Additional Problems for Self Practice (APSP)

✍ Marked Questions may have for Revision Questions.

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Marks: 100 **Max. Time : 1 Hour**

Important Instructions:

A. General :

1. The test paper is of **1** hour duration.
2. The Test Paper consists of **25** questions and each questions carries **4** Marks. Test Paper consists of **Two** Sections.

B. Test Paper Format and its Marking Scheme:

1. Section-1 contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which **ONE** is correct. For each question in Section-1, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. In all other cases, minus one **(–1)** mark will be awarded.
2. Section-2 contains **5** questions. The answer to each of the question is a **Numerical Value**. For each question in Section-2, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. No negative marks will be answered for incorrect answer in this section. In this section answer to each question is **NUMERICAL VALUE** with two digit integer and decimal upto two digit. If the numerical value has more than two decimal places **truncate/round-off** the value to **TWO** decimal placed.

SECTION-1

This section contains **20** multiple choice questions. Each questions has four choices (1), (2), (3) and (4) out of which Only **ONE** option is correct.

1.✍ The standard electrode potentials (reduction) of Pt/Fe^{3+}, Fe^{2+} and Pt/Sn^{4+}, Sn^{2+} are + 0.77 V and 0.15 V respectively at 25° C. The standard EMF of the reaction $Sn^{4+} + 2Fe^{2+} \longrightarrow Sn^{2+} + 2Fe^{3+}$ is

(1) – 0.62 V (2) – 0.92 V (3) + 0.31 V (4) + 0.85 V

2.✍ Which is/are correct among the following?

Given, the half cell emf's $E^0_{Cu^{+2}\,|\,Cu} = 0.337$, $E^0_{Cu^{+1}\,|\,Cu} = 0.521$

(1) Cu^{+1} disproportionates (2) Cu and Cu^{2+} comproportionates.

(3) $E^0_{Cu\,|\,Cu^{+2}} + E^0_{Cu^{+1}\,|\,Cu}$ is positive (4) (1) and (3) Both

3. How many g of silver will be displaced from a solution of AgNO$_3$ by 4 g of magnesium?

(1) 18 g (2) 4 g (3) 36 g (4) 16 g

4. The electrode potentials for $Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)}$ and $Cu^+_{(aq)} + e^- \longrightarrow Cu_{(s)}$ are +0.15 V and + 0.50V respectively. The value of $E^o_{Cu^{2+}/Cu}$ will be :

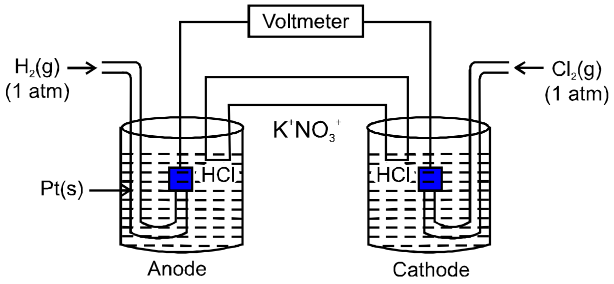
(1) 0.500 V (2) 0.325 V (3) 0.650 V (4) 0.150 V

5.✍ How much will the reduction potential of a hydrogen electrode change when its solution initially at pH = 0 is neutralised to pH = 7 at 25^{o}C ?

(1) Increases by 0.059 V (2) Decreases by 0.059 V

(3) Increases by 0.41 V (4) Decreases by 0.41 V

6. Consider the following Galvanic cell as shown in figure. By what will value the cell voltage change when concentration of ions in anodic and cathodic compartments are both increased by factor of 10 at 298 K
(1) + 0.591 V
(2) – 0.0591 V
(3) – 0.1182 V
(4) 0 V

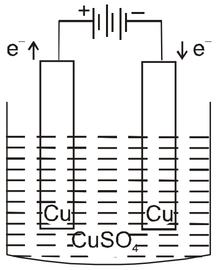


7.✍ In a cell that utilise the reaction : $Zn\ (s) + 2H^+\ (0.1M) \longrightarrow Zn^{2+}\ (aq) + H_2\ (g)$
addition of 0.1 M H_2SO_4 to cathode compartment will :
(1) increase the cell emf and shift equilibrium to the left.
(2) lower the cell emf and shift equilibrium to the right.
(3) increase the cell emf and shift equilibrium to the right.
(4) lower the cell emf and shift equilibrium to the left.

8. The chemical reaction, $2AgCl(s) + H_2\ (g) \longrightarrow 2HCl\ (aq) + 2Ag\ (s)$
taking place in a galvanic cell (under standard condition) is represented by the notation.
(1) Pt(s) | H_2 (g), 1 bar | 1 M KCl (aq) | AgCl(s) | Ag (s)
(2) Pt(s) | H_2 (g), 1 bar | 1 M HCl (aq) | 1 M Ag^+ (aq) | Ag (s)
(3) Pt(s) | H_2 (g), 1 bar | 1 M HCl (aq) | AgCl (s) | Ag (s)
(4) Pt(s) | H_2 (g), 1 bar | 1 M HCl (aq) | Ag (s) | AgCl (s)

9.✍ For the cell, Pt | H_2 (g) | H^+ (aq) || Cu^{2+} (aq) | Cu (s) ; $E^o_{Cu/Cu^{2+}} = -0.34$ V.
Then calculate approximate value of K_{eq} ?
(1) 5×10^{12} (2) 2×10^{11} (3) 2×10^{-11} (4) 5×10^{-12}

10.✍ In the given figure, the electrolytic cell contains 1 L of an aqueous 1 M Copper (II) sulphate solution. If 0.4 mole of electrons are passed through cell, the concentration of copper ion after passage of the charge will be :
(1) 0.4 M
(2) 0.8 M
(3) 1.0 M
(4) 1.2 M



11.✍ Cost of electricity for the production of 'X' litre H_2 at NTP at cathode is Rs. X. Then cost of electricity for the production 'X' litre O_2 gas at NTP at anode will : (assume 1 mole of electrons as one unit of electricity)
(1) 2X (2) 4X (3) 16X (4) 32X

12.✍ A current of 0.1 A was passed for 965 second through a solution of Cu^+ solution and 0.03175 g of copper was deposited on the cathode. Calculate the current efficiency for the copper deposition. (Cu – 63.5)
(1) 79% (2) 39.5 % (3) 63.25% (4) 50%

13. A current of 9.95 amp following for 10 minutes, deposits 3 g of a metal. Equivalent weight of the metal is :
(1) 12.5 (2) 18.5 (3) 21.5 (4) 48.5

14. The specific conductance of a N/10 KCl at 25°C is 0.0112 $ohm^{-1}\ cm^{-1}$. The resistance of cell containing solution at the same temperature was found to be 55 ohms. The cell constant will be
(1) 6.16 cm^{-1} (2) 0.616 cm^{-1} (3) 0.0616 cm^{-1} (4) 616 cm^{-1}

15. The equivalent conductance of a N/10 NaCl solution at 25ºC is $10^{-2}\ Sm^2eq^{-1}$. Resistance of solution contained in the cell is 50 Ω. Cell constant is:
(1) 50 m^{-1} (2) $50 \times 10^{-6}\ m^{-1}$ (3) $50 \times 10^{-3}\ m^{-1}$ (4) $50 \times 10^{3}\ m^{-1}$

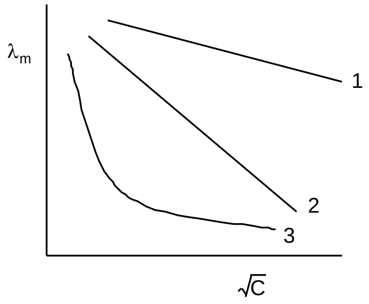
16.✍ For an NaCl (aq.) solution, which of the following quantities go to zero as NaCl concentration goes to zero? (Assume the solvent's contribution to conductivity has been subtracted off).
(1) $\wedge_m$ (2) κ (3) $\lambda_m(Na^+)$ (4) $\lambda_m(C\ell^-)$

17. Find the value of λ^{α}_{eq} for potashalum.

Given : $\lambda^{\alpha}_{m(K^+)} = 73.5\ \Omega^{-1}cm^2\ mol^{-1}$, $\lambda^{\alpha}_{m(Al^{+3})} = 198\ \Omega^{-1}cm^2\ mol^{-1}$, $\lambda^{\alpha}_{m(SO_4^{-2})} = 160\ \Omega^{-1}cm^2\ mol^{-1}$

(1) $145.6\Omega^{-1}cm^2\ eq^{-1}$	(2) $1165\ \Omega^{-1}cm^2\ eq^{-1}$
(3) $532\ \Omega^{-1}cm^2\ eq^{-1}$	(4) $195.5\ \Omega^{-1}cm^2\ eq^{-1}$

18. A graph of molar conductivity of three electrolytes (NaCl, HCl and NH_4OH) is plotted against $\sqrt{C}$



Which of the following options is correct ?

