.

Statement -2 : The standard oxidation potential of copper is less than the standard oxidation potential of water and standard reduction potential of copper is greater than the standard reduction potential of water.

19. **Statement -1** : In case of weak electrolytes, the molar conductivity increases with decrease in concentration of the solution.

Statement -2 : On dilution there occurs a decrease in number of ions present per unit volume.

MARK YOUR RESPONSE	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ
	19. ⓐⓑⓒⓓ				

D MULTIPLE CORRECT CHOICE TYPE

Each of these questions has 4 choices (a), (b), (c) and (d) for its answer, out of which ONE OR MORE is/are correct.

1. During conductance measurement of an electrolyte (based upon Wheatstone bridge principle), alternating current is used because direct current leads to the complications :
(a) Polymerization
(b) Ionization
(c) Electrolysis resulting in the change of concentration and in consequence the resistance
(d) Polarisation at the electrodes resulting in the change of resistance.

2. For a solution of an electrolyte at a particular concentration and temperature, which of the following is not the function of cell constant ?
(a) specific conductance
(b) molar conductance
(c) equivalent conductance
(d) conductance

3. The correct sequence of ionic radii (r's) and ionic conductance (λ's) of the hydrated ions $Li^+_{(aq)}$, $Na^+_{(aq)}$ and $K^+_{(aq)}$ is / are :
(a) $r_{Li^+} < r_{Na^+} < r_{K^+}$
(b) $r_{Li^+} > r_{Na^+} > r_{K^+}$
(c) $\lambda_{Li^+} > \lambda_{Na^+} > \lambda_{K^+}$
(d) $\lambda_{Li^+} < \lambda_{Na^+} < \lambda_{K^+}$

4. On passing 0.5 mole of electrons through $CuSO_4$ and $Hg_2(NO_3)_2$ solutions in series using inert electrodes:
(a) 0.5 mol of Cu deposited
(b) 0.5 mol of Hg deposited
(c) 0.125 mol of O_2 produced in each solution
(d) 0.5 mol of O_2 produced in each solution

5. If same quantity of electricity is passed through three electrolytic cells containing $FeSO_4$, $Fe_2(SO_4)_3$, and $Fe(NO_3)_3$, then
(a) The amounts of iron deposited in $FeSO_4$ and $Fe_2(SO_4)_3$ are equal
(b) The amount of iron deposited in $FeSO_4$ is 1.5 times of the amount of iron deposited in $Fe(NO_3)_3$
(c) The amounts of iron deposited in $Fe_2(SO_4)_3$ and $Fe(NO_3)_3$ are equal
(d) The same amount of gas is evolved in all three cases at the anode.

MARK YOUR RESPONSE	1. ⓐⓑⓒⓓ	2. ⓐⓑⓒⓓ	3. ⓐⓑⓒⓓ	4. ⓐⓑⓒⓓ	5. ⓐⓑⓒⓓ

6. H_2 and O_2 gases will evolve at the cathode and anode respectively during the electrolysis of aqueous solutions of :

(a) KNO_3, Pt electrodes

(b) $AgNO_3$, Ag electrodes

(c) $CuSO_4$, Cu electrodes

(d) Na_2SO_4, inert electrodes

7. Which is/are true about the salt bridge ?

(a) Any salt can be employed to construct the salt bridge

(b) Only salts containing cation and ion having equal ionic mobilities can be employed

(c) During the operation of cell, anions of the salt rush into the anodic half cell and cations into the cathodic half cell to maintain the electrical neutrality of the two solutions

(d) Salt bridge gives rise to liquid-liquid junction potential.

8. Which of the following changes will cause the free energy of the cell reaction to decrease :

$$\text{Zn} \mid \text{ZnSO}_{4(aq)}(x_1M) \parallel \text{HCl}_{(aq)}(x_2M) \mid \text{H}_{2(g)}, \text{Pt}$$

(a) Increase in the volume of HCl solution from 100 ml to 200 ml

(b) Increase in pressure of hydrogen from 1 atm to 2 atm

(c) Increase in molarity x_2 from 0.1 to 1 M

(d) Decrease in molarity x_1 from 1M to 0.1 M

9. If 90g of water is electrolysed completely with 50% current efficiency

(a) 10 Faraday of electricity will be consumed

(b) 20 Faraday of electricity will be consumed

(c) 168 L (STP) of gases will be produced

(d) 84 L (STP) of gases will be produced.

10. In order to obtain more useful work from the electrochemical cell :

$$\text{Zn}_{(s)} \mid \text{Zn}^{2}_{(aq)}(1.0M) \parallel \text{Cu}^{2}_{(aq)}(1.0M) \mid \text{Cu}_{(s)} \text{ one should :}$$

(a) increase both $[Zn^{2+}]$ and $[Cu^{2+}]$ to 2.0 M

(b) decrease $[Zn^{2+}]$ to 0.1 M

(c) increase $[Cu^{2+}]$ to 2.0 M

(d) reduce both $[Zn^{2+}]$ and $[Cu^{2+}]$ to 0.1 M

11. Which of the following cells give the cell potentials to be their standard values ?

(a) $\text{Zn}_{(s)} \mid \text{Zn}^{2}_{(aq)}(0.01M) \parallel \text{H}_3\text{O}_{(aq)}(0.1M) \mid \text{H}_{2(g)}(1\text{atm}), \text{Pt}$

(b) $\text{Cu}_{(s)} \mid \text{Cu}^{2}_{(aq)}(0.25M) \parallel \text{Ag}_{(aq)}(0.5M) \mid \text{Ag}$

(c) $\text{Cd}_{(s)} \mid \text{Cd}^{2}_{(aq)}(0.01M) \parallel \text{pH} \quad 1 \mid \text{H}_{2(g)}(1\text{atm}), \text{Pt}$

(d) $\text{Zn}_{(s)} \mid \text{Zn}^{2}_{(aq)}(0.1M) \parallel \text{pH} \quad 1 \mid \text{H}_{2(g)}(1\text{atm}), \text{Pt}$

12. For the galvanic cell :

$\text{Al}_{(s)} \mid \text{Al}^{3}_{(aq)}(0.1M) \parallel \text{Ag}_{(aq)}(0.1M) \mid \text{Ag}_{(s)}$, which of the following is/are correct ?

(a) Reaction quotient $Q = 1.0 \times 10^{-2}$

(b) $\log_{10}Q = 2$

(c) $Q = 1.0 \times 10^3$

(d) $Q = 1.0 \times 10^2$

13. During the working of a galvanic cell and with the passage of time :

(a) spontaneity of the cell reaction decreases, E_{cell} decreases

(b) Reaction quotient Q decreases, E_{cell} increases

(c) Reaction quotient Q increases, E_{cell} decreases

(d) At equilibrium, $Q = K_e$, $E_{cell} = 0$

14. Which of the following is/are concentration cell(s) ?

(a) $\underset{\text{molality } m_1}{\text{Pb (Hg)}} \mid \text{Pb}^{2}_{(aq)} \mid \underset{\text{molality } m_2}{\text{Pb (Hg)}}$

(b) Pt, H_2(1 atm) | HCl | Cl_2(1 atm), Pt

(c) Pt, H_2(2atm) | HCl | H_2(1atm), Pt

(d) $\text{Ag}_{(s)}, \text{AgCl}_{(s)} \mid \underset{m_1}{\text{KCl}} \parallel \underset{m_2}{\text{KCl}} \mid \text{AgCl}_{(s)}, \text{Ag}_{(s)}$

15. Which of the following expression(s) represent the voltage of cell at 298 K :

$$\text{Ag}_{(s)} \mid \underset{\substack{\text{Saturated (1)}\\ \text{solution}}}{\text{AgI}} \parallel \underset{\substack{\text{Saturated (2)}\\ \text{solution}}}{\text{Ag}_2\text{C}_2\text{O}_4} \mid \text{Ag}_{(s)}$$

(a) $E_{cell} \quad 0.0592 \log \dfrac{[\text{Ag} \quad]_1}{[\text{Ag} \quad]_2}$

(b) $E_{cell} \quad 0.0592 \log \dfrac{[\text{Ag} \quad]_2}{[\text{Ag} \quad]_1}$

(c) $E_{cell} \quad 0.0592 \log \dfrac{K_{sp}(\text{Ag}_2\text{C}_2\text{O}_4)}{K_{sp}(\text{AgI})}$

(d) $E_{cell} \quad 0.0592 \log \dfrac{[2K_{sp}(\text{Ag}_2\text{C}_2\text{O}_4)]^{1/3}}{[K_{sp}(\text{AgI})]^{1/2}}$

MARK YOUR RESPONSE	6. ⓐⓑⓒⓓ	7. ⓐⓑⓒⓓ	8. ⓐⓑⓒⓓ	9. ⓐⓑⓒⓓ	10. ⓐⓑⓒⓓ
	11. ⓐⓑⓒⓓ	12. ⓐⓑⓒⓓ	13. ⓐⓑⓒⓓ	14. ⓐⓑⓒⓓ	15. ⓐⓑⓒⓓ

16. Consider the cell :

$Ag_{(s)} \mid AgCl(\text{saturated solution}) \parallel AgNO_{3(aq)}(1.0M) \mid Ag_{(s)}$

EMF of the above cell is given by

$(K_{sp} \text{ of } AgCl = 1.0 \times 10^{-10} M^2)$

(a) $E_{cell} = E^{\circ}_{Ag} + 0.0592 \log[K_{sp}(AgCl)]^{1/2}$

(b) $E_{cell} = 0.0592 \log \dfrac{1}{[K_{sp}(AgCl)]^{1/2}}$

(c) $E_{cell} = 0.0592 \times 5\ V$

(d) $E_{cell} = 296\ mV$

17. During the working of the cell

$Pb - Hg\,(1.0\text{ M}) \mid Pb^{2+}_{(aq)}(1M) \parallel Pb^{2+}_{(aq)}(1M) \mid Pb - Hg(0.5M)$

(a) $[Pb^{2+}]$ in right half cell decreases
(b) $[Pb^{2+}]$ in left half cell decreases
(c) $[Pb^{2+}]$ does not change in either of the half cells
(d) Molality of lead amalgam in right half cell increases while that of left half cell decreases

18. Consider the cell : Ag (s), AgCl (s) | KCl (1.0 M) | $Hg_2Cl_{2(s)}, Hg_{(\ell)}$

The cell potential

(a) increases on increasing concentration of Cl^- ions
(b) decreases on decreasing concentration of Cl^- ions
(c) is independent of concentration of Cl^- ions
(d) is independent of amounts of AgCl and Hg_2Cl_2

19. Choose the correct statement

(a) The normal calomel electrode contains electrolyte solution that is 1.0 N in KCl.
(b) The standard calomel electrode contains electrolyte solution that is saturated with KCl.
(c) The standard reference potential of normal calomel electrode is 0.3356 V.
(d) The standard refrence potential of normal calomel electrode is 0.2415 V.

20. Choose the correct statements (s)

(a) $\text{Cell constant} = \dfrac{\text{specific conductivity}}{\text{observed conductivity}}$

(b) Equivalent conductivity = observed conductivity × cell constant × volume in cc containing 1 g -equivalent of electrolyte

(c) Conductivity water is obtained by redistilling water from an alkaline solution of $KMnO_4$. The distillate which is condensed in platinum black tin condenser is known as conductivity water

(d) Molecular conductivity = Equivalent conductivity × Number of equivalents per mole of an electrolyte.

21. Select the correct statements

(a) Ostwald first showed the applicability of law of mass action to solution of weak electrolytes
(b) Ostwald's dilution law is applicable to weak electrolytes
(c) In case of a weak electrolyte, the degree of dissociation is proportional to the square root of dilution
(d) none of the above is correct

22. Whenever the electrical energy i.e., nFE is equal, or greater or less than the heat of reaction ($-\Delta H$) depends upon the sign of $\left(\dfrac{\partial E}{\partial T}\right)_P$ i.e., upon the sign of temperature coeffiecient of the e.m.f of the cell. If $\left(\dfrac{\partial E}{\partial T}\right)_P > 0$, then

(a) the e.m.f of the cell will increase with increase of temperature
(b) the electrical energy will be greater than the heat of reaction
(c) additional energy will be supplied to the cell by surroundings
(d) If no additional energy is supplied by surroundings, temperature of the cell will fall during its working .

23. Choose the correct statements :

(a) Ag in a solution of $AgNO_3$ is an electrode of the first type i.e., electrode reversible w.r.t cations
(b) Ag in $AgNO_3$ solution is an electrode which is known as metal -metal ion electrode
(c) Calomel electrode is an example of an electrode reversible with respect to anions
(d) Hydrogen electrode is an electrode that is reversible with respect to anion

MARK YOUR RESPONSE	16. ⓐⓑⓒⓓ	17. ⓐⓑⓒⓓ	18. ⓐⓑⓒⓓ	19. ⓐⓑⓒⓓ	20. ⓐⓑⓒⓓ
	21. ⓐⓑⓒⓓ	22. ⓐⓑⓒⓓ	23. ⓐⓑⓒⓓ		

E

MATRIX-MATCH TYPE

Each question contains statements given in two columns, which have to be matched. The statements in Column-I are labeled A, B, C and D, while the statements in Column-II are labelled p, q, r, s and t. Any given statement in Column -I can have correct matching with ONE OR MORE statement(s) in Column-II. The appropriate bubbles corresponding to the answers to these questions have to be darkened as illustrated in the following example:
If the correct matches are A–p, s and t; B–q and r; C–p and q; and D–s then the correct darkening of bubbles will look like the given.

	p	q	r	s	t
A	●	○	○	●	●
B	○	●	●	○	○
C	●	●	○	○	○
D	○	○	○	●	○

1. **Match the following :**

Column I	**Column II**
(A) Λ°_m $(NaNO_3)$	p. can be obtained by Kohlraush law
(B) Λ°_m (C_2H_5COOH)	q. can be obtained by extrapolating Λ_m *vs.* (molarity)$^{1/2}$ graph to zero molarity
(C) Ionic mobility	r. contribution by the ion to Λ°_m
(D) Ionic conductance	s. velocity of the ion under electric field of 1 $V\,cm^{-1}$.

2. **Match the following listed in column I with those listed in column II.**

Column I	**Column II**
(A) Λ_m of KCl increases on dilution	p. is a linear graph
(B) Λ_m CH_3COOH increases on dilution	q. is a nonlinear graph
(C) Λ_m of KCl versus (molarity)$^{1/2}$	r. due to increased degree of ionization
(D) Λ_m of CH_3COOH versus (molarity)$^{1/2}$	s. due to weakening of inter-ionic attractions

3. For the galvanic cell $Ag\,|\,Ag^+_{(aq)}\ (0.1M)\ ||\ Cd^{2+}_{(aq)}\ (0.1\ M)\ |\ Cd$

$(E^\circ_{Ag^+/Ag} = 0.80\ V,\ E^\circ_{Cd^{2+}/Cd} = -0.40\ V)$,

Match the following :

Column I	**Column II**
(A) The cell reaction	p. –1.17 *V*
(B) Reaction quotient	q. –1.20 *V*
(C) The cell potential	r. Non-spontaneous
(D) The standard cell potential	s. 1/10

4. **Match the reaction quotients listed in Column II with the cell reactions listed in Column I :**

Column I	**Column II**
(A) $Al/Al^{3+}\ (0.1M)\ ||\ Cu^{2+}\ (0.2\ M)\ |\ Cu$	p. 1.0
(B) $Cd/Cd^{2+}\ (0.1M)\ ||\ Fe^{3+}\ (0.01M),\ Fe^{2+}\ (0.1M)\ |\ Pt$	q. 0.001
(C) $Cd/Cd^{2+}\ (0.01\ M)\ ||\ Ag^+\ (0.1\ M)\ |\ Ag$	r. 1.25
(D) $Pt,\ H_2\ (10\ atm)\ |\ H^+\ (0.1M)\ ||\ H^+\ (1M)\ |\ H_2\ (1atm),\ Pt$	s. 10

MARK YOUR RESPONSE

1.

	p	q	r	s
A	○	○	○	○
B	○	○	○	○
C	○	○	○	○
D	○	○	○	○

2.

	p	q	r	s
A	○	○	○	○
B	○	○	○	○
C	○	○	○	○
D	○	○	○	○

3.

	p	q	r	s
A	○	○	○	○
B	○	○	○	○
C	○	○	○	○
D	○	○	○	○

4.

	p	q	r	s
A	○	○	○	○
B	○	○	○	○
C	○	○	○	○
D	○	○	○	○

5. Consider the reduction reactions :

(i) $Sn^{2+} + 2e^- \longrightarrow Sn;\ E° = -0.14\ V$ (ii) $Sn^{4+} + 2e^- \longrightarrow Sn^{2+};\ E° = 0.13\ V$

Match the following

Column I	**Column II**
(A) $E°_{Sn^{4+}/Sn}$	p. +0.005 V
(B) Standard oxidation potential of Sn to Sn (+IV)	q. –0.005 V
(C) Disproportionation of Sn^{2+}	r. Spontaneous
(D) Oxidation of Sn to Sn^{4+}	s. Non-spontaneous

6. Match the following :

Column I	**Column II**
(A) Maximum potential for H-electrode at $p_{H_2} = 1$ atm	p. $-0.414\ V$
(B) Minimum potential for H-electrode at $p_{H_2} = 1$ atm	q. $-0.018\ V$
(C) Potential of H-electrode set up in 1 M KCl and $p_{H_2} = 1$ atm	r. $-0.827\ V$
(D) Potential of H-electrode set up in 1.0 M HCl and $p_{H_2} = 4$ atm	s. $0.0\ V$

7. Match the following :

Column I	**Column II**
(A) E_{cell} when salt bridge is removed	p. Reversible ion – Cl^-
(B) Junction potential in a cell with no salt bridge	q. Reversible ion – H^+
(C) Calomel electrode	r. Zero volt
(D) Quinhydrone electrode	s. Non-zero, opposing E_{cell}

8. Match the following, given that

$$E°_{Cu^{2+}/Cu} = 0.34V,\ E°_{Cl_2/Cl^-} = 1.36V,\ E°_{Br_2/Br^-} = 1.08V,\ E°_{I_2/I^-} = 0.54V$$

Column I	**Column II**
(A) $Cu^{2+} + 2Cl^- \longrightarrow Cu + Cl_2$	p. Can produce electricity in a galvanic cell
(B) $Cl_2 + Cu \longrightarrow Cu^{2+} + 2Cl^-$	q. Can be made to occur in electrolytic cell
(C) $2I^-$ + Starch solution + Chlorine water	r. Appearance of brown colour
(D) $2Br^- + CCl_4$ + Chlorine water	s. Appearance of violet colour

9.

Column A **(Electrolyte Subjected to electrolysis)**	**Column B** **(Species obtained at the electrode)**
(A) Dil HCl solution	p. At anode $O_2(g)$ is evolved
(B) Dil NaCl solution	q. At Cathode $H_2(g)$ is evolved
(C) Conc. NaCl solution	r. At anode $Cl_2\ (g)$ is evolved
(D) Fairly concentrated $AgNO_3$ solution	s. At cathode Ag(s) is deposited

MARK YOUR RESPONSE

5.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

6.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

7.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

8.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

9.

	p	q	r	s
A	ⓟ	ⓠ	ⓡ	ⓢ
B	ⓟ	ⓠ	ⓡ	ⓢ
C	ⓟ	ⓠ	ⓡ	ⓢ
D	ⓟ	ⓠ	ⓡ	ⓢ

F

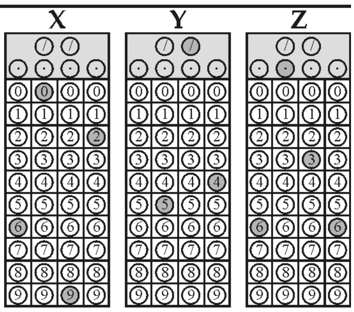
NUMERIC/INTEGER ANSWER TYPE

The answer to each of the questions is either numeric (eg. 304, 40, 3010, 3 etc.) or a fraction (2/3, 23/7) or a decimal (2.35, 0.546).

The appropriate bubbles below the respective question numbers in the response grid have to be darkened.

For example, if the correct answers to question X, Y & Z are 6092, 5/4 & 6.36 respectively then the correct darkening of bubbles will look like the following.

For single digit integer answer darken the extreme right bubble only.



1. A saturated solution of AgBr and AgCNS is prepared. Find the conductivity of this solution. Given K_{sp} (AgBr) = 5×10^{-13} ; $K_{sp}(AgCNS) = 1\times10^{-12}$

$$\lambda^\circ_{Ag^+} = 6\times10^{-3}\,s\,m^2 mol^{-1};$$

$$\lambda^\circ_{Br^-} = 8\times10^{-3}\,s\,m^2 mol^{-1};$$

$$\lambda^\circ_{CNS^-} = 7\times10^{-3}\,s\,m^2 mol^{-1}$$

Give your answer in terms of 10^{-7} s/m.

2. An excess of liquid mercury is added to an acidified solution of $1.0\times10^{-3}\,M\,Fe^{3+}$. It is found that 5% of Fe^{3+} remains at equilibrium of the following reaction

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}$$

Calculate $E^\circ_{Hg_2^{2+}/Hg}$, given that $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77V.$

3. During recharging of a lead storage battery, the density of sulphuric acid increased from 1.140 g mL^{-1} to 1.284 g mL^{-1}. Before recharging, sulphuric acid solution was 20% by mass and after recharging the acid solution was 38% by mass. The battery holds 3.0 L of the acid solution and the volume practically remained constant during recharge. How long (hours) would it take to charge the battery with a current of 5 A with 96.5% efficiency ?

4. Compute the electrode potential of the half cell set up, immersing a silver wire in a solution which is 0.10 M $AgNO_3$ and 1.00 M NH_3. Given that instability constant of the complex ion $Ag(NH_3)_2^+$ is 6.0×10^{-8} and

$$E^\circ_{Ag^+/Ag} = 0.80V.$$

5. Consider the cell

Pt, $H_{2(g)}$ (1 atm) | $HCl_{(aq)}$ (1.0M) | $Cl_{2(g)}$ (1 atm), Pt

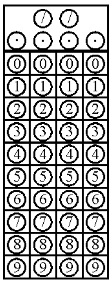
Given that

$$E^\circ_{Cl_2/Cl^-} = 1.36V\ ; \left(\frac{dE^\circ_{cell}}{dT}\right)_p = -1.25\times10^{-3}\,VK^{-1}$$

Calculate the standard enthalpy of the cell reaction in terms of 10^2 kJ.

MARK YOUR RESPONSE

1.



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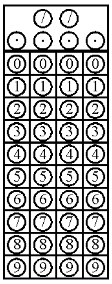
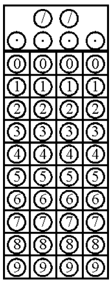
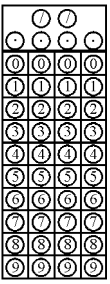


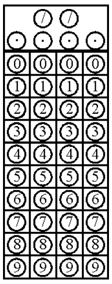
3.



4.



5.