	(1)	(2)	(3)		(1)	(2)	(3)
(1)	NaCl	HCl	NH_4OH	(2)	NH_4OH	NaCl	HCl
(3)	HCl	NaCl	NH_4OH	(4)	NH_4OH	HCl	NaCl

19. 0.1 molar solution NaCl filled in different conductivity cell. Order of equivalent conductance of NaCl solution is :

	Cell – 1	**Cell – 2**	**Cell – 3**
A	5 cm^2	6 cm^2	10 cm^2
l	2 cm	3 cm	4 cm^2
Equivalents : conductance	a	b	c

A = Area of cross section, l = distance between two electrode.

(1) Cell – 1 > Cell – 2 > Cell – 3	(2) Cell – 1 = Cell – 2 = Cell – 3
(3) Cell – 1 > Cell – 3 < Cell – 2	(4) None of these

20. Acetic acid is titrated with NaOH solution. Which of the following statement is correct for this titration?
(1) conductance increases upto equivalence point, then it decreases
(2) conductance increases upto equivalence point, then it increases
(3) first conductance increases slowly upto equivalence point and then increases rapidly
(4) first conductance increases slowly upto equivalence point and then drops rapidly .

SECTION-2

This section contains **5** questions. Each question, when worked out will result in **Numerical Value**.

21.

$$\begin{tikzcd} ClO_3^- \arrow[r, "0.54\ V"] \arrow[rrr, bend right, "E°"'] & ClO^- \arrow[r, "0.45\ V"] \arrow[rr, bend right, "0.76\ V"'] & \frac{1}{2}Cl_2 \arrow[r, "1.07V"] & Cl^- \end{tikzcd}$$

The E° in the given figure is X. Report the answer as 10X.

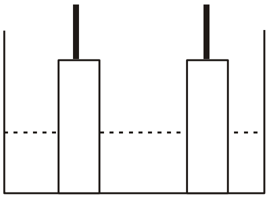
22. The standard reduction potential for Zn^{+2}/Zn ; Ni^{+2}/Ni ; and Fe^{+2}/Fe are –0.76V, –0.23V, –0.44V respectively. In how many of the following, the reaction $X + Y^{+2} \longrightarrow X^{+2} + Y$ will be non-spontaneous:

	X	Y
(I)	Ni	Fe
(II)	Ni	Zn
(III)	Fe	Zn
(VI)	Zn	Ni

23. A current is passed through 2 voltameters connected in series. The first voltameter contains XSO_4 (aq.) and second has Y_2SO_4 (aq.). The relative atomic masses of X and Y are in the ratio of 2 : 1. The ratio of the mass of X liberated to the mass of Y liberated is a : b. Find a + b

24.✍ The ratio of wt. deposited of metal x, y, z on passing electric charge in ratio of 1 : 2 : 3 respectively is 3 : 2 : 1 then the ratio of equivalent weights for the above metals respectively is a : b : c. Find a + b + c

25.✍ A resistance of 50Ω is registered when two electrodes are suspended into a beaker containing a dilute solution of a strong electrolyte such that exactly half of the them are submerged into solution as shown in figure. If the solution is diluted by adding pure water (negligible conductivity) so as to just completely submerge the electrodes, the new resistance offered by the solution would be :



Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.										
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.										
Que.	**21**	**22**	**23**	**24**	**25**					
Ans.										

PART - II : JEE (MAIN) / AIEEE OFFLINE PROBLEMS (PREVIOUS YEARS)

1. For the following cell with hydrogen electrodes at two different pressure $p_1$and p_2,

$$\underset{p_1}{\mathrm{Pt} \mid \mathrm{H_2(g)}} \mid \underset{1M}{\mathrm{H^+(aq)}} \mid \underset{p_2}{\mathrm{H_2(g)}} \mid \mathrm{Pt}$$

emf is given by : **[AIEEE 2002, 3/225]**

(1) $\frac{RT}{F}\log_e\frac{p_1}{p_2}$ (2) $\frac{RT}{2F}\log_e\frac{p_1}{p_2}$ (3) $\frac{RT}{F}\log_e\frac{p_2}{p_1}$ (4) $\frac{RT}{2F}\log_e\frac{p_2}{p_1}$

2. Which of the following reactions is possible at anode : **[AIEEE 2002, 3/225]**

(1) $2\,Cr^{3+} + 7H_2O \rightarrow Cr_2O_7^{2-} + 14H^+$ (2) $F_2 \rightarrow 2F^-$

(3) $\frac{1}{2}O_2 + 2H^+ \rightarrow H_2O$ (4) displacement reaction

3. For a cell given below : **[AIEEE 2002, 3/225]**

$$\underset{-}{\mathrm{Ag} \mid \mathrm{Ag^+}} \parallel \underset{+}{\mathrm{Cu^{2+}} \mid \mathrm{Cu}}$$

$Ag^+ + e^- \longrightarrow Ag$ $E^o = x$

$Cu^{2+} + 2e^- \longrightarrow Cu,$ $E^o = y$

The value of E^o_{cell} is :

(1) x + 2y (2) 2x + y (3) y –x (4) y – 2x

4. For a cell reaction involving a two electron change, the standard emf of the cell is found to be 0.295 V at 25°C. The equilibrium constant of the reaction at 25°C will be : **[AIEEE 2003, 3/225]**

(1) 1×10^{-10} (2) 29.5×10^{-2} (3) 10 (4) 1×10^{10}

5. Standard electrode potentials of three metals A, B and C are +0.5 V, –3.0 V and –1.2 V respectively. The reducing power of these metals is in the order : **[AIEEE 2003, 3/225]**

(1) B > C > A (2) A > B > C (3) C > B > A (4) A > C > B

6. Consider the following Eº values :

$E^0_{Fe^{3+}/Fe^{2+}} = +0.77$ V ; $E^0_{Sn^{2+}/Sn} = -0.14$ V

Under standard conditions, the cell potential for the reaction given below is : **[AIEEE 2004, 3/225]**

$Sn_{(s)} + 2Fe^{3+}_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + Sn^{2+}_{(aq)}$

(1) 1.68 V (2) 1.40 V (3) 0.91 V (4) 0.63 V

7. The limiting molar conductivities Λ^o for NaCl, KBr and KCl are 126, 152 and 150 S cm^2 mol^{-1} respectively. The value of Λ^o for NaBr is : **[AIEEE 2004, 3/225]**

(1) 128 S cm^2 mol^{-1} (2) 176 S cm^2 mol^{-1} (3) 278 S cm^2 mol^{-1} (4) 302 S cm^2 mol^{-1}

8. In a cell that utilizes the reaction $Zn_{(s)} + 2H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$, addition of H_2SO_4 to cathode compartment will : **[AIEEE 2004, 3/225]**

(1) lower the E and shift equilibrium to the left.
(2) lower the E and shift the equilibrium to the right.
(3) increase the E and shift the equilibrium to the right.
(4) increase the E and shift the equilibrium to the left.

9. The $E^0_{M^{3+}/M^{2+}}$ values for Cr, Mn, Fe and Co are – 0.41, + 1.57, + 0.77 and + 1.97 V respectively. For which one of these metals, the change in oxidation state from +2 to +3 is easiest :**[AIEEE 2004, 3/225]**

(1) Cr (2) Mn (3) Fe (4) Co

10. Aluminium oxide may be electrolysed at 1000ºC to furnish aluminium metal (At.Mass of Al = 27 amu ; 1 Faraday = 96,500 Coulombs). The cathode reaction is $Al^{3+} + 3e^- \rightarrow Al^0$. To prepare 5.12 kg of aluminium metal by this method, one would require : **[AIEEE–2005, 3/225]**

(1) 5.49×10^7 C of electricity (2) 1.83×10^7 C of electricity
(3) 5.49×10^4 C of electricity (4) 5.49×10^{10} C of electricity

11. The molar conductivities Λ^0_{NaOAc} and Λ^0_{HCl} at infinite dilution in water at 25°C are 91.0 and 426.2 Scm^2/mol respectively. To calculate Λ^0_{HOAc}, the additional value required is : **[AIEEE–2006, 3/165]**