Answerkey

A SINGLE CORRECT CHOICE TYPE

1.	d	**2.**	d	**3.**	b	**4.**	c	**5.**	c	**6.**	b	**7.**	c	**8.**	d	**9.**	d	**10.**	d
11.	d	**12.**	c	**13.**	b	**14.**	d	**15.**	d	**16.**	d	**17.**	b	**18.**	b	**19.**	b	**20.**	c
21.	c	**22.**	c	**23.**	b	**24.**	a	**25.**	b	**26.**	c	**27.**	d	**28.**	c	**29.**	c	**30.**	d
31.	b	**32.**	c	**33.**	d	**34.**	c	**35.**	b	**36.**	c	**37.**	d	**38.**	c	**39.**	d	**40.**	c
41.	b	**42.**	d	**43.**	c	**44.**	c	**45.**	b	**46.**	c	**47.**	d	**48.**	c	**49.**	d	**50.**	c
51.	c	**52.**	b	**53.**	b	**54.**	b	**55.**	d	**56.**	b	**57.**	b	**58.**	c	**59.**	b	**60.**	d
61.	a	**62.**	c	**63.**	c	**64.**	b	**65.**	d	**66.**	d	**67.**	a	**68.**	b	**69.**	c	**70.**	d
71.	c	**72.**	b	**73**	c	**74**	c	**75**	c	**76**	d	**77**	c	**78**	b	**79**	b	**80**	d
81	c	**82**	d	**83**	d	**84**	d	**85**	c	**86**	b	**87**	d	**88**	c	**89**	d	**90**	b
91	d	**92**	c	**93**	d	**94**	c	**95**	b	**96**	d	**97**	b	**98**	c				

B COMPREHENSION TYPE

1	(d)	**6**	(a)	**11**	(a)	**16**	(b)	**21**	(a)	**26**	(b)
2	(b)	**7**	(b)	**12**	(b)	**17**	(d)	**22**	(b)	**27**	(a)
3	(a)	**8**	(c)	**13**	(b)	**18**	(d)	**23**	(a)	**28**	(b)
4	(d)	**9**	(b)	**14**	(d)	**19**	(d)	**24**	(a)	**29**	(c)
5	(b)	**10**	(c)	**15**	(a)	**20**	(b)	**25**	(c)	**30**	(a)

C REASONING TYPE

1	(c)	**4**	(b)	**7**	(a)	**10**	(c)	**13**	(d)	**16**	(d)	**19**	(b)
2	(a)	**5**	(c)	**8**	(a)	**11**	(d)	**14**	(b)	**17**	(a)		
3	(d)	**6**	(b)	**9**	(a)	**12**	(b)	**15**	(c)	**18**	(c)		

D MULTIPLE CORRECT CHOICE TYPE

1.	c,d	**2.**	a,b,c	**3.**	b,d	**4.**	b,c	**5.**	b,c,d	**6.**	a,d	**7.**	b,c	**8.**	c,d	**9.**	b,c	**10.**	b,c
11.	a,b,c	**12.**	b,d	**13.**	a,c,d	**14.**	a,c,d	**15.**	b,d	**16.**	b,c,d	**17.**	a,d	**18.**	c,d	**19.**	a,b,d	**20.**	a,b,c,d
21.	a,b,c	**22.**	a,b,c,d	**23.**	a,b,c														

E MATRIX-MATCH TYPE

1. **A - q ; B - p ; C - s ; D - r**

2. **A - s ; B - r ; C - p ; D - q**

3. **A - r ; B - s ; C - p ; D - q**

4. **A - r ; B - s ; C - p ; D - q**

5. **A - q ; B - p; C - s; D - r**

6. **A-s; B-r; C-p; D-q**

7. **A - r; B - s; C - p; D - q**

8. **A-q, B-p, C-s, D-r**

9. **A - p, q ; B - p, q ; C - q, r ; D - p, s**

F NUMERIC/INTEGER ANSWER TYPE

1	164	**2**	0.793	**3**	44.2	**4**	0.38	**5**	3.344

Solutions

A SINGLE CORRECT CHOICE TYPE

2. **(d)** On pulling out one of the electrodes the electric field applied to the solution disappears and hence the ions start moving randomly.

3. **(b)** On dilution number of ions per unit volume of solution decreases. Hence resistance to passage of electric current increases i.e., conductance (reciprocal of resistance) decreases. Also conductively (conductance per unit volume) decreases. Both equivalent and molar conductance increase due to increase in total number of ions in the solution.

5. **(c)** On dilution, degree of ionization of a weak electrolyte increases but not proportionately to volume. Hence total number of ions in solution increases but per unit volume decreases.

7. **(c)** Absolute ionic mobility is the speed of ion under an electric field of 1V cm^{-1} (unit electric field).

8. **(d)** $[Co(NH_3)_6]Cl_3$ ionizes as :

$[Co(NH_3)_6]Cl_3 \rightarrow [Co(NH_3)_6]^{3+} + 3\,Cl^-$

Greater the charge of the ions and greater their number, the higher will be the conductivity.

9. **(c)** A plot of $\lambda_m\ V_s \sqrt{C}$ is linear with negative slope.

10. **(d)** HCN is weak electrolyte. The relationship holds good only for strong electrolytes.

12. **(c)** Ionic mobility is the velocity of ion under a potential gradiant of 1 Vm^{-1}.

13. **(b)** Li^+ ion, being smallest in size, gets hydrated to the maximum extent and hence Li^+_{aq} has the largest size amongst the cations of the given electrolytes.

14. **(d)** λ_m for NaOH $= \dfrac{1000k}{\text{molarity}} = \dfrac{\dfrac{1000\times xz}{y}}{0.1} \quad \left(k = \dfrac{xz}{y}\right)$

15. (d) The plot of λ_m for NH_4OH (being weak electrolyte) *versus* (molarity)$^{1/2}$ is not linear and can not be extrapolated to zero molarity.

16. **(d)** $\lambda_m^\infty(BaSO_4) = \lambda^\infty_{Ba^{2+}} + \lambda^\infty_{SO_4^{2-}}$

$$= \lambda_m^\infty(BaCl_2) + \lambda_m^\infty(H_2SO_4)^- - 2\lambda^\infty_{(HCl)}$$

$$= x_1 + x_2 - 2x_3;\quad \overset{\circ}{\lambda}_e = \frac{1}{2}\overset{\circ}{\lambda}_m(\text{BaSO}_4)$$

17. **(b)** Solubility $S = \dfrac{1000k}{\overset{\circ}{\lambda}_{AgCl}} = \dfrac{1000\times 2.6\times 10^{-6}}{\overset{\circ}{\lambda}_{Ag^+} + \overset{\circ}{\lambda}_{Cl^-}}$

$$= \frac{2.6\times 10^{-3}}{63+67} = 2\times 10^{-5}\,\text{mol L}^{-1};\ K_{sp} = S^2$$

18. **(b)** $\lambda_m(CH_3COOH) = \dfrac{1000k}{0.1} = \dfrac{1000\times 3.9\times 10^{-4}}{0.1}$

$$= 3.9\,\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$$

$$\alpha_{CH_3COOH} = \frac{\lambda_m}{\overset{\circ}{\lambda}_m} = \frac{3.9}{\overset{\circ}{\lambda}_{CH_3COO^-} + \overset{\circ}{\lambda}_{H^+}}$$

$$= \frac{3.9}{41+349} = 1.0\times 10^{-2} = 1\%$$

19. **(b)** Upto equivalence point highly mobile H^+ get replaced by much less mobile K^+ ions. Hence resistance of solution increases. After equivalence point resistance decreases due to unreacted K^+ and highly mobile OH^- ions.

20. **(c)** $NH_4OH + HCl \rightarrow NH_4Cl + H_2O$:

Before equivalence point conductance increases slowly due to the formation of highly ionizable NH_4Cl in place of weakly ionizable NH_4 OH. Beyond equivalence point conductance increases rapidly due to unreacted H^+ ions (highly mobile) and Cl^- ions.

22. **(c)** $\lambda_m = \dfrac{1000k}{0.1} = \dfrac{1000\times 3.75\times 10^{-4}}{0.1} = 3.75;$

$$\alpha = \frac{\lambda_m}{\lambda_m^\infty} = \frac{3.75}{250} = 1.5\times 10^{-2};$$

$K_a = C\alpha^2 = 0.1\times(1.5\times 10^{-2})^2 = 2.25\times 10^{-5}$

26. **(c)** The cations will be liberated in the sequence of decreasing reduction potentials. Cations having E° value $< -0.83V$ (reduction potential of water) will not be liberated from aqueous solutions.

27. **(d)** Since $\overset{\circ}{E}_{Na^+/Na} = -2.71V$ < reduction potential of water (= – 0.83V), water will be reduced to H_2 and OH^- at the cathode. Although

$$\overset{\circ}{E}_{OX}(H_2O) = -1.23\,V > \overset{\circ}{E}_{Cl^-/Cl_2} = (-1.36\,V),$$

water will not be oxidised at the anode due to over potential of oxygen at platinum surface but Cl^- will be oxidised to Cl_2.

28. **(c)** $Ar-NO_2+6H^++6e^-\longrightarrow Ar-NH_2+2H_2O$

$W=zQ\eta=\frac{\text{molar mass}\times 2\times 96500}{6\times 96500}\times\frac{50}{100}\Rightarrow$ molar mass $=6W=6\times 20.50\text{ g}=123\text{g}$

29. **(c)** Anode :

$$Pb_{(s)}+H_2SO_{4(aq)}\longrightarrow PbSO_{4(s)}+2H^+_{(aq)}+2e^-$$

Cathode :

$$PbO_{2(s)}+H_2SO_{4(aq)}+2H^++2e^-\longrightarrow PbSO_{4(s)}+2H_2O$$

2 mol of H_2SO_4 consumed ≡ 4 equiv. of H_2SO_4 $\equiv 2\times 96500\,C$.

Hence, equiv. of H_2SO_4 consumed

$$=\frac{4\times 100\times 10^{-3}\times 9.65\times 10^5}{2\times 96500}=2;$$

decrease in normality = 2/5.

30. **(d)** (A) Cathode : $Cu^{2+}_{(aq)}+2e^-\longrightarrow Cu_{(s)}$

Anode : $H_2O\longrightarrow 2H^++\frac{1}{2}O_2+2e^-$ p^H decreases.

(B) Cathode : $Cu^{2+}_{(aq)}+2e^-\longrightarrow Cu_{(s)}$

Anode : $Cu_{(s)}\longrightarrow Cu^{2+}_{(aq)}+2e^-$ pH remains unchanged.

(C) Cathode : $2H_2O+2e^-\longrightarrow H_2+2OH^-_{(aq)}$

Anode : $2Cl^-\longrightarrow Cl_{2\,(aq)}+2e^-$ pH increases.

32. **(c)** Cathode : $2H_2O+2e^-\longrightarrow H_{2(g)}+2OH^-_{(aq)}$

Anode : $H_2O\longrightarrow 2H^+_{(aq)}+\frac{1}{2}O_{2(g)}+2e^-$

Volume of $H_2=\frac{22400\times 1\times 965}{2\times 96500}=112\text{ml}$; Volume of O_2 = 56 ml; Total volume = 112 + 56 ml

33. **(d)** $K_2SO_{4(aq)}$: At cathode :

$$2H_2O+2e^-\longrightarrow H_{2(g)}+2OH^-_{(aq)}$$

At anode : $H_2O\longrightarrow 2H^+_{(aq)}+\frac{1}{2}O_{2(g)}+2e^-$

Cathodic reduction of MnO_4^- :

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

If V L = Volume of H_2(STP), then $V+V/2=1.68$
$\Rightarrow V=1.12$L

Quantity of electricity passed for the liberation of 12 L (STP) of H_2

$$=\frac{2F}{22.4}\times 1.12=0.1F$$

Moles of MnO^-_4 reduced $=\frac{1}{5F}\times 0.1F=0.02$

34. **(c)** Cathode : $2H_2O+2e^-\longrightarrow H_2+2OH^-$;

z for H_2 in terms of cm^3 (STP)

$$=\frac{22400}{2\times 96500}=\frac{112}{965}cm^3c^{-1}$$

Hence, $V(H_2)=1.12cm^3=zit\times\frac{96.5}{100}$

$$=\frac{112}{965}\times i\times 1\times\frac{96.5}{100}\Rightarrow i=10A$$

35. **(b)** Cathode : $2H_2O+2e^-\longrightarrow H_2+2OH^-$;

Anode : $2Cl^-\longrightarrow Cl_2+2e^-$

Mol of OH^- formed $=zit=\frac{1\times 5\times 965}{96500}=0.05$;

$[OH^-]=\frac{0.05}{0.5}=1\times 10^{-1}$; $|H^+|=1.0\times 10^{-13}$

36. **(c)** $NaCl_{(aq)}$ (cathode) :

$$2H_2O+2e^-\longrightarrow H_{2(g)}+2OH^-_{(aq)}$$

$CuSO_{4(aq)}$ (cathode) : $Cu^{2+}_{(aq)}+2e^-\longrightarrow Cu_{(s)}$

Equivalents of OH^- = mole of OH^- formed

$$=\frac{600\times 1}{1000}=0.6$$

Equivalents of Cu deposited $=\frac{31.8}{63.6/2}=1.0$;

Current efficiency $=\frac{0.6\times 100}{1}\%=60\%$

37. **(d)** Cathode : $2H_2O+2e^-\longrightarrow H_2+2OH^-$

Anode : $H_2O\longrightarrow 2H^++\frac{1}{2}O_2+2e^-$

Under identical conditions of T and P, volume of H_2 produced is twice that of O_2 formed and hence cost would be half. Hence, cost of 10L of $H_2=10\,x/2$

38. **(c)** $Mn_3O_4 \longrightarrow 3MnO_4^{2-}$; change in O.N. of Mn per mol of $Mn_3O_4 = 3\times\left(6-\frac{8}{3}\right)=10$

Hence, 1 mol of $Mn_3O_4 \equiv 10$ equivalents $\equiv 10\,F$

39. **(d)** $Cu^{2+}+2e^- \longrightarrow Cu$; mol of Cu^{2+} deposited $=\frac{1\times48250}{2\times96500}=0.25$; molarity $=\frac{0.25}{0.5}=0.5$

40. **(c)** pH will remain practically constant due to buffer action.

41. **(b)** Cell reaction : $3Cu^{2+}_{(aq)}+2Cr_{(s)}\longrightarrow 3Cu_{(s)}+2Cr^{3+}_{(aq)}$;

$$Q=\frac{[Cr^{3+}]^2}{[Cu^{2+}]^3}=\frac{0.1^2}{0.5^3}=0.08$$

43. **(c)** $Fe^{2+}+2e^-\longrightarrow Fe_{(s)}, E^\circ = x_1V$ ......(i)

$Fe^{3+}+e^-\longrightarrow Fe^{2+}, E^\circ = x_2V$ ......(ii)

(i)+(ii), $Fe^{3+}+3e^-\longrightarrow Fe_{(s)}, E^\circ = x_3V$

hence $3x_3 = 2x_1+x_2 \Rightarrow x_3=(2x_1+x_2)/3V$

44. **(c)** Net cell reaction :

$$Cd_{(s)}+2Ag^+_{(aq)}\longrightarrow Cd^{2+}_{(aq)}+Ag_{(s)}$$

$$E_{cell}=E^\circ_{cell}-\frac{0.0592}{2}\log\frac{[Cd^{2+}]}{[Ag^+]^2}$$

45. **(b)** Cell reactoin : $Pb_{(s)}+Cu^{2+}_{(aq)}\longrightarrow Pb^{2+}_{(aq)}+Cu_{(s)}$

$$E_{cell}=E^\circ_{cell}+\frac{0.0592}{2}\log\frac{[Cu^{2+}]}{[Pb^{2+}]}$$

46. **(c)** $2H^+_{(aq)}+2e^-\longrightarrow H_{2(g)}; E=E^\circ-\frac{0.0592}{2}\log\frac{P_{H_2}}{[H^+]^2}$

$$=-\frac{0.0592}{2}\log\frac{1}{[H^+]^2}$$

$=-0.0592\,pH=-0.0592\times7=-0.414\,V$ (pH of $KCl_{(aq)}=7$)

48. **(c)** Anode : $2Cl^-_{(aq)}\longrightarrow Cl_{2(g)}(P_1 atm)+2e^-$

Cathode : $Cl_{2(aq)}(P_2 atm)+2e^-\longrightarrow 2Cl^-_{(aq)}$

Cell reaction : $Cl_{2(g)}(P_2 atm)\longrightarrow Cl_{2(aq)}(P_1 atm)$

$E_{cell}=\frac{0.0592}{2}\log\frac{P_2}{p_1}$; For positive E_{cell}, $p_2>p_1$

49. **(d)** $E_{cell}=0.0592\log\frac{[Ag^+]cathode}{[Ag^+]anode}=0.0592\log\frac{1}{K_{sp}(AgCl)}$

$$=0.0592\log\frac{1}{1\times10^{-10}}=0.592V$$

$\left([Ag^+]_{anode}=\frac{K_{sp}}{[Cl^-]}=K_{sp}\right)$ $[Cl^-]=1$ M

50. **(c)** Greater the standard reduction potential, stronger will be the oxidizing agent.

The reaction will be spontaneous in backward direction.

51. **(c)** Equivalent mass of metal $=\frac{3.80}{0.2}=19=\frac{57}{n}\Rightarrow n=3$

(n = valency)

52. **(b)** $E=E^\circ-\frac{0.0592}{2}\log\frac{[Mn^{2+}]}{[H^+]^4}$

$$=E^\circ-\frac{0.0592\times4}{2}\log\frac{[Mn^{2+}]^{1/4}}{[H^+]}$$

$=E^\circ-0.0592\times2(\log[Mn^{2+}]^{1/4}+pH)$

$\Delta E=E_2-E_1=0.0592\times2(pH_1-pH_2)=0.118\times1\ V$

53. **(b)** $E=E^\circ-\frac{0.0592}{2}\log\frac{[QH_2]}{[Q][H^+]^2}=E^\circ-0.0592pH$

$=0.699-0.0592\times4=0.463V$

54. **(b)** $-\Delta G^\circ=nFE^\circ_{cell}$

55. **(d)** $MX_{(s)}+e^-\longrightarrow M_{(s)}+X^-_{(aq)}$, $E^\circ=0.207V$ ......(i)

$M^+_{(aq)}+e^-\longrightarrow M_{(s)}; E^\circ=0.799V$ ......(ii)

(i) – (ii) $MX_{(s)}\longrightarrow M^+_{(aq)}+X^-_{(aq)}$;

$E^\circ_{cell}=0.207-0.799=-0.592V$

$E_{cell}=0=E^\circ_{cell}-0.0592\log[M^+_{(aq)}]\times[X^-_{(aq)}]$

$=-0.592=0.0592\log K_{sp}$

$\log K_{sp}=-10, K_{sp}=1.0\times10^{-10}$; solubility $=\sqrt{K_{sp}}$

$=\sqrt{1.0\times10^{-10}}=1.0\times10^{-5}$ mol L^{-1}

57. **(b)** In concentration all the spontaneous process is physical in nature involving transfer of matter from higher concentration to lower concentration in indirect manner.

58. **(c)** $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}, E^\circ = 0.0V$ ......(i)

$2D^+_{(aq)} + 2e^- \longrightarrow D_{2(g)}, E^\circ = -0.003V$ ......(ii)

$\text{(i)} - \text{(ii)},\ 2H^+_{(aq)} + D_{2(g)} \longrightarrow H_{2(g)} + 2D^+_{(aq)},$

$E^\circ_{\text{cell}} = 0.003V$

$$E_{\text{cell}} = 0 = E^\circ_{\text{cell}} - \frac{0.0592}{2}\log\frac{P_{H_2} \times [D^+_{(aq)}]^2}{P_{D_2}[H^+_{(aq)}]^2};$$

$$\log\frac{[D^+_{(aq)}]}{[H^+_{(aq)}]} = \frac{E^\circ_{\text{cell}}}{0.0592} = \frac{0.003}{0.0592} = 0.05$$

59. **(b)** $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{2}\log\frac{[Hg^{2+}_{2(aq)}]}{[Ag^+_{(aq)}]^2}$

$$= (0.80 - 0.785) - \frac{0.0592}{2}\log\frac{10^{-1}}{(10^{-3})^2} = -0.133V$$

hence backward reation is spontaneous.

60. **(d)** $E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{1}\log\frac{[Cu^{2+}_{(aq)}]}{[Cu^+_{(aq)}]^2}$

when $\frac{[Cu^{2+}_{(aq)}]}{[Cu^+_{(aq)}]^2} = K_e, E_{\text{cell}} = 0$

Hence, $\log K_e = \frac{E^\circ_{\text{cell}}}{0.0592} = \frac{0.52 - 0.16}{0.0592}$

$= 6.08;\ K_e = 1.2 \times 10^6$

61. **(a)** $-\Delta G^\circ$ = electrical work done $= nFE^\circ_{cell} = 2 \times 96500 \times (1.36 - 0.27)J = 210.37\,kJ$

62. **(c)** Cell reaction : $3Y^{2+} + 2X \longrightarrow 2X^{3+} + 3Y$

$[n = 6, E^\circ_{\text{cell}} = 0.34 - (-1.66)V] = 2.00\ V$

Hence, $\frac{0.0592}{n}\log K_e = E^\circ_{\text{cell}} = 2$

$$\log K_e = \frac{2 \times 6}{0.0592} = 202.7$$

63. **(c)** $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

$$E = E^\circ - \frac{0.0592}{2}\log\frac{P_{H_2}}{(H^+_{(aq)})^2} = 0.0296\log\frac{2}{1^2} = 8.9mV$$

64. **(b)** $\Delta H = \Delta G + T\Delta S = -nFE_{\text{cell}} - T\left[\frac{d(\Delta G)}{dT}\right]_P$

$$= -nFE_{\text{cell}} - T\left[\frac{d(-nFE_{\text{cell}})}{dT}\right]_P$$

$$= nF[T\left(\frac{dE_{\text{cell}}}{dT}\right)_P - E_{\text{cell}}]$$

65. **(d)** $\Delta G = \Delta H - T\Delta S = \Delta H + T\left(\frac{d\Delta G}{dT}\right)_P$

$$= \Delta H + T\left[\frac{d(-nFE_{\text{cell}})}{dT}\right]_P = \Delta H - nFT\left(\frac{dE_{\text{cell}}}{dT}\right)_P$$

or $\left(\frac{dE_{\text{cell}}}{dT}\right)_P = \frac{\Delta H - \Delta G}{nFT} = \frac{T\Delta S}{nFT} = \frac{\Delta S}{nF}$

66. **(d)** $K^+_{(aq)}$ and $Zn^{2+}_{(aq)}$ can not lose electron(s). Fe has greater tendency to lose electrons than Cu.

$[E^\circ_{Fe/Fe^{2+}}(= 0.44V) > E^\circ_{Cu/Cu^{2+}}(= -0.34V)]$

67. **(a)** Only $H_3O^+_{(aq)}$ can take up electrons whereas other species can not.

69. **(c)** The standard oxidation potentials of Fe, I^- and Cl^- are 0.44, –0.54 and –1.36 V respectively. Hence, their reducing powers will be in the order : $Fe > I^- > Cl^-$

71. **(c)** In $H_2 - O_2$ fuel cell, anode :

$H_{2(g)} + 2OH^-_{(aq)} \longrightarrow 2H_2O_{(\ell)} + 2e^-$

Cathode : $H_2O + \frac{1}{2}O_{2(g)} + 2e^- \longrightarrow 2OH^-_{(aq)}$

Hence, net reaction : $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(\ell)}$

$$E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.0592}{2}\log P_{H_2} P_{O_2}^{1/2}$$

72. **(b)** For reaction (a), $E^\circ_{\text{cell}} = 0.33 - 0.44 = -0.11V$
Hence, non-spontaneous.
For reaction (b) $E^\circ_{\text{cell}} = 0.44 - 0.33 = 0.11V$
Hence, spontaneous.
For the given cell $E^\circ_{\text{cell}} = E_R - E_L = 0.33 - 0.44$
Cell is wrongly represented.