(1) $\Lambda^0_{H_2O}$ (2) Λ^0_{KCl} (3) Λ^0_{NaOH} (4) Λ^0_{NaCl}

12. Given data is at 25°C :

$Ag + I^- \rightarrow AgI + e^-$; E° = 0.152 V
$Ag \rightarrow Ag^+ + e^-$; E° = – 0.800 V

What is the value of log K_{sp} for AgI : (Take $\frac{0.474}{0.059} = 8.065$) **[AIEEE–2006, 3/165]**

(1) – 8.12 (2) + 8.612 (3) – 37.83 (4) – 16.13

13. Resistance of a conductivity cell filled with a solution of an electrolyte of concentration 0.1 M is 100 Ω. The conductivity of this solution is 1.29 Sm^{-1}. Resistance of the same cell when filled with 0.02 M of the same solution is 520 Ω. The molar conductivity of 0.02 M solution of the electrolyte will be : (Take $\frac{129}{520} = 0.248$) **[AIEEE–2006, 3/165]**

(1) 124×10^{-4} Sm^{2}mol^{-1} (2) 1240×10^{-4} Sm^{2}mol^{-1}
(3) 1.24 Sm^{2}mol^{-1} (4) 12.4×10^{-4} Sm^{2}mol^{-1}

14. The equivalent conductances of two strong electrolytes at infinite dilution in H_2O (where ions move freely through a solution) at 25°C are given below : **[AIEEE–2007, 3/120]**

$\Lambda^0_{CH_3COONa} = 91.0$ Scm^2/equiv and $\Lambda^0_{HCl} = 426.2$ Scm^2/equiv

What additional information/quantity one needs to calculate Λ^o of an aqueous solution of acetic acid :

(1) The limiting equivalent conductance of H^+ ($\lambda^\circ_{H^+}$) (2) Λ^o of chloroacetic acid ($ClCH_2COOH$)
(3) Λ^o of NaCl (4) Λ^o of CH_3COOK

15. The cell Zn | Zn^{2+}(1M) || Cu^{2+}(1M) | Cu : (E°_{cell} = 1.10V) was allowed to completely discharge at 298 K. The relative concentration of Zn^{2+} to Cu^{2+} $\left(\frac{[Zn^{2+}]}{[Cu^{2+}]}\right)$ is : (Take $\frac{1.1}{0.059}$ = 18.65) **[AIEEE–2007, 3/120]**

(1) $10^{37.3}$ (2) 9.65×10^4 (3) antilog (24.08) (4) 37.3

16. Given : $E^0_{Cr^{3+}/Cr} = -0.72$, $E^0_{Fe^{2+}/Fe} = -0.42$ V

The potential for the cell Cr | Cr^{3+}(0.1 M) || Fe^{2+}(0.01 M) | Fe at 298 K is :

(Take $\frac{2.303\ R\ (298)}{F} = 0.06$) **[AIEEE–2008, 3/105]**

(1) 0.339 V (2) – 0.339 V (3) – 0.26 V (4) 0.26 V

17. Given : $E^0_{Fe^{3+}/Fe} = -0.036$ V, $E^0_{Fe^{2+}/Fe} = -0.439$ V

The value of standard electrode potential for the change, $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$ will be :

(1) 0.385V (2) 0.770V (3) –0.270V (4) –0.072V

18. The Gibbs energy for the decomposition of Al_2O_3 at 500ºC is as follows : **[AIEEE–2010, 4/144]**

$\frac{2}{3} Al_2O_3 \rightarrow \frac{4}{3} Al + O_2$; $\Delta_rG = +\ 966$ kJmol^{-1}. The potential difference needed for electrolytic reduction of Al_2O_3 at 500ºC is at least :

(1) 4.5 V (2) 3.0 V (3) 2.5 V (4) 5.0 V

19. The reduction potential of hydrogen half-cell will be negative, if : **[AIEEE–2011(1), 4/120]**

(1) $p(H_2)$ = 1 atm and $[H^+]$ = 2.0 M (2) $p(H_2)$ = 1 atm and $[H^+]$ = 1.0 M

(3) $p(H_2)$ = 2 atm and $[H^+]$ = 1.0 M (4) $p(H_2)$ = 2 atm and $[H^+]$ = 2.0 M

20. The standard reduction potentials for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are –0.76, – 0.23 and –0.44 V respectively. The reaction $X + Y^{2+} \rightarrow X^{2+} + Y$ will be spontaneous, when : **[AIEEE 2012, 4/120]**

(1) X = Ni, Y = Fe (2) X = Ni, Y = Zn (3) X= Fe, Y = Zn (4) X= Zn, Y = Ni

21. Given : $E^0_{Cr^{3+}/Cr} = -0.74$ V ; $E^0_{MnO_4^-/Mn^{2+}} = 1.51$ V

$E^0_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33$ V ; $E^0_{Cl/Cl^-} = 1.36$ V

Based on the data given above, strongest oxidising agent will be : **[JEE(Main) 2013, 4/120]**

(1) Cl (2) Cr^{3+} (3) Mn^{2+} (4) MnO_4^-

22. Resistance of 0.2 M solution of an electrolyte is 50 Ω. The specific conductance of the solution is 1.4 S m^{-1}. The resistance of 0.5 M solution of the same electrolyte is 280 Ω. The molar conductivity of 0.5 M solution of the electrolyte in S m^2 mol^{-1} is : **[JEE(Main) 2014, 4/120]**

(1) 5×10^{-4} (2) 5×10^{-3} (3) 5×10^3 (4) 5×10^2

23. The equivalent conductance of NaCl at concentration C and at infinite dilution are Λ_C and Λ_∞, respectively. The correct relationship between Λ_C and Λ_∞ is given as : (where the constant B is positive) **[JEE(Main) 2014, 4/120]**

(1) $\Lambda_C = \Lambda_\infty + (B)C$ (2) $\Lambda_C = \Lambda_\infty - (B)C$ (3) $\Lambda_C = \Lambda_\infty - (B)\sqrt{C}$ (4) $\Lambda_C = \Lambda_\infty + (B)\sqrt{C}$

24. The metal that cannot be obtained by electrolysis of an aqueous solution of its salts is : **[JEE(Main) 2014, 4/120]**

(1) Ag (2) Ca (3) Cu (4) Cr

25. Given below are the half-cell reactions : **[JEE(Main) 2014, 4/120]**

$Mn^{2+} + 2e^- \longrightarrow Mn$; $E^o = -1.18$ V

$2(Mn^{3+} + e^- \longrightarrow Mn^{2+})$; $E^o = +1.51$ V

The E^o for $3Mn^{2+} \longrightarrow Mn + 2Mn^{3+}$ will be :

(1) –2.69 V ; the reaction will not occur
(2) –2.69 V ; the reaction will occur
(3) –0.33 V ; the reaction will not occur
(4) –0.33 V ; the reaction will occur

26. Two Faraday of electricity is passed through a solution of $CuSO_4$. The mass of copper deposited at the cathode is : (at. mass of Cu = 63.5 amu) **[JEE(Main) 2015, 4/120]**

(1) 0 g
(2) 63.5 g
(3) 2 g
(4) 127 g

27. Galvanization is applying a coating of : **[JEE(Main) 2016, 4/120]**

(1) Cr
(2) Cu
(3) Zn
(4) Pb

28. Given

$$E^o_{Cl_2/Cl^-} = 1.36 \text{ V}, \ E^o_{Cr^{3+}/Cr} = -0.74 \text{ V}$$

$$E^o_{Cr_2O_7^{2-}/Cr^{3+}} = 1.33 \text{ V}, \ E^o_{MnO_4^-/Mn^{2+}} = 1.51 \text{ V}$$

Among the following, the strongest reducing agent is : **[JEE(Main) 2017, 4/120]**

(1) Mn^{2+}
(2) Cr^{3+}
(3) Cl^-
(4) Cr

29. How long (approximate) should water be electrolysed by passing through 100 amperes current so that the oxygen released can completely burn 27.66 g of diborane? **[JEE(Main)-2018, 4/120]**
(Atomic weight of B = 10.8u)

(1) 3.2 hours
(2) 1.6 hours
(3) 6.4 hours
(4) 0.8 hours

PART - III : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. The increase in the equivalent conductance of a salt solution on dilution is due to increase in the **[NSEC-2000]**

(A) attraction between the ions
(B) degree of ionization of the salt
(C) molecular attraction
(D) association of the salt

2. When 96500 coulombs of electricity are passed through a nickel sulphate solution, the amount of nickel deposited will be **[NSEC-2000]**

(A) 1.0 mol
(B) 0.5 mol
(C) 0.1 mol
(D) 2.0 mol **[NSEC-2000]**

3. When a piece of copper wire is immersed in a silver nitrate solution, the colour of the solution turns blue due to **[NSEC-2000]**