73. **(c)** The greater the number of ions given by one formula unit and larger the charge on each ion, the greater will be the molar conductance. *III* - No ion; *I* - 1 cation and 1 anion with unit charges; *IV* - 1 cation and 1 anion with charges of 2 units each; *II* - 3 cations and 2 anions with charges of 2 and 3 units.

74. **(c)** Volume of plated layer = $10^2 \times 5 \times 10^{-3} = 0.5\ \text{cm}^3$;
Mass of metal = 0.5 × 10.8 = 5.4 g

$$W = \frac{E \times Q}{96500} \times \frac{96.5}{100} = \frac{108 \times Q \times 96.5}{96500 \times 100} \Rightarrow Q = 5000\,\text{C}$$

75. **(c)** Let $C\,\text{mol}\,\text{L}^{-1}$ be the concentration of H^+ & OH^- ions in water. Then,

$$\lambda_m(\text{water}) = \frac{1000\kappa}{C} = \frac{1000 \times 6.6 \times 10^{-8}}{C}$$

$$\Rightarrow C = \frac{6.6 \times 10^{-5}}{\lambda_m(\text{water})} = \frac{6.6 \times 10^{-5}}{\lambda_m^{\infty}(\text{water})} = \frac{6.6 \times 10^{-5}}{350 + 200}$$

$$= 1.2 \times 10^{-7}\,\text{mol}\,\text{L}^{-1};\quad K_w = (1.2 \times 10^{-7})^2$$

77. **(c)** $$E_{\text{cell}} = 0.059 \log \frac{[H^+]_{\text{cathode}}}{[H^+]_{\text{anode}}}$$

$$= 0.059 \log \frac{1}{[H^+]_{\text{anode}}} = 0.295\ \text{(given)}$$

$$\Rightarrow [H^+]_{\text{anode}} = 1.0 \times 10^{-5}\,\text{M}$$

$$\sqrt{K_a C} = \sqrt{K_a \times 0.01} = 1.0 \times 10^{-5}$$

$$K_a = 1.0 \times 10^{-8}$$

78. **(b)** $$E_{\text{cell}} = 0.0592\,(\text{pH}_{\text{anode}} - \text{pH}_{\text{cathode}})$$

$$= 0.0592\,(\text{pH}_{\text{anode}} - 0) = 0.296\,\text{V (given)}$$

$$\Rightarrow \text{pH}_{\text{anode}} = 5;$$

$$\text{pH(acid buffer)} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 5$$

or $$4.699 + \log \frac{[\text{Salt}]}{[\text{Acid}]} = 5,$$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = 0.3010 \Rightarrow \frac{[\text{Salt}]}{[\text{Acid}]} = 2$$

79. **(b)** Reduction reaction at electrode;

$$Hg_2Cl_{2(s)} + 2e^- \longrightarrow 2Hg_{(\ell)} + 2Cl^-_{(aq)}$$

$$E_{Hg_2Cl_2/Hg,Cl^-} = E^\circ - \frac{0.059}{2} \log[Cl^-]^2$$

$$= E^\circ - 0.059 \log[Cl^-]$$

80. **(d)** For a buffer of weak acid and its salt,

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Hence, $$(\text{pH})_1 = \text{pK}_a + \log \frac{y}{x} \qquad \text{.................... (i)}$$

$$(\text{pH})_2 = \text{pK}_a + \log \frac{x}{y} \qquad \text{.................. (ii)}$$

Adding (i) and (ii),

$$\text{pK}_a = \frac{1}{2}[(\text{pH})_1 + (\text{pH})_2] \qquad \text{.................. (iii)}$$

Oxidation reaction at H-electrode :

$$H_{2(g)} \rightarrow 2H^+ + 2e^-$$

$$E_{OX} = E^\circ - \frac{0.059}{2} \log \frac{[H^+]^2}{P_{H_2}} = 0.059\,\text{pH} \qquad \text{...(iv)}$$

$$(E^\circ = 0,\ P_{H_2} = 1\,\text{atm})$$

From (iii) and (iv), $$\text{pK}_a = \frac{1}{2}\frac{(E_1 + E_2)}{0.059} = \frac{E_1 + E_2}{0.118}$$

81. **(c)** The electrode at higher value of pK_b of the base will act as cathode.

$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{[H^+]^2_{\text{cathode}}}{[H^+]^2_{\text{anode}}}$$

$$= \frac{0.059}{2} \log \frac{[OH^-]^2_{\text{anode}}}{[OH^-]^2_{\text{cathode}}} = \frac{0.059}{2} \log \frac{K_{b(1)}C}{K_{b(2)}C}$$

$$= \frac{0.059}{2}(\text{pK}_{b(2)} - \text{pK}_{b(1)})$$

$$= \frac{0.059}{2} \times (5 - 3) = 0.059\text{V}$$

82. **(d)** Reduction reaction :

$$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}$$

$$E_{Cl_2/Cl^-} = E^\circ_{Cl_2/Cl^-} - \frac{0.059}{2} \log \frac{[Cl^-]^2}{P_{Cl_2}}$$

$$= 1.36 - \frac{0.059}{2} \log \frac{(1.0 \times 10^{-3})^2}{10}$$

$$= 1.36 - \frac{0.059}{2} \log 10^{-7} = 1.57\,\text{V}$$

83. **(d)** Minimum is the concentration of H^+ ions at the anode, the maximum would be e.m.f.

For H^+ concentration cell,

$$E_{cell} = 0.059 \log \frac{[H^+]_{cathode}}{[H^+]_{anode}}$$

$$= -0.059 \log [H^+]_{anode} \qquad \left([H^+]_{cathode} = 1\right)$$

84. **(d)** In Cl_2 concentration cell (I) reduction will take place at higher pressure of chlorine. In Cl^- ion concentration cell (II) reduction will occur at lower $[Cl^-]$.

85. **(d)** $E_{cell} = \frac{0.059}{2} \log \frac{[H^+]^2_{cathode}}{[H^+]^2_{anode}}$

$$= 0.059 \log \frac{[H^+]_{cathode}}{[H^+]_{anode}}$$

$$[H^+]_{cathode} = \sqrt{K_a C} = \sqrt{4 \times 10^{-5} \times 0.1}$$

$$= 2 \times 10^{-3} M$$

$$[H^+]_{anode} = \frac{K_w}{[OH^-]_{anode}} = \frac{10^{-14}}{\sqrt{K_b C}}$$

$$= \frac{10^{-14}}{\sqrt{2.5 \times 10^{-5} \times 1}} = 2 \times 10^{-12}$$

Hence, $E_{cell} = 0.059 \log \frac{2 \times 10^{-3}}{2 \times 10^{-12}} = 0.532\, V$

86. **(b)** Anode : $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$

Cathode : $Ag^+_{(aq)} + e^- \rightarrow Ag$

Moles of Cu^{2+} produced $= \frac{1 \times 9.65 \times 1000}{2 \times 96500} = 0.05$

$[Cu^{2+}] = 1.0 + 0.05 = 1.05\, M$

Moles of Ag^+ reduced $= \frac{1 \times 9.65 \times 1000}{96500} = 0.1$

$[Ag^+] = 1.0 - 0.1 = 0.9\, M$

87. **(d)** Potential gradient $= \frac{50}{10} = 5$ volt cm^{-1}

Ionic mobility of $Ba^{2+} = \frac{x}{5} cm^2\, V^{-1} s^{-1}$

Ionic mobility of $Cl^- = \frac{y}{5} cm^2\, V^{-1}\, s^{-1}$

Equivalent ionic conductance of Ba^{2+} ion

$$= 96500 \times \frac{x}{5} ohm^{-1} cm^2 equiv^{-1}$$

Equivalent ionic conductance of Cl^- ion

$$= 96500 \times \frac{y}{5} ohm^{-1} cm^2 equiv^{-1}$$

$$\lambda_m (BaCl_2) = 2 \times [\lambda_e (Ba^{2+}) + \lambda_e (Cl^-)]$$

$$= 2 \times 96500 \frac{(x+y)}{5} = 38600 (x+y)\, ohm^{-1} cm^2 mol^{-1}$$

88. **(c)** $Cu^{2+} + e^- \rightarrow Cu^+$; $E^\circ = x_1 V$

$\Delta G^\circ_1 = -Fx_1$ .... (i)

$In^{3+} + 2e^- \rightarrow In^+$; $E^\circ = x_2 V$

$\Delta G^\circ_2 = -2Fx_2$ .... (ii)

$In^{2+} + e^- \rightarrow In^+$; $E^\circ = x_3 V$

$\Delta G^\circ_3 = -Fx_3$ .... (iii)

From equation (i) + (iii) – (ii),

$In^{2+} + Cu^{2+} \rightarrow In^{3+} + Cu^+$, $\Delta G^\circ = -FE^\circ$

Hence, $\Delta G^\circ = -FE^\circ = \Delta G^\circ_1 + \Delta G^\circ_3 - \Delta G^\circ_2$

$= -F(x_1 + x_3 - 2x_2)$ or $E^\circ = x_1 + x_3 - 2x_2$ Volt

89. **(d)** $E^\circ = 0.15 - 0.40 - 2(-0.42) = 0.59\, V$

$$\Delta G^\circ = -nFE^\circ = -1 \times 96500 \times 0.59\, J$$

$$= -0.59 \times 96.5\, kJ$$

90. **(d)** (I) $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$

$$= E^\circ_{Sn^{4+}/Sn^{2+}} - E^\circ_{Fe^{3+}/Fe^{2+}} = 0.10 - 0.77 = -0.67\, V$$

Negative E°_{cell}, and hence no feasibility of the reaction.

(II) $E^\circ_{cell} = E^\circ_{Cu^+/Cu} - E^\circ_{Cu^{2+}/Cu^+} = 0.52 - 0.15 = 0.37 V$

Positive E°_{cell} and hence the disproportionation reaction is feasible.

92. **(c)** As per reaction in (c), reduction occurs at iodine electrode and oxidation at bromine electrode.

Hence, $E^\circ_{cell} = E^\circ_{I_2/I^-} - E^\circ_{Br_2/Br^-}$

$$= 0.54 - 1.09 = -0.55 V$$

The negative cell potential suggests the non-spontaneity of the reaction. In other cases E_{cell} will be positive.

94. **(c)** The cell reaction is

$$\frac{1}{2}\text{Pb} + \text{AgCl} \rightarrow \text{Ag} + \frac{1}{2}\text{PbCl}_2$$

The reaction requires 1 Faraday for its completion (i.e., $n = 1$)

and $\Delta G = \Delta H - TnF\left(\frac{\partial E}{\partial T}\right)_P$

$$\Delta S = nF\left(\frac{\partial E}{\partial T}\right)_P$$

$$\therefore \quad \Delta S = \frac{1 \times 96500 \times (-1.8 \times 10^{-4})}{4.2} \qquad [\,1 \text{ Cal} = 4.2\text{J}]$$

$= -4.14$ Cal/degree

95. **(b)** Let the concentration of mercurous ions in $\frac{N}{20}$ Solution be C_1 and that in $\frac{N}{2}$ solution be C_2. Then, emf of cell is given by $E = \frac{0.0591}{n}\log\frac{C_2}{C_1}$

But $\frac{C_2}{C_1} = \frac{1/2}{1/20} = 10$

Hence, $E = 0.029 = \frac{0.0591}{n}\log\frac{C_1}{C_1} = \frac{0.0591}{n}\log 10$

or $n = 2$

Thus, the valency of mercurous ion is +2 and it should be represented as Hg_2^{2+}.

96. **(d)** All the given statements are correct

97. **(b)** It is the correct statement.