(A) oxidation of silver
(B) reduction of copper
(C) oxidation of copper
(D) formation of soluble complex

4. The reduction potentials of Zn, Cu, Fe and Ag are in the order : **[NSEC-2001]**

(A) Zn,Cu,Fe,Ag
(B) Cu,Ag,Fe,Zn
(C) Ag,Cu,Fe,Zn
(D) Fe,Zn,Cu, Ag

5. The standard reduction potentials of Cu^{2+}/Cu and Cu^+/Cu are 0.339 V and 0.518 V respectively. The standard electrode potential of Cu^{2+}/Cu^+ half cell is : **[NSEC-2001]**

(A) 0.16 V
(B) 0.827 V
(C) 0.184 V
(D) 0.490 V

6. How many coulombs are required for oxidation of 1 mole of H_2O to O_2 ? **[NSEC-2001]**

(A) 3.86×10^5C
(B) 9.65×10^4C
(C) 1.93×10^5C
(D) 4.825×10^4C

7. The metal which can not be obtained by electrolysis of its aqueous salt solution is : **[NSEC-2001]**

(A) Au
(B) Al
(C) Ag
(D) Cu

8. The units of conductivity are : **[NSEC-2001]**

(A) $\text{Siemen}^{-1}.\text{cm}^{-1}$.
(B) Siemen.cm
(C) Siemen.cm^{-1}
(D) $\text{Semen.cm}^{-2}.\text{mol}^{-1}$

9. The calomel electrode used a reference elecrode contains : **[NSEC-2001]**
(A) PbO_2-$PbSO_4$ mixture (B) $HgCl_2$
(C) Hg_2Cl_2 (D) $ZnCl_2$

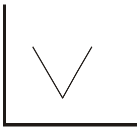
10. KCl is used in a salt bridge because : **[NSEC-2001]**
(A) it forms a good jelly with agar-agar
(B) it is strong electrolyte
(C) it is a good conductor of elelctric current
(D) the transference number of K^+ and Cl^- ions are almost equal

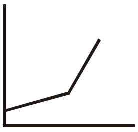
11. During the electrolysis of fused NaCl, the reaction occurring at the anode is : **[NSEC-2001]**
(A) reduction of Na^+ ions (B) oxidation of Cl^- ions
(C) oxidation of Na^+ ions (D) reduction of Cl^- ions

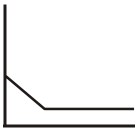
12. On electrolysis, one mole of chromium ions will be deposited by : **[NSEC-2001]**
(A) three moles of electrons (B) two moles of electrons
(C) one mole of electrons (D) six moles of electrons

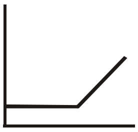
13. The quantity of electricity which deposits 1.08 g of silver from $AgNO_3$ solution is : **[NSEC-2002]**
(A) 96500 coulombs (B) 9650 coulombs (C) 965 coulombs (D) 96.5 coulombs.

14. In the conductometric titration of CH_3 COOH vs NaOH, the titration curve obtained will be of the type **[NSEC-2002]**

(A) 

(B) 

(C) 

(D) 

15. The standard reduction potentials at 298 K for the half reactions are: **[NSEC-2002]**
(a) $Zn^{2+}{}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$; –0.762 V (b) $Cr^{3+}{}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$; – 0.740 V
(c) $2H^+{}_{(aq)} + 2e^- \rightarrow H_{2(g)}$; 0.000 V (d) $Fe^{3+}{}_{(aq)} + e^- \rightarrow Fe^{2+}{}_{(aq)}$; 0.770 V
Which is the strongest reducing agent?
(A) $Zn_{(s)}$ (B) $Cr_{(s)}$ (C) $H_{2(g)}$ (D) $Fe^{2+}{}_{(aq)}$.

16. The molar conductivities of H^+, Li^+ and Na^+ ions in aqueous solutions at infinite dilution are in the order : **[NSEC-2003]**
(A) $H^+ > Li^+ > Na^+$ (B) $H^+ < Li^+ < Na^+$ (C) $H^+ > Na^+ > Li^+$ (D) $Na^+ > H^+ > Li^+$.

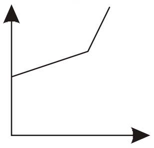
17. $Fe^{2+} + 2e \rightarrow Fe$ .....(i)
$Fe^{3+} + e \rightarrow Fe^{2+}$ .....(ii)
The standard potentials (in volt) corresponding to the reactions (i) and (ii) are E_1 and E_2 respectively. The value (in volt) of the standard potential corresponding to the reaction $Fe^{3+} + 3e \rightarrow Fe$ is **[NSEC-2003]**
(A) (E_1+E_2) (B) $(2E_1+E_2)/3$ (C) $(E_1 + 2E_2)/2$ (D) $(E_1+E_2)/3$.

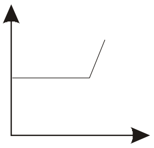
18. The standard reduction potentials of Cu^{2+}, Zn^{2+}, Sn^{2+} and Ag^+ are 0.34, –0.76, –0.14 and 0.80 V respectively. The storage that is possible without any reaction is for **[NSEC-2003]**
(A) $CuSO_4$ solution in a zinc vessel (B) $AgNO_3$ solution in a zinc vessel
(C) $AgNO_3$ solution in a tin vessel (D) $CuSO_4$ solution in a silver vessel.

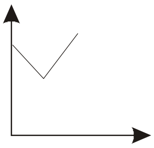
19. A certain current passed through $CuSO_4$ solution for 100 seconds deposits 0.3175 g of copper. The current passed (in A) is **[NSEC-2004]**
(A) 4.83 (B) 9.65 (C) 0.963 (D) 0.483

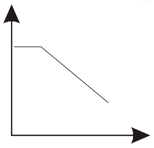
20. The salt that can be used in the salt bridge of an electrochemical cell is **[NSEC-2004]**
(A) $FeCl_3$ (B) AgCl (C) CH_3COONa (D) KNO_3.

21. The conductometric titration curve (of conductance vs mL of NaOH) obtained when acetic acid is titrated against NaOH is **[NSEC-2005]**

(A) 

(B) 

(C) 

(D) 

22. In an alkaline energy cell the overall cell reaction is as follows :

$Zn(s) + 2MnO2(s) + 2H_2O \rightarrow Zn(OH)_2(s) + 2MnO(OH)$.

Which of the following reactions is taking place at the cathode? **[NSEC-2005]**

(A) $2MnO_{2(s)} + 2H_2O + 2e \rightarrow Zn(OH)_2(s) + 2MnO(OH)_{(s)}$

(B) $2MnO_{2(s)} + 2H_2O + 2e \rightarrow 2MnO(OH)_{(s)} + 2OH^-_{(aq)}$

(C) $Zn_{(s)} + 2OH^-_{(aq)} \rightarrow Zn(OH)_{2(s)} + 2e$

(D) $Zn(OH)_{2(s)} + 2e \rightarrow Zn_{(s)} + 2OH^-_{(aq)}$.

23. What is the charge on an ion of tin if 7.42 g of metallic tin is deposited by passage of 24125 coulombs through a solution containing the ion ? **[NSEC-2005]**

(A) +1 (B) +3 (C) +2 (D) +4.

24. The cell potential (E) and free energy change (ΔG) accompanying an electrochemical reaction, are related by **[NSEC-2005]**
[NSEC-2005]

(A) $\Delta G = nFE$ (B) $\Delta G = nFE$ (C) $\Delta G = nFlogE$ (D) $\Delta G = nF\sqrt{logE.}$.

25. The mass of the copper, in grams, deposited during the passage of 2.5 ampere current through a Cu(II) sulphate solution for 1 hour is **[NSEC-2006]**

(A) 5.96 (B) 29.8 (C) 2.98 (D) 59.6

26. The standard reduction potentials of Fe^{2+}/Fe and Cu^{2+}/Cu electrodes are –0.44 and 0.34 volts, respectively. The following reaction would occur **[NSEC-2006]**

(A) copper will reduce Fe^{2+} ions (B) iron will reduce Cu^{2+} ions

(C) iron will oxidise copper metal (D) Cu^{2+} ions will reduce Fe^{2+}.

27. Rusting of iron is due to the formation of **[NSEC-2006]**

(A) hydrated ferrous oxide (B) hydrated ferric oxide

(C) only ferric oxide (D) a mixture of ferric oxide and $Fe(OH)_3$.

28. If the equilibrium constant of the disproportionation reaction

$Hg_2^{2+} = Hg^0 + Hg^{2+}$

at 298 K is 0.0795, the standard e.m.f. of the reaction is **[NSEC-2006]**

(A) –0.065 V (B) –0.212 V (C) 0.125 V (D) 0.110 V

29. The voltage for the cell: $Fe /Fe^{2+}(0.001M) // Cu^{2+}(0.10M) /Cu^{2+} (0.10\ M) / Cu^{2+} (0.10\ M) / Cu$ is 0.807 V at 25°C. What is the value of E° ? **[NSEC-2007]**

(A) 0.629 V (B) 0.689 V (C) 0.748 V (D) 0.866 V

30. A current of 2.0 A is used to plate Ni(s) from 500mL of a 1.0 M Ni^{2+} aqueous solution. What is the $[Ni^{2+}]$ after 3.0 hours ? **[NSEC-2007]**

(A) 0.39 M (B) 0.46 M (C) 0.78 M (D) 0.89 M

31. Nickel metal is added to a solution containing1.0 M $Pb^{2+}_{(aq)}$ and 1.0 M $Cd^{2+}_{(aq)}$. Use the standard reduction potential to determine which of the following reaction (s) will occur. **[NSEC-2008]**

Reaction 1 : $Ni_{(s)} + Pb^{2+}_{(aq)} \rightarrow Pb_{(s)} + Ni^{2+}_{(aq)}$

Reaction 2 : $Ni_{(s)} + Cd^{2+}_{(aq)}\ Cd_{(s)} + Ni^{2+}_{(aq)}$

Reactions :

$Pb^{2+}_{(aq)} + 2e = Pb_{(s)}$ $E° = -0.13$ V

$Ni^{2+}_{(aq)} + 2e = Ni_{(s)}$ $E° = -0.23$ V

$Cd^{2+}_{(aq)} + 2e = Cd_{(s)}$ $E° = -0.40$ V

(A) 1 only (B) 2 only (C) both 1 and 2 (D) neither 1 nor 2

32. An electrochemical cell constructed for the reaction, $Cu^{2+}{}_{(aq)} + M_{(s)} \rightarrow Cu_{(s)} + M^{2+}{}_{(aq)}$ has an E° = 0.75 V. The standard reduction potential for $Cu^{2+}{}_{(aq)}$ is 0.34 V. What is the standard reduction potential for $M^{2+}{}_{(aq)}$? **[NSEC-2008]**
(A) 1.09 V (B) 0.410 V (C) – 0410 V (D) – 1.09 V

33. An electric current is passed through a silver voltameter connected to a water voltameter. 0.324 g of silver was deposited on the cathode of the silver voltameter. The volume of oxygen evolved at NTP is : **[NSEC-2009]**
(A) 5.6 cm^3 (B) 16.8 cm^3 (C) 11.2 cm^3 (D) 22.4 cm^3

34. The amount of copper (At. wt. 63.54) deposited by passing 0.2 faraday of electricity through copper sulphate is **[NSEC-2009]**
(A) 3.175 g (B) 6.350 g (C) 31.75 g (D) 63.35 g

35. When aqueous solution of sodum chloride is electrolysed using platinum electrode the cathode reaction is, **[NSEC-2009]**
(A) $Na^+ + e^- \longrightarrow Na$ (B) $H_2O + e^- \longrightarrow \frac{1}{2} H_2 + OH^-$
(C) $Na^+ + OH^- \longrightarrow Na^+ + OH^- + e^-$ (D) $Na^+ + H_2O + e^- \longrightarrow Na + H^+ + OH^-$

36. The standard electrode potential values for four metals K, L, M and N are respectively, –3.05, –1.66, –0.40 and +0.80V. The best reducing agent is – **[NSEC-2009]**
(A) L (B) K (C) N (D) M

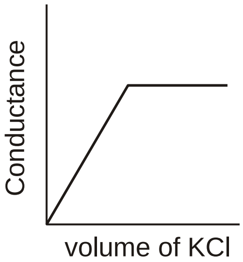
37. $10Cl^-\,(aq) + 2MnO_4^-\,(aq) + 16H^+\,(aq) \longrightarrow 5Cl_2\,(g) + 2Mn^{2+}\,(aq) + 8H_2O\,(l)$ **[NSEC-2009]**
The value of E° for the above reaction at 25°C is 0.15V. Hence, the value of K for this reaction is:
(A) 2.4×10^{25} (B) 4.9×10^{12} (C) 1.2×10^5 (D) 3.4×10^2

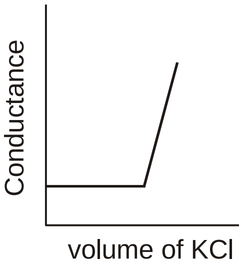
38. Adding powdered Pb and Fe to a solution containing 1 M each of Pb^{2+} and Fe^{2+} ions would result in the formation of – ($E^0_{Pb^{2+}/Pb} = -0.126V$ and $E^0_{Fe^{2+}/Fe} = -0.44V$) **[NSEC-2010]**
(A) more of Pb and Fe^{2+} ions (B) more of Fe and Pb^{2+} ions
(C) more of Pb and Fe (D) more of Pb^{2+} and Fe^{2+} ions

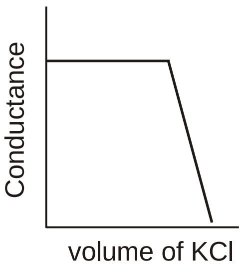
39. The cell $Al_{(s)}|Al^{3+}{}_{(aq)}$ (0.001 M) | | $Cu^{2+}{}_{(aq)}$ (0.10 M) | $Cu_{(s)}$ has a standard cell potential E° = 2.00 V at 25°C. The cell potential at the given concentration will be : **[NSEC-2010]**
(A) 2.07 V (B) 2.03 V (C) 1.97 V (D) 1.94 V

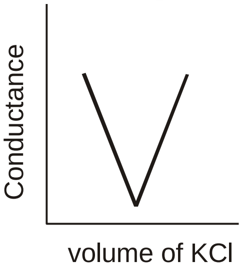
40. The mass of copper deposited when a current of 10A is passed through a solution of copper(II) nitrate for 30.6s is **[NSEC-2010]**
(A) 0.101 g (B) 0.201 g (C) 0.403 g (D) 6.04 g

41. In the conductometric titration of silver nitrate against KCl, the graph obtained is **[NSEC-2011]**

(A) 

(B) 

(C) 

(D) 

42. Th emf of the cell (Zn | $ZnSO_4$(0.1M) || $CdSO_4$ (0.01M) | Cd) is **[NSEC-2011]**
($E^o_{Zn^{2+}/Zn} = -0.76$ V, $E^o_{Cd^{2+}/Cd} = 0.40$ V at 298 K)
(A) +0.33 V (B) +0.36 V (C) +1.13 V (D) –0.36 V

43. The conductivity of a metal decreases with increase in temperature because : **[NSEC-2012]**
(A) the kinetic energy of the electrons increases (B) the movement of electrons becomes haphazard
(C) the ions start vibrating (D) the metal becomes hot and starts emiting radiation

44. The amount of electricity required to deposit 1.0 mole of aluminium from a solution of $AlCl_3$ will be : **[NSEC-2012]**

(A) 1 faraday (B) 3 faradays (C) 0.33 faraday (D) 1.33 faraday

45. Which is the strongest oxidising agent among the species given below? **[NSEC-2013]**

(i) In^{3+} $E^o = -1.34V$ (ii) Au^{3+} $E^o = 1.40V$

(iii) Hg^{2+} $E^o = 0.867V$ (iv) Cr^{3+} $E^o = -0.786V$

(A) Cr^{3+} (B) Au^{3+} (C) Hg^{2+} (D) In^{3+}

46. Which of the following aqueous solution has the lowest electrical conductance ? **[NSEC-2013]**

(A) 0.01M $CaCl_2$ (B) 0.01M KNO_2 (C) 0.01M CH_3COOH (D) 0.01M CH_3COCH_3

47. The value of the constant in Nernst equation

$$E = E^o - \frac{\text{constant}}{n} \ln Q \text{ at } 25^oC \text{ is :}$$ **[NSEC-2013]**

(A) 0.592 (B) 0.0592 (C) 0.296 (D) 0.0296

48. When zinc rod is directly placed in copper sulphate solution **[NSEC-2013]**

(A) the blue colour of the solution starts intensifying

(B) the solution remains electrically neutral

(C) the temperature of the solution falls

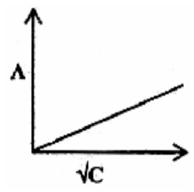
(D) the weight of zinc rod starts increasing