98. **(c)** We know $\Delta G° = -\ nFE°$

$$\therefore \quad E° = -\frac{\Delta G°}{nF}$$

$$= +\frac{237.2 \times 1000\text{J}}{2 \times 96500} = 1.23\text{ V} \qquad [\because n = 2)$$

B COMPREHENSION TYPE

1. **(d)** In the H_2 - O_2 fuel cell, H_2 undergoes oxidation and O_2 undergoes reduction.

$E_{cell} = 1.23\text{ V} = E_{cathode} - E_{anode} = 0.40 - E_{anode}$

$\Rightarrow E_{anode} = -0.83\text{ V}$

2. **(b)** $\Delta G° = -nF\,E^o_{cell} = -(4) \times (96500C)(1.23\ V)\text{ J}.\ (n = 4)$

3. **(a)** Under ideal conditions, electrical work $= \Delta G = -23.7\text{kJ}$

Hence, number of moles of H_2 needed

$$= \frac{-23.7}{-237.39} = 0.1$$

V_{H_2} at 25°C and 1 atm $= \frac{nRT}{P} = 0.1 \times 0.0821 \times 298$

$= 2.45\,L$

4. **(d)** In the overall cell reaction concentration of OH^- ions is not involved. Hence, cell potential is independent of OH^- concentration.

5. **(b)** $\Delta S° = \frac{\Delta H° - \Delta G°}{T}$

$$= \frac{-285.8 \times 10^3 - (-237.39) \times 10^3}{298} = -162\ \text{JK}^{-1}$$

7. **(b)** Since Ksp of AgI is lower than that of AgCl, I^- ions will be precipitated first, which is complete at the inflexion point B. The precipitation of AgCl then commences at the point B.

8. **(c)** Precipitation of Cl^- starts after I^- ions are precipitated. Precipitation of I^- ions is complete at point B. Hence at point A, I^- ion is in small amount and Cl^- is almost unchanged from the start.

9. **(b)** In the solution containing three ions, I^-, Br^- and Cl^- the precipitation will be in this very order (Ksp : AgI < AgBr < AgCl). Thus, third end point (point of inflexion in the titration curve) will be obtained between points B and D.

10. **(c)** Moles of $AgNO_3$ added between the point B and point D correspond to the precipitation of Cl^- ions. Hence, the concentration of second precipitant (Cl^- ions) = moles of $AgNO_3$ added between B and D divided by volume of original solution in L.

11. **(a)** $KCl_{(aq)} + AgNO_{3(aq)}$ (excess)

$$\longrightarrow AgCl_{(s)} + KNO_{3(aq)}$$

The unreacted $AgNO_3$ is back titrated with KSCN solution.

$$AgNO_{3(aq)} + KSCN_{(aq)} \longrightarrow AgSCN_{(s)} + KNO_{3(aq)}$$

When Ag^+ ions are completely precipitated as AgSCN, the excess SCN^- ion reacts with Fe^{3+} to give red colour.

$$Fe^{3+}_{(aq)} + SCN^-_{(aq)} \longrightarrow Fe(SCN)^{2+}_{(aq)} \text{ red colour}$$

12. **(b)** Since *Ksp* (AgI) << *Ksp* (AgCl), I^- ions must be completely precipitated before the commencement of precipitation of Cl^- ions at point *B*. But in actual practice some Cl^- ions start precipitating along with I^- ions, thus consuming more volume of $AgNO_3$ than with same amount of KI alone. Thus, the calculated concentration of I^- ions in the mixture will be slightly greater than the actual value.

14. **(d)** $\therefore$ Anodic reaction : $Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$

$E° = -0.447$

Cathodic reaction : $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

$E° = 1.229 V$

$E°_{cell} = E°_{cathode} - E°_{anode}$

(both reduction potentials)

$= 1.229 - (-0.447)\ V = 1.676\ V$

15. **(a)** $Pb^{2+}{}_{(aq)} + Cu_{(s)} \longrightarrow Pb_{(s)} + Cu^{2+}{}_{(aq)}$

$E°_{cell}$ for this reaction $= E°_{Pb^{2+}/Pb^-} - E°_{Cu^{2+}/Cu}$

$= -0.126 - 0.342 = -0.468$ V.

Negative cell potential implies that the above cell reaction will not be spontaneous. In other words Cu can not act as sacrificial electrode for lead.

16. **(b)** Anodic reaction at iron hull :

$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$$

Fe oxidized in 1hour

$$= ZIt = \frac{55.85 \times 0.5 \times 1 \times 60 \times 60}{2 \times 96500} = 0.52g$$

17. **(d)** At the bottom of ocean, there is less availability of O_2. Hence, the reduction reaction

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ occurs to a small extent.

18. **(d)** $E°_{cell}$ for the reaction :

$$Fe_{(s)} + 2M^+{}_{(aq)} \longrightarrow Fe^{2+}_{(aq)} + M_{(s)}$$

will be maximum if metal M^+ is Ag^+ ion.

19. **(d)** Since $E°_{Cu^{2+}/Cu} > E°_{H^+/H_2}$, copper will not reduce H^+ into H_2.

20. **(b)** $Pb_{(s)} + 2H^+_{(aq)} \longrightarrow Pb^{2+} + H_2$

$$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{H^+/H^-} - \overset{\circ}{E}_{Pb^{2+}/Pb} = 0 - (-0.13) = 0.13 \text{ V}$$

Since $\overset{\circ}{E}_{cell} > 0$, the reaction would be spontaneous.

21. **(a)** For the cell reaction $Br_2 + Ni_{(s)} \longrightarrow Ni^{2+} + 2Br^-$,

$$\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{Br_2/Br^-} - \overset{\circ}{E}_{Ni^{2+}/Ni}$$

$= 1.09 - (-0.25) = 1.34$ V

$= E_{Br_2/Br^-} - E_{Ni^{2+}/Ni} = E_{Br_2/Br^-} - 0.0$

$\Rightarrow E_{Br_2/Br^-} = 1.34$ V

22. **(b)** $\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{F_2/F^-} - \overset{\circ}{E}_{Br^2/Br^-} = 2.87 - 1.09 = 1.78$ V

23. **(a)** For the reaction during electrolysis :

$$Na^+ + Cl^- \longrightarrow Na + \frac{1}{2}Cl_2$$

$$E_{cell} = \overset{\circ}{E}_{Na^+/Na} - \overset{\circ}{E}_{Cl_2/Cl^-} = -2.71 - 1.36 = -4.07 \text{ V}$$

24. **(a)**

25. **(c)** For a concentration cell, we have

$$E = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

$\therefore \quad 0.1182 = \dfrac{0.0591}{1}\log\dfrac{0.001}{C_1}$ [Here $n = 1$]

or $\log\dfrac{0.001}{C_1} = \dfrac{0.1182}{0.0591} = 2$

or $\log\dfrac{0.001}{C_1} = \log 10^2$

[Taking anti log of both sides 2 = log 10^2]

or $C_1 = \dfrac{0.001}{10^2} = 10^{-5}$ moles/litre

26. **(b)** Using the relation

$$E = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

$$E = \frac{0.0591}{n}\log\frac{0.1}{0.001}$$

$= 0.0591 \log 100$

$= 0.0591 \times 2$ [log 100 = 2]

$= 0.1182$ V.

27. **(a)** Since 0.1*M* $AgNO_3$ is 82% dissociated, so

$$[Ag^+] = \frac{0.1 \times 82}{100}$$

$= 0.082$ mole/litre

Let C_1 be the concentration of Ag^+ on right hand side due to solubility of AgCl. The EMF of cell is

$$E = \frac{0.0591}{n}\log\frac{C_2}{C_1}$$

or $$0.45 = \frac{0.0591}{1}\log\frac{0.082}{C_1} \qquad (\because n = 1)$$

or $C_1 = 2.008 \times 10^{-9}$ mole/litre

$0.1M$ KCl is 85% dissociated, so $[Cl^-] = \dfrac{0.1 \times 85}{100}$

$= 0.085$ mole/litre

∴ Solubility product $= [Ag^+]\,[Cl^-]$

$= 2.0 \times 10^{-9} \times 0.085 = 1.7 \times 10^{-10}$

28. **(b)** The heat or enthalpy of the reaction

$$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$= nF\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right]$$

$= 2 \times 96500\,(298 \times 0.000174 - 0.9647)$ (4.18J = Cal)

$= -42148$ Cal.

29. **(c)** The cell reactions for the passage of 2 Faradays, are

(1) $Pb_{(s)} + 2Ag\,Cl_{(s)} \rightarrow PbCl_{2(s)} + 2Ag_{(s)}$; $\Delta H_1 = ?$

(2) $Pb_{(s)} + 2Ag\,I_{(s)} \rightarrow PbI_{2(s)} + 2Ag_{(s)}$; $\Delta H_2 = ?$

(1) – (2) gives

$PbI_{2(s)} + 2AgCl_{(s)} \rightarrow PbCl_{2(s)} + 2AgI_{(s)}$

$\Delta H = \Delta H_1 - \Delta H_2$

$$\Delta H_1 = nF\left[T\left(\frac{\partial E_1}{\partial T}\right) - E_1\right]$$

$$= \frac{2 \times 96500\left[298 \times (-0.000186) - 0.4902\right]}{4.18}$$

$= -25183$ Cal

$$\Delta H_2 = nF\left[T\left(\frac{\partial E_2}{\partial T}\right) - E_2\right]$$

$$= \frac{2 \times 96500\left[298(-0.000127) - 0.2111\right]}{4.18}$$

$= -11489$ Cal

Hence, $\Delta H = \Delta H_1 - \Delta H_2 = -25183 - (-11489)$ Cal

$= -13694$ Cal.

30. **(a)** The reaction in Daniel's cell is

$$Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)} \qquad (n = 2)$$

Heat of the reaction may be expressed as

$$\Delta H = nF\left[T\left(\frac{\partial E}{\partial T}\right)_P - E\right]$$

$$= 2 \times 96500\left[\frac{288 \times \left(-4.28 \times 10^{-4}\right) - 1.0934}{4.18}\right]$$

$= -56187$ Cal

C REASONING TYPE

1. **(c)** On dilution, number of ions per millilitre decreases. Total number of ions increases only in case of weak electrolytes.
2. **(a)** Reason is the correct explanation of Assertion.
3. **(d)** Conductivity of solutions of different electrolytes in the same solvent and at a given temperature is different.
4. **(b)** The nature of the cathode can affect the order of discharge of ions.
5. **(c)** Electrons are not tightly held but are free to flow. Instead, kernels start vibrating which create hinderance to the flow of electrons. In case of electrolytes, dissociation and ionic mobilities increase with temperature.
6. **(b)** If redox reaction is spontaneous, ΔG is –ve and hence E^o is positive.

   $-\Delta G^o = nFE^o$ cell
7. **(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."
8. **(a)** At cathode : $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu(s)$ (Reduction)

   At anode : $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$ (Oxidation)
9. **(a)** $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

   As the time passes, concentration of Zn^{2+} keeps on increasing while that 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.
10. **(c)** On doubling the concentrations, the EMF will remain unchanged because $\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ will remain same.

Effect of concentration on electrode potential is found by Nernst equation.

11. **(d)** In dry cell, zinc acts as anode and carbon (graphite) rod as cathode. Dry cell has a potential of nearly 1.5 V.

12. **(b)** KCl/NaCl/NH_4Cl etc. cannot be used as salt bridge in a cell containing silver as one of the electrodes because they react to form a precipitate of AgCl.

13. **(d)** Production of electricity by thermal plants is not a very efficient method as a lot of heat energy is lost.

14. **(b)** Cathode : $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Anode : $4H_2O(l) + 4e^- \longrightarrow 2H_2 + 4OH^-(aq)$

Overall reaction being : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

15. **(c)** 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.

16. **(d)** Assertion is false, reason is true

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

18. **(c)** **Assertion** is true and reason is false

19. **(b)** Both assertion and reason are correct and reason is not the correct explanation of assertion.