49. For the following cell at 25ºC the E.M.F. is : [If $E^o_{M^{2+}/M} = 0.347$ V] **[NSEC-2014]**

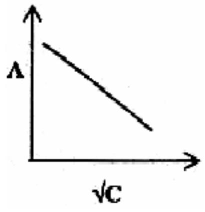
$$M_{(S)} \mid M^{2+} (1M) \parallel M^{2+} (0.01M) \mid M_{(S)}$$

(A) 0.089V (B) 0.598V (C) 0.251V (D) 0.764V

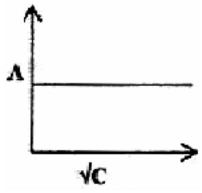
50. For a strong electrolyte, the change in the molar conductance with concentration is represented by : **[NSEC-2014]**



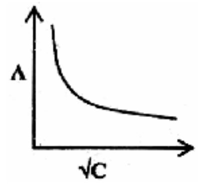
(I)



(II)



(III)



(IV)

(A) I (B) II (C) III (D) IV

51. The specific conductance of 0.01M solution of the weak monobasic acid is 0.20×10^{-3} Scm^{-1}. The dissociation constant of the acid is [Given: $\Lambda^o_{HA} = 400$ Scm^2mol^{-1}] **[NSEC-2014]**

(A) 5×10^{-2} (B) 2.5×10^{-5} (C) 5×10^{-4} (D) 2.5×10^{-11}

52. The reaction given below is the cell reaction in a galvanic cell.

$$Cd(s) + Sn^{2+}(aq) \rightarrow Cd^{2+}(aq) + Sn(s)$$

Where, $[Cd^{2+}] = 0.1$ M and $[Sn^{2+}] = 0.025$ M

Given: $E^0_{Cd^{2+}/Cd} = -0.403V$, $E^0_{Sn^{2+}/Sn} = -0.136V, F = 96485 Cmol^{-1}$

At 25ºC, the free energy change for this reaction is : **[NSEC-2014]**

(A) − 48.05 KJ (B) − 54.96 KJ (C) − 100.58 KJ (D) − 107.46 KJ

53. A current of 5.0 A flows for 4.0 h through an electrolytic cell containing a molten salt of metal M. This results in deposition of 0.25 mol of the metal M at the cathode. The oxidation state of M in the molten salt is (1 Faraday = 96485 C mol^{-1}) **[NSEC-2015]**

(A) +1 (B) +2 (C) +3 (D) +4

54. The limiting molar conductivities of KCl, KNO_3, and $AgNO_3$ are 149.9, 145.0 and 133.4 S cm^2 mol^{-1}, respectively, at 25ºC. The limiting molar conductivity of AgCl at the same temperature in S cm^2 mol^{-1} is **[NSEC-2015]**

(A) 128.5 (B) 138.3 (C) 161.5 (D) 283.3

55. The emf of a cell corresponding to the following reaction is 0.199 V at 298 K. **[NSEC-2015]**
$Zn\ (S) + 2\ H^+\ (aq) \rightarrow Zn^{2+}\ (0.1\ M) + H_2\ (g)$ $(E^o_{Zn/Zn^{2+}} = 0.76V)$
The approximate pH of the solution n at the electrode where hydrogen is being produced is (p_{H2} = 1 atm).
(A) 3 (B) 9 (C) 10 (D) 11

56. The standard electrode potentials, E° of Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe at 300 K are +0.77 V and –0.44 V, respectively. The E° of Fe^{3+}/Fe at the same temperature is **[NSEC-2015]**
(A) 1.21 V (B) 0.33 V (C) –0.036 V (D) 0.036 V

57. Three Faradays of electricity are passed through aqueous solutions of $AgNO_3$, $NiSO_4$ and $CrCl_3$ kept in three vessels using inert electrodes. The ratio (in moles) in which the metals Ag, Ni and Cr are deposited is : **[NSEC-2016]**
(A) 1 : 2 : 3 (B) 3 : 2 : 1 (C) 6 : 3 : 2 (D) 2 : 3 : 6

58. The standard potentials (E°) of MnO_4^-/Mn^{2+} and MnO_2/Mn^{2+} half cells in acidic medium are 1.51 V and 1.23 V respectively at 298 K. The standard potential of MnO_4^-/MnO_2 half-cell in acidic medium at the same temperature is : **[NSEC-2016]**
(A) 5.09 V (B) 1.70 V (C) 0.28 V (D) 3.34 V

59. Given the E_0 values for the half reactions :
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$, 0.15 V
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$, 0.92 V
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$, 1.45 V
Which of the following statements is true? **[NSEC-2016]**
(A) Sn^{2+} is a stronger oxidizing agent than Pb^{4+} (B) Sn^{2+} is a stronger reducing agent than Hg_2^{2+}
(C) Hg^{2+} is a stronger oxidizing agent than Pb^{4+} (D) Pb^{2+} is a stronger reducing agent than Sn^{2+}

60. The conductivity of 0.10 M KCl solution at 298 K is 1.29×10^{-2} S cm^{-1}. The resistance of this solution is found to be 28.44 Ω. Using the same cell, the resistance of 0.10 M NH_4Cl solution is found to be 28.50 Ω. The molar conductivity of NH_4Cl solution in S cm^2 mol^{-1} is : **[NSEC-2016]**
(A) 0.130 (B) 13 (C) 130 (D) 1300

61. Which of the following statements is not correct regarding the galvanic cells ? **[NSEC-2016]**
(A) Oxidation occurs at the anode.
(B) Ions carry current inside the cell.
(C) Electrons flow in the external circuit from cathode to anode.
(D) When the cell potential is positive, the cell reaction is spontaneous.

62. When a medal is electroplated with silver (Ag) **[NSEC-2017]**
(A) The medal is the anode (B) Ag metal is the cathode
(C) The solution contains Ag^+ ions (D) The reaction at the anode is $Ag^+ + e^- \rightarrow Ag$

Use the table given below to answer questions 63 and 64

Reaction	**E_0/V**
$Ag \rightarrow Ag^+ + e^-$	–0.80
$Cr^{3+} + 3e^- \rightarrow 3Cr$	–0.74
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.76
$I_2(s) + 2e^- \rightarrow 2\ I^-$	0.54
$Co^{2+} + 2e^- \rightarrow Co$	–0.28
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.26

63. The best reducing agent among the following is **[NSEC-2017]**
(A) Ag^+ (B) Zn^{2+} (C) Cr^{3+} (D) I^-

64. E° of the given cell is : **[NSEC-2017]**
$Ni\ |\ (Ni^{+2}, 1.0\ M)\ ||\ (Co^{+2}, 1.0\ M)\ |\ Co$
(A) +0.02V (B) –0.02V (C) –0.54V (D) +0.54V

65. The reduction of O_2 to H_2O in acidic solution has a standard reduction potential of 1.23 V. If the pH of the acid solution is increased by one unit, half cell potential will **[NSEC-2017]**

$O_2(g) + 4H^+(aq) + 4e^- \longrightarrow 2H_2O(l)$

(A) decrease by 59 mV (B) increase by 59 mV
(C) decrease by 236 mV (D) increase by 236 mV

66. From the given standard electrode potentials **[NSEC-2018]**

$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$ $E^o = 0.15V$
$Br_2(l) + 2e^- \rightarrow 2Br^-(aq)$ $E^o = 1.07V$

The approximate free energy change of the process $2Br^-(aq) + Sn^{4+}(aq) \rightarrow Br_2(l) + Sn^{2+}(aq)$ is

(A) 117.6 kJ (B) 355 kJ (C) –177.6 kJ (D) –355 kJ

67. Concentration of K^+ ions inside a biological cell was found to be 25 times higher than that outside. The magnitude of the potential difference between the two sides of the cell is close to (2.303 RT/F-can be taken as 59 mV; difference in concentrations of other ions can be taken as negligible) **[NSEC-2018]**

(A) 4.2 mV (B) 195 mV (C) 82 mV (D) –82 mV

68. The standard redox potential for the reaction $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ is –1.23V. If the same reaction is carried out at 25ºC and at pH = 7, the potential will be **[NSEC-2018]**

(A) –0.82 V (B) –3.28V (C) 0.82V (D) –1.18V

69. The standard electrode potential (E°) of the Daniel cell is 1.1 V and the overall cell reaction can be represented as $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$. Under which of the following conditions will the cell potential be higher than 1.1 V ? **[NSEC-2018]**

(A) 1.0 M Zn^{2+}, 1.0 M Cu^{2+} (B) 1.2 M Zn^{2+}, 1.2 M Cu^{2+}
(C) 0.1 M Zn^{2+}, 1.0 M Cu^{2+} (D) 1.0 M Zn^{2+}, 0.01 M Cu^{2+}