D MULTIPLE CORRECT CHOICE TYPE

2. **(a)** Specific conductance $(\kappa) = \dfrac{\text{cell constant } (K)}{R \text{ (resistance)}}$;

$$\lambda_m = \frac{1000\kappa}{\text{molarity}};\ \lambda_e = \frac{1000K}{\text{Normality}}$$

Conductance = 1/R

3. **(b, d)** Smaller is the size of an ion having fixed charge, greater will be the extent of hydration and hence greater will be the size of the hydrated ion. Ionic conductance is inversely related to the size of hydrated ion.

4. **(b, c)** Cathode : $Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$

1 mole of Cu deposited ≡ 2 mole of electrons

$Hg^{2+}_{2(aq)} + 2e^- \longrightarrow 2Hg_{(\ell)}$

1 mole of $Hg_{(\ell)}$ deposited ≡ 1 mole of electrons

Anode (each cell) :

$2H_2O_{(\ell)} \longrightarrow 4H^+_{(aq)} + O_{2(g)} + 4e^-$;

1 mole of O_2 ≡ 4 mol of electrons

5. **(b, c, d)** Cathode : $Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$

$Fe^{3+}_{(aq)} + 3e^- \longrightarrow Fe_{(s)}$

Anode (in all the three cases) :

$H_2O_{(\ell)} \longrightarrow 2H^+_{(aq)} + \frac{1}{2}O_{2(g)} + 2e^-$

6. **(a)** Cathode : $2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^-$

Anode : $H_2O \rightarrow 2H^+ + \frac{1}{2}O_{2(g)} + 2e^-$

(b) Cathode : $Ag^2 + e^- \rightarrow Ag_{(s)}$

Anode : $Ag_{(s)} \rightarrow Ag^+ + e^-$

(c) Cathode : $Cu^{2+} + 2e^- \rightarrow Cu_{(s)}$

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

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

Anode : $H_2O \rightarrow 2H^+ + HO_2 + 2e^-$

8. **(c, d)** The cell reaction is :

$$2H^+_{(aq)} + Zn_{(s)} \rightarrow H_{2(s)} + Zn^{2+}_{(aq)}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} + \frac{0.0591}{2}\log\frac{[H^+]^2}{[Zn^{2+}]P_{H_2}}$$

9. **(b, c)** $2H_2O \rightleftharpoons 2H^+_{(aq)} + 2OH^-_{(aq)}$

Cathode : $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

Anode : $2OH^-_{(aq)} \longrightarrow H_2O_{(\ell)} + \frac{1}{2}O_{2(g)} + 2e^-$

1 mole of H_2O electrolysed ≡ 2 mol of electrons ≡ 2 F (effeciency = 100%)

1 mole of H_2O electrolysed ≡ 4 mol of electrons ≡ 4 F (effeciency = 50%)

Hence, 5 mole of H_2O ≡ 5 × 4 = 20F

Volume of gases (STP) = 5 × [22.4 + 11.2] = 168.0 L

11. **(a,b,c)** (a) Cell reaction :

$$2H_{(aq)}\quad Zn_{(s)} \longrightarrow H_{2(g)}\quad Zn^{2}_{(aq)}$$

Reaction quotient,

$$Q\quad \frac{P_{H_2}\times[Zn^{2}\ \ ]}{[H\ \ ]^{2}}\quad \frac{1\times 0.01}{0.1^{2}}\quad 1,\ \log Q = 0$$

(b) Cell reaction :

$$2Ag_{(aq)}\quad Cu_{(s)} \longrightarrow Cu^{2}_{(aq)}\quad 2Ag_{(s)}$$

$$Q\quad \frac{[Cu^{2}\ \ ]}{[Ag\ \ ]^{2}}\quad \frac{0.25}{(0.5)^{2}}\quad 1$$

(c) Cell reaction :

$$2H_{(aq)}\quad Cd_{(s)} \longrightarrow H_{2}\quad Cd^{2}_{(aq)}$$

$$Q\quad \frac{P_{H_2}\times[Cd^{2}\ \ ]}{[H\ \ ]^{2}}\quad \frac{1\times 0.01}{0.1^{2}}\quad 1$$

(d) Cell reaction :

$$2H_{(aq)}\quad Zn_{(s)} \longrightarrow H_{2}\quad Zn^{2}_{(aq)}$$

$$Q\quad \frac{P_{H_2}\times[Zn^{2}\ \ ]}{[H\ \ ]^{2}}\quad \frac{1\times 0.1}{0.1^{2}}\quad 10$$

12. **(b,d)** $Al_{(s)}\quad 3Ag_{(aq)} \longrightarrow Al^{3}_{(aq)}\quad 3Ag_{(s)}$

$$Q\quad \frac{[Al^{3}\ \ ]}{[Ag\ \ ]^{3}}\quad \frac{0.1}{0.1^{3}}\quad 10^{2}$$

15. **(b,d)** It is the concentration cell in respect to Ag^+ ions.

$$\text{Hence, } E_{cell}\quad 0.0592\log\frac{[Ag\ \ ]_2}{[Ag\ \ ]_2}$$

$$K_{sp}(Ag_2C_2O_4)\quad [Ag\ \ ]^{2}_{2}[C_2O^{2-}_{4}]$$

$$= [Ag\ \ ]^{2}_{2}\times\frac{[Ag\ \ ]_2}{2}$$

or $\quad [Ag\ \ ]_2\quad \left[2K_{sp}(Ag_2C_2O_4)\right]^{1/3}$

$$K_{sp}\,(AgI)\quad [Ag^{+}]_1[I^{-}]$$

$$= [Ag^{+}]^{2}$$

or $\quad [Ag\ \ ]_1\quad [K_{sp}(AgI)]^{1/2}$

16. **(b, c, d)** It is concentration cell with respect to Ag^+ ions.

$[Ag^+]_{anode} = [K_{sp}\,[AgCl]]^{1/2} = (1.0 \times 10^{-10})^{1/2}\,M$

$= 1.0 \times 10^{-5}\,M$

$[Ag^+]_{cathode} = 1.0\,M$

$E_{cell} = 0.0592 \log [Ag^+]_{cathode}/[Ag^+]_{anode}$

17. **(a, d)** At higher concentration of metal amalgam, oxidation of the metal occurs whereas at lower concentration of amalgam, reduction of metal ions in the solution takes place.

18. **(c, d)** Cathodic reaction :

$$Hg_2Cl_{2(s)}\quad 2e^{-} \rightarrow 2Hg_{(\ell)}\quad 2Cl^{-}$$

Anodic reaction :

$$2Ag_{(s)}\quad 2Cl^{-} \rightarrow 2AgCl_{(s)}\quad 2e^{-}$$

Cell reaction ;

$$Hg_2Cl_{2(s)}\quad 2Ag_{(s)} \rightarrow 2Hg_{(\ell)}\quad 2AgCl_{(s)}$$

In case of same concentration of Cl^- ions in the two half cells, E_{cell} is independent of $[Cl^-]$. Other substances are either pure solids or liquids, which have unit activities irrespective of their amounts. Hence E_{cell} is independent of the amounts of pure solids or liquids involved in the reaction.

19. **(a,b,d)** The standard refrence potential of normal calomel electrode is 0.2415 V.

20. **(a,b,c,d)** All the given statements are correct.

21. **(a,b,c)** For a weak electralyte $K\quad \frac{\alpha^{2}}{V}$

$$\text{or}\quad \alpha\quad (KV)^{\frac{1}{2}}$$

$$\text{or}\quad \alpha\quad K_1(V)^{\frac{1}{2}}$$

$$\text{or}\quad \alpha\quad (V)^{\frac{1}{2}}$$

22. **(a,b,c,d)** All these are correct.

23. **(a,b,c)** Hydrogen electrode is an electrode that is reversible with respect to cation (H^+ ion).

E MATRIX-MATCH TYPE

1. **A - q ; B - p ; C - s ; D - r**

(A) For strong electrolytes λ_m and molarity (C) are related by Onsagar's eq. as :

$$\lambda^{o}{}_{m} = \lambda^{\circ}{}_{m} - k\sqrt{C}$$

A plot of λ_m *Vs* $\sqrt{C}$ (abscissa) would be a straight line with intercept on y-axis = $\overset{\circ}{\lambda}_m$

(B) For weak electrolytes (like C_2H_5COOH), λ_m *Vs* $\sqrt{C}$ is a curve which can not be extrapolated to $C = 0$.

From Kohlrausch law, λ° (C_2H_5COOH)

$$= \overset{\circ}{\lambda}_{C_2H_5COO^-} + \overset{\circ}{\lambda}_{H^+}$$

2. **A - s ; B - r ; C - p ; D - q**

KCl is a strong electrolyte and CH_3COOH a weak electrolyte. See Q.1

3. **A - r ; B - s ; C - p ; D - q**

(A) For the Cell reaction :

$$Cd^{2+}{}_{(aq)} + 2Ag_{(s)} \longrightarrow 2Ag^{+}{}_{(aq)} + Cd_{(s)}$$

$$E^\circ{}_{cell} = E^\circ{}_{cathode} - E^\circ{}_{anode} = -0.40 - 0.80 = -1.20\ V$$

Since $\overset{\circ}{E}_{cell}$ is negative, the reaction will be non-spontaneous.

(B) Reaction quotient (Q) = $\dfrac{[Ag^+]^2}{[Cd^{2+}]} = \dfrac{0.1 \times 0.1}{0.1} = 0.1$

(C) $E_{cell} = \overset{\circ}{E}_{cell} - \dfrac{0.0591}{2}\log\dfrac{[Ag^+]}{[Cd^{2+}]}$

$$= -1.20V - \frac{0.0591}{2}\log\frac{0.1^2}{0.1} = -1.17V$$

(D) See (A)

4. **A - r ; B - s ; C - p ; D - q**

(A) $2Al + 3Cu^{2+} \longrightarrow 2Al^{3+} + 3Cu$

$$Q = \frac{[Al^{3+}]^2}{[Cu^{2+}]^3} = \frac{0.1 \times 0.1}{0.2 \times 0.2 \times 0.2} = 1.25$$

(B) $Cd_{(s)} + 2Fe^{3+}{}_{(aq)} \longrightarrow Cd^{2+}{}_{(aq)} + 2Fe^{2+}{}_{(aq)}$

$$Q = \frac{[Cd^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2} = \frac{0.1 \times 0.1^2}{0.01^2} = 10$$

(C) $Cd_{(s)} + 2Ag^{+}{}_{(aq)} \longrightarrow Cd^{2+} + 2Ag_{(s)}$

$$Q = \frac{[Cd^{2+}]}{[Ag^+]^2} = \frac{0.01}{0.1^2} = 1$$

(D) $H_2(10atm) + 2H^+(1M) \longrightarrow$

$$2H^{+}{}_{(aq)}(0.1M) + H_2(1\ atm)$$

$$Q = \frac{[H^+]^2{}_{right} \times P_{H_2(right)}}{[H^+]^2{}_{left} \times P_{H_2(left)}} = \frac{0.1^2 \times 1}{1.0^2 \times 10} = 0.001$$

5. **A - q ; B - p; C - s; D - r**

(A) $Sn^{2+} + 2e^- \longrightarrow Sn;\ E^\circ = -0.14V$ ......(*i*)

$Sn^{4+} + 2e^- \longrightarrow Sn^{2+};\ E^\circ = 0.13V$ .....(*ii*)

(i) + (ii), $Sn^{4+} + 4e^- \longrightarrow Sn$;

$$E^\circ = \frac{n_1E^\circ{}_1 + n_2E^\circ{}_2}{4} = \frac{2 \times (-0.14) + 2 \times 0.13}{4}$$

$= -0.005\ V$

Hence, $E^\circ_{Sn^{4+}/Sn} = -0.005V$

(B) $\overset{\circ}{E}_{Sn/Sn^{4+}} = -\overset{\circ}{E}_{Sn^{4+}/Sn} = 0.005V$

(C) Disproportionation reaction :

$$2Sn^{2+} \longrightarrow Sn^{4+} + Sn$$

$$E^{o}{}_{cell} = E^{o}{}_{Sn^{2+}/Sn} - E^{o}{}_{Sn^{4+}/Sn^{2+}}$$

= $-0.14 - 0.13 = -0.27V$; the reaction is non-spontaneous

Since $\overset{\circ}{E}_{Sn/Sn^{4+}} > 0$, oxidation of Sn to Sn^{4+} will be spontaneous.