70. An electrochemical cell was constructed with Fe^{2+}/Fe and Cd^{2+}/Cd at 25ºC with initial concentrations of $[Fe^{2+}]$ = 0.800 M and $[Cd^{2+}]$ = 0.250 M. The EMF of the cell when $[Cd^{2+}]$ becomes 0.100 M is

Half cell	Eº(V)
$Fe^{2+}(aq)/Fe(s)$	– 0.44
$Cd^{2+}(aq)/Cd(s)$	– 0.40

[NSEC-2019]

(A) 0.013 V (B) 0.011 V (C) 0. 051 V (D) 0.022 V

71. Molten NaCl is electrolysed for 35 minutes with a currect of 3.50 A at 40ºC and 1 bar pressure. Volume of chlorine gas evolved in this electrolysis is **[NSEC-2019]**

(A) 0.016 L (B) 0.98 L (C) 9.8 L (D) 1.96 L

72. If the standard electrode potentials of Fe^{3+}/Fe and Fe^{2+}/Fe are –0.04 V and –0.44 V respectively then that of Fe^{3+}/Fe^{2+} is **[NSEC-2019]**

(A) 0.76 V (B) –0.76 V (C) 0.40 V (D) –0.40 V

PART - IV : HIGH LEVEL PROBLEMS (HLP)

THEORY

Solubility product and EMF (Metal-Metal Insoluble Salt Electrode) :

- A half cell containing metal M and its sparingly soluble salt MA in a saturated solution. i.e M(s) | MA (satd) or a metal, its sparingly soluble salt in contact with a solution of a soluble salt NaA of the same anion, i.e. M(s) | MA(s) | NaA is set up.
- The solubility product of a sparingly doubles salt is a kind of equilibrium constant.

$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$ $K_{sp} = [M^+][X^-]$

At Anode

- $M(s) \rightleftharpoons M^+(aq) + e^-$

At Cathode

- $e^- + MX(s) \rightleftharpoons M(s) + X^-(aq)$

Overall reaction : $MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$
Cell representation : M | M^+(saturated sol.) || NaA | MX(s) | M (s)

$E^o_{cell} = E^\circ_{red} - E^\circ_{ox}$

From thermodynamics $\Delta G^\circ = -nFE^\circ$
$\Delta G^\circ = -2.303\ RT \log K_{sp}$

combining both equations $-2.303\ RT \log K_{sp} = -nFE^\circ$

or $$E^\circ = \frac{2.303\ \ RT}{nF} \log K_{sp}$$

$$E^\circ = \frac{0.0591}{n} \log K_{sp} \quad \text{at } 25^\circ C$$

Solved Examples

Example Calculate K_{sp} if ($PbSO_4$) E_{cell} at 298 K of this electrode is 0.236 V
$Pb(s)\ |PbSO_4(s)|Na_2SO_4(aq)||Pb(NO_3)|Pb(s)$
0.01 M 0.1 M

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log \left[\frac{0.01}{0.1}\right]$$

$$0.236 = E^0_{cell} + \frac{0.059}{2}$$

$$E^0_{cell} = 0.236 - 0.03 = 0.206$$

Solution I Let it be conc. cell

Anode $Pb(s) \rightarrow Pb^{2+}_{(a)} + 2e^-$

Cathode $Pb^{2+}_{(s)} + 2e^- \rightarrow Pb(s)$

$$Pb^{2+}_{(c)} \rightleftharpoons Pb^{2+}_{(a)}$$

$$E_{cell} = E^0_{cell} - \frac{0.059}{2} \log\left[\frac{(Pb^{2+})_a}{(Pb^{2+})_c}\right]$$

$$0.236 = \frac{0.059}{2} \log\left[\frac{(Pb^{2+})_a}{(Pb^{2+})_c}\right]$$

$(Pb^{2+})_a = 10^{-9}M$

$K_{sp} = (Pb^{2+})_a\ (SO_4^{2-})_a = 10^{-11}$

Solution II **Let if it is not a conc cell**

Anode : $Pb(s) + SO_4^{2-}\ (aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode : $Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$

$$Pb^{2+}(c) + SO_4^{2-}\ (a) \rightarrow PbSO_4(s)$$

$$E^0_{cell} = E^0_{Pb^{2+}/Pb} - E^0_{SO_4^{2-}|\,PbSO_4|Pb} = E^0_{Pb^{2+}|Pb} - \left[E^0_{Pb^{2+}|Pb^+} + \frac{0.059}{2}\log\ K_{sp}\right]$$

$$E^0_{cell} = -\frac{0.059}{2} \log K_{sp}$$

$$0.236 = \frac{0.059}{2} \log K_{sp} - \frac{0.059}{2} \log\left[\frac{1}{(Pb^{2+})_c (SO_4^{2-})a}\right] = \log\left[\frac{K_{SP}}{0.1 \times 0.01}\right] = \log\left[\frac{K_{SP}}{10^{-3}}\right] \log 10^{-8}$$

$K_{sp} = 10^{-11}$

Calomel Electrode :

- A calomel electrode consists of a platinum electrode dipping into mercury in contact with calomel (dimercury (I) chloride, Hg_2Cl_2) and potassium chloride solution.
- Usually the solution is saturated with potassium chloride.

- The cell has $E^0 = 0.28$ V (with respect of SHE) at 25°C

Standard (normal) calomel electrode when $[Cl^-] = 1M = 1N$

At Anode	**At Cathode**
$2Hg(\ell) \rightarrow Hg_2^{2+}(aq) + 2e^-$	$Hg_2^{2+} + 2e^- \rightarrow 2Hg(\ell)$
$Hg_2^{2+}(aq) + 2Cl^- \rightarrow Hg_2Cl_2(s)$	$Hg_2Cl_2 \rightarrow Hg_2^{2+}(aq) + 2Cl^-(aq)$
$2Hg(\ell) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s) + 2e^-$	$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(\ell) + 2Cl^-$
● Cell representation	● Cell representation
Pt(s) |Hg(ℓ) | Hg_2Cl_2(s) | Cl^-(aq)|| cathode	(Anode) || Cl^-(aq) | Hg_2Cl_2|Hg(ℓ) | Pt(s)
$E^0_{Hg\,|\,Hg_2Cl_2\,/\,Cl^-}$ = SOP	$E^0_{Cl^-|Hg_2Cl_2|Hg(\ell)}$ = SRP

$$E_{Cl^-/Hg_2Cl_2/Hg} = E^0_{Cl^-/Hg_2Cl_2/Hg} - \frac{RT}{F}\ell n[Cl^-]$$

$$E_{M^{n+}/M(Hg)Pt} = E^0_{M^{n+}/M(Hg)Pt} - \frac{RT}{F}\ \ell n\left[\frac{1}{M^{n+}}\right]$$

Thermodynamics of Cell Potential :

We know that :

$$\Delta G^0 = -nFE^0_{cell}$$

$$\Delta G = -\,nFE_{cell}$$

$$G = H - TS$$

From thermodynamics H = E + PV enthalpy function.

Substituting G = E + PV – TS

By partial differentiation

$dG = dE + PdV + VdP - TdS - SdT$ ...... (i)

according to **1st law** of thermodynamics

$E = q + W$ $dW = -PdV$

$dE = dq - PdV$

$dq = dE + PdV$ ...... (ii)

according to **2nd law**

$ds = \frac{dq}{T} = dq = Tds$ ...... (iii)

From (i), (ii) and (iii)

$dG = VdP - SdT$

at constant pressure, which is actually the condition for all normal cell reaction.

$dG = -SdT$

$$S = \frac{-dG}{dT}$$

$$\Delta S = -\frac{d(\Delta G)}{dT}$$

$\Delta G = -\,nFE_{cell}$

$\Delta S = +nF\ \dfrac{dE_{cell}}{dT}$

$\dfrac{dE_{cell}}{dT}$ = temperature cofficient of cell reaction.

$\Delta G = \Delta H - T\Delta S$

$\Delta H = -\,nF\,E_{cell} + nFT\ \dfrac{dE_{cell}}{dT}$

Kirchoff's equation

$\Delta Cp = \dfrac{d}{dT}\ (\Delta H)$

$\Delta Cp = Cp\text{ (of products)} - Cp\text{ (of reactants)} = \dfrac{-nFdE_{cell}}{dT} + nFT\ \dfrac{d^2E_{cell}}{dT^2} + \dfrac{+nFdE_{cell}}{dT}$

$\Delta Cp = nFT\ \dfrac{d^2E_{cell}}{dT^2}$

SUBJECTIVE QUESTIONS

1. Determine range of E° values for this reaction $X^{2+}_{aq.} + 2e^- \longrightarrow X(s)$ for given conditions:

(a) If the metal X dissolve in HNO_3 but not in HCl it can displace Ag^+ ion but not Cu^{2+} ion.