6. **A-s; B-r; C-p; D-q**

(A) $2H^+ + 2e^- \longrightarrow H_2$

$$E_{H^+/H_2} = E^o - \frac{0.0591}{2}\log\frac{P_{H2}}{[H^+]^2}$$

$$= 0 - \frac{0.0591}{2}\log\frac{1}{[H^+]^2} = 0.0591 \quad \log \quad [H^+]$$

Since maximum activity of $H^+ = 1$, So $E_{H^+/H_2} = 0$

(B) $[H^+]_{\min imum} = 10^{-14} M$;

$$E_{\text{minimum}} = 0.0591 \log 10^{-14} = -0.0591 \times (-14)$$

$$= -0.827 \; V$$

(C) For $KCl_{(aq)}$ $[1M]$, pH = 7 $[H^+] = 10^{-7} M$

Hence, $E = 0.0591 \log 10^{-7} = 0.0591 \times (-7)$

$$= -0.414 \; V$$

(D) $E = -\frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2}$

$$= \frac{-0.0591}{2}\log\frac{4}{1^2} = -0.0591 \log 2$$

$$= -0.0591 \times 0.301 = -0.018 V$$

7. **A - r; B - s; C - p; D - q**

(A) On removing the salt bridge the circuit is broken. Hence $E_{cell} = 0$

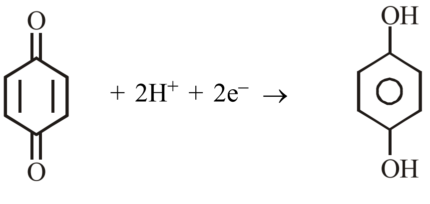
(B) In the absence of salt bridge, junction potential comes into play. It opposes the cell potential.

(C) Calomel electrode :

$$Hg_2Cl_{2(s)} + 2e^- \longrightarrow 2Hg_{(l)} + 2Cl^-_{(aq)}$$

The electrode is reversible to Cl^- ion.

(D) Quinhydrone electrode :



Quinone [Q] Hydroquinone [QH_2]

$$E_{Quin} = E^o_{Quin} - \frac{0.0591}{2}\log\frac{[QH_2]}{[Q]\times[H^+]^2}$$

$$= E^o_{Quin} + 0.0591 \quad \log \quad [H^+]$$

Quinhydrone is the equimolar mixture of Q and QH_2. Hence $[Q] = [QH_2]$

The electrode is reversible to H^+ ion.

8. **A-q, B-p, C-s, D-r**

(A) For the cell reaction

$$Cu^{2+} + 2Cl^- \longrightarrow Cu + Cl_2$$

$$E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Cl_2/Cl^-} = 0.34 - 1.36 = -1.02 \, V$$

Thus, the reaction would be non-spontaneous and can be made to occur by applying potential greater than 1.02 V.

(B) E°_{Cell} for the reaction :

$$Cu + Cl_2 \longrightarrow Cu^{2+} + 2Cl^- \text{ is} 1.02 V.$$

Hence, this reaction is spontaneous and can be used to produce electricity in a galvanic cell.

(C) $2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$

$$E^\circ_{Cell} = E^\circ_{Cl_2/Cl^-} - E^\circ_{I_2/I^-} = 1.36 - 0.54 = 0.82V$$

The reaction is feasible and liberated I_2 gives violet colour with starch solution.

(D) $2Br^- + Cl_2 \longrightarrow Br_2 + 2Cl^-$

$$E^\circ_{Cell} = 1.36 - 1.08 = 0.28 V$$

The reaction is spontaneous. Liberated Br_2 dissolves in CCl_4 to produce brown colour.

F NUMERIC/INTEGER ANSWER TYPE

1. $AgBr_{(s)} \rightleftharpoons Ag^+ + Br^-$; $[Ag^+][Br^-] = 5.0\times10^{-13}$ .... (i)

$AgCNS_{(s)} \rightleftharpoons Ag^+ + CNS^-$

$[Ag^+][CNS^-] = 1\times10^{-12}$ .... (ii)

From (i) and (ii), $\frac{[CNS^-]}{[Br^-]} = \frac{1\times10^{-12}}{5\times10^{-13}} = 2$ .... (iii)

For electrical neutrality of the solution,

$[Ag^+] = [Br^-] + [CNS^-]$

or $\frac{[Ag^+]}{[Br^-]} = 1 + \frac{[CNS^-]}{[Br^-]} = 1 + 2 = 3$

Hence, $[Ag^+] = 3[Br^-]$ .... (iv)

From (i) & (iv), $[Br^-] = 4.1\times10^{-7}\ \text{mol L}^{-1}$

$= 4.1\times10^{-4}\ \text{mol m}^{-3}$ $(\because 1\text{L} = 10^{-3}\text{m}^3)$ ....(v)

From (iii) & (v), $[CNS^-] = 2\times4.1\times10^{-7}$

$= 8.2\times10^{-7}\ \text{mol L}^{-1} = 8.2\times10^{-4}\ \text{mol m}^{-3}$

and $[Ag^+] = [Br^-] + [CNS^-] =$

$4.1\times10^{-4} + 8.2\times10^{-4} = 12.3\times10^{-4}\ \text{mol m}^{-3}$

Specific conductance or conductivity (κ) = Molar conductance × molar concentration

$\kappa(Ag^+) = \lambda^\circ_{Ag} \times [Ag^+]$

$= 6.0\times10^{-3}\ \text{sm}^2\text{mol}^{-1} \times 12.3\times10^{-4}\ \text{mol m}^{-3}$

$= 73.8\times10^{-7}\ s\,m^{-1}$

$\kappa(Br^-) = \lambda^\circ_{Br^-} \times [Br^-]$

$= 8\times10^{-3}\ \text{s m}^2\text{mol}^{-1} \times 4.1\times10^{-4}\ \text{mol m}^{-3}$

$= 32.8\times10^{-7}\ \text{s m}^{-1}$

$\kappa(CNS^-) = \lambda^\circ_{CNS^-} \times [CNS^-]$

$= 7\times10^{-3}\ \text{s m}^2\text{mol}^{-1} \times 8.2\times10^{-4}\ \text{mol m}^{-3} = 57.4\ \text{s m}^{-1}$

Total conductivity of solution

$= \kappa(Ag^+) + \kappa(Br^-) + \kappa(CNS^-)$

$= 73.8\times10^{-7} + 32.8\times10^{-7} + 57.4\times10^{-7}\ \text{s m}^{-1}$

$= \mathbf{164.0}\times10^{-7}\ \text{s m}^{-1}$

2. The cell reaction is:

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}$$

	$2Fe^{3+}$	Hg_2^{2+}	$2Fe^{2+}$
Initial	1.0×10^{-3}M	0	0
Equib. conc.	$1.0\times10^{-3} - 2x$	x	$2x$

$[Fe^{3+}]_{Equi} = 1.0\times10^{-3} - 2x$

$= 1.0\times10^{-3} \times \frac{5}{100} = 5\times10^{-5}\text{M} \Rightarrow x = 4.75\times10^{-4}\text{M}$

$[Hg_2^{2+}] = x = 4.75\times10^{-4}\text{M}$

$[Fe^{2+}] = 2x = 2\times4.75\times10^{-4} = 9.50\times10^{-4}\text{M}$

Oxidation reaction: $2Hg \longrightarrow Hg_2^{2+} + 2e^-$

Reduction reaction: $2Fe^{3+} + 2e^- \longrightarrow 2Fe^{2+}$

K_{eq} for the cell reaction $= \frac{[Hg_2^{2+}][Fe^{2+}]^2}{[Fe^{3+}]^2}$

$= \frac{4.75\times10^{-4}\times(9.5\times10^{-4})^2}{(5\times10^{-5})^2} = 0.1715\text{M}$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log K_e$ [At equib. $E_{cell} = 0.0$]

$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Hg_2^{2+}/Hg} - \frac{0.0591}{2}\log 0.1715$

$E^\circ_{Hg_2^{2+}/Hg} = E^\circ_{Fe^{3+}/Fe^{2+}} - \frac{0.0591}{2}\log 0.1715$

$= 0.77 - 0.0295\log 0.1715 = \mathbf{0.793}\boldsymbol{V}$.

3. Mass of H_2SO_4 solution before recharge

$= 3000\times1.140 = 3420$ g

Mass of H_2SO_4 in this solution = $\frac{20}{100} \times 3420 = 684\text{g}$

Mass of H_2SO_4 solution after recharge
$= 3000 \times 1.284 = 3852$ g

Mass of H_2SO_4 in this solution $= \frac{38}{100} \times 3852 = 1463.76\text{g}$

Increase in mass of $H_2SO_4 = 1463.76 - 684 = 779.76\text{g}$
During recharge of battery, the following reactions occur.

Cathodic reaction: $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{2-}$

Anodic reaction:

$PbSO_4 + 2H_2O \longrightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

Net reaction: $2PbSO_4 + 2H_2O \longrightarrow PbO_2 + 2H_2SO_4$

2 mol of H_2SO_4 are produced per 2 mole of electrons.
Using faraday's first law,

$w = zit$ or $779.76 = \frac{2 \times 98}{2 \times 96500} \times 5 \times t_{(s)}$

$\Rightarrow t = 159135$ sec. = **44.20 hrs.**

4. Dissociation of the complex ion is as:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + NH_3$$

Instability constant, $K_{ins} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$

Since K_{ins} of the complex ion is of the order of 10^{-8}, the complex ion is highly stable and almost all Ag^+ ions would exist in the form of complex ion.

Hence, $[Ag(NH_3)_2^+] = 0.10M$

$[NH_3] = 1.00 - 2 \times 0.10 = 0.80M$

$K_{ins} = 6.0 \times 10^{-8} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]} = \frac{[Ag^+] \times 0.80^2}{0.10}$

or $|Ag^+| = 0.94 \times 10^{-8} M$

The half cell reaction is : $Ag^+ + e^- \longrightarrow Ag_{(s)}$

$$E_{Ag^+/Ag} = E^\circ_{Ag^+/Ag} + \frac{0.0591}{1} \log[Ag^+]$$

$= 0.80 + 0.0591 \log 0.94 \times 10^{-8} = \mathbf{0.38\ V}$

5. Cathodic reaction: $Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$

Anodic reaction: $H_{2(g)} \longrightarrow 2H^+_{(aq)} + 2e^-$

$$E^\circ = E^\circ_{cell} = E^\circ_{Cl_2/Cl^-} - E^\circ_{H^+/H_2} = 1.36 - 0 = 1.36V$$

From Gibbs-Helmholtz equation,

$$\Delta G^\circ = \Delta H^\circ + T\left[\frac{d(\Delta G^\circ)}{dT}\right]_p \quad \text{.........(i)}$$

But $\Delta G^\circ = -nFE^\circ$

Hence (i) becomes, $-nFE^\circ = \Delta H^\circ + T\left[\frac{d(-nFE^\circ)}{dT}\right]_p$

$$-nFE^\circ = \Delta H^\circ - nFT\left(\frac{dE^\circ}{dT}\right)_p$$

$$\Delta H^\circ = -nF\left[E^\circ - T\left(\frac{dE^\circ}{dT}\right)_p\right]$$

$= -2 \times 96500\,[1.36 - 298 \times (-1.25 \times 10^{-3})]$
$= -3.3437 \times 10^5$ J $= \mathbf{-3.344 \times 10^2}$ **kJ.**

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