(b) If the metal X in HCl acid producing $H_2(g)$ but does not displace either Zn^{2+} or Fe^{2+}.

Given : $E^o_{Ag^+/Ag} = 0.8V$, $E^o_{Fe^{2+}/Fe} = -0.44V$,

$E^o_{Cu^{2+}/Cu} = 0.34V$, $E^o_{NO_3^-/NO} = 0.96V$, $E^o_{Zn^{2+}/Zn} = -0.76V$

2. The standard reduction potential of TiO^{2+} and Ti^{3+} are given by

$TiO^{2+} + 2H^+ + e^- \longrightarrow Ti^{3+} + H_2O$ $E^o = 0.10$ V

$Ti^{3+} + 3e^- \longrightarrow Ti$ $E^o = -1.21$ V

Find the standard reduction potential of TiO^{2+} to Ti.

3. The standard oxidation potential for the half–cell

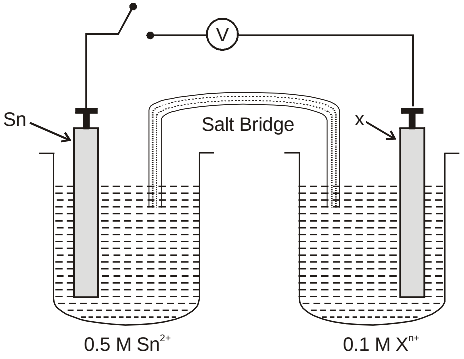
$NO_2^-\ (g) + H_2O \longrightarrow NO_3^-(aq) + 2H^+\ (aq) + 2e$ is -0.78 V.

Calculate the reduciton potential in 9 molar H^+ assuming all other species at unit concentration. What will be the reduction potential in neutral medium ?

4. Calculate the electrode potential at 25^0C of Cr^{3+}, $Cr_2O_7^{2-}$ electrode at pOH = 11 in a solution of 0.01 M both in Cr^{3+} and $Cr_2O_7^{2-}$.

$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 2Cr^{3+} + 7H_2O$ $E^0 = 1.33$ V.

5. An electrochemical cell is constructed with an open switch as shown below:



When the switch is closed, mass of tin-electrode increase. If E^o (Sn^{2+} / Sn) = – 0.14 V and for E^o (X^{n+} / X) = – 0.78 V and initial emf of the cell is 0.65 V, determine n and indicate the direction of electron flow in the external circuit.

6. Equinormal Solutions of two weak acids, HA (pK_a = 3) and HB (pK_a = 5) are each placed in contact with standard hydrogen electrode at 25°C (T = 298 K). When a cell is constructed by interconnecting them through a salt bridge find the e.m.f. of the cell.

7. In two vessels each containing 500ml water, 0.5m mol of aniline ($K_b = 10^{-9}$) and 25 m mol of HCl are added separately. Two hydrogen electrodes are constructed using these solutions. Calculate the emf of cell made by connecting them appropriately.

8. Write cell reaction from given cell diagrams
(A) $Cu\,|\,Cu^{2+}\,||\,Cl^-\,|\,Hg_2Cl_2\,|\,Hg\,|\,Pt$
(B) Ag (s) | $AgIO_3$ (s)|Ag^+, HIO_3 || Zn^{2+} | Zn (s)
(C) Mn (s) | Mn $(OH)_2$ (s) Mn^{2+}, OH^- || Cu^{2+}|Cu (s)

9. For the galvanic cell : Ag | AgCl (s)|KCl (0.2M) || KBr (0.001M) |AgBr (s) |Ag,
Calculate the EMF generated? (Take $\frac{2.303RT}{F} = 0.06$)
[$K_{sp(AgCl)} = 10^{-10}$; $K_{sp(AgBr)} = 10^{-13}$]

10. Given, E° = –0.27 V for the Cl^- | $PbCl_2$ |Pb couple and – 0.12 V for the Pb^{2+} | Pb couple, determine K_{sp} for $PbCl_2$ at 25°C ? (Take $\frac{2.303RT}{F} = 0.06$)

11. The pK_{sp} of AgI is 16. if the E° value for Ag^+ | Ag is 0.8 V. Find the E° for the half cell reaction AgI(s) + $e^- \rightarrow Ag + I^-$? (Take $\frac{2.303RT}{F} = 0.06$)

12. The EMF of the standard weston cadmium cell Cd (12.5%) in Hg | $3CdSO_4$, $8H_2O$ (solid) | saturated solution of $CdSO_4$ || Hg_2SO_4(s) | Hg is 1.0180 volts at 25° C and the temperature coefficient of the cell, $\left(\frac{\partial E}{\partial T}\right)_P = -4.0 \times 10^{-5}$ V/degree. Calculate ΔG, ΔH and ΔS for the reaction in the cell when n = 2.

13. ΔH for the reaction $Ag(s) + \frac{1}{2}Hg_2Cl_2(s) \longrightarrow AgCl(s) + Hg(\ell)$ is +1280 cal at 25°C. This reaction can be conducted in a cell for which the emf = 0.0455 volt at this temperature. Calculate the temperature coefficient of the emf.

14. The standard electromotive force of the cell :
Fe | Fe^{2+} (aq) | | Cd^{2+} | Cd is 0.0372 V
The temperature coefficient of e.m.f. is –0.125 V K^{-1}. Calculate the quantities ΔG^o, ΔH^o and ΔS^o at 25ºC.

15. The voltage of a certain cell has standred potential at 25ºC and 20ºC are 0.3525 V and 0.3533 V respectively. If the number of electrons involved in the overall reactions are two, calculate ΔG^o, ΔS^o and ΔH^o at 25ºC.

16. A metal is known to form fluoride MF_2. When 10A of electricity is passed through a molten salt for 330 sec., 1.95g of metal is deposited. Find the atomic weight of M. What will be the quantity electricity required to deposit the same mass of Cu from $CuSO_4$?

17. Find the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of CH_3COONa at 250ºC and 1 atm.

18. One of the methods of preparation of per disulphuric acid, $H_2S_2O_8$, involve electrolytic oxidation of H_2SO_4 at anode ($2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$) with oxygen and hydrogen as by-products. In such an electrolysis, 9.722 L of H_2 and 2.35L of O_2 were generated at STP. What is the weight of $H_2S_2O_8$ formed ?

19. The standard reduction potential values, E^o (Bi^{3+} / Bi) and E^o (Cu^{2+} /Cu) are 0.226V and 0.344V respectively. A mixture of salts of bismuth and copper at unit concentration each is electrolysed at 25°C. To what value can $[Cu^{2+}]$ be brought down before bismuth starts to deposit, in electrolysis.

20. Calculate the dissociation constant ($k_{dissociation}$) of water at 25°C from the following data :

Specific conductance of $H_2O = 5.8 \times 10^{-8}$ mho cm^{-1}, $\lambda^{\infty}_{H^+} = 350.0$ and $\lambda^{\infty}_{OH^-} = 198.0$ mho cm^2 mol^{-1}

21. **(a)** Calculate ΔG^o of the following reaction :

$$Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$$

Given : $\Delta G^o(AgCl) = -109$ kJ/mole, $\Delta G^o(Cl^-) = -129$ kJ/mole, $\Delta G^o(Ag^+) = 77$ kJ/mole.

Represent the above reaction in form of a cell.

Calculate E^o of the cell. Find $\log_{10}K_{sp}$ of AgCl at 25ºC.

(b) 6.539×10^{-2} g of metallic Zn (atomic mass = 65.39 amu) was added to 100 mL of saturated solution of AgCl.

Calculate $\log_{10}\dfrac{[Zn^{2+}]}{[Ag^+]^2}$ at equilibrium at 25ºC, given that :

$Ag^+ + e^- \longrightarrow Ag$ $\quad E^o = 0.80$ V

$Zn^{2+} + 2e^- \longrightarrow Zn$ $\quad E^o = -0.76$ V

Also find how many moles of Ag will be formed. (Take $\dfrac{114}{193} = 0.59$, $\dfrac{1.56}{0.059} = 26.44$) **[JEE 2005, 6/60]**

ONLY ONE OPTION CORRECT TYPE

22. The standard potential of the reaction $H_2O + e^- \rightarrow \frac{1}{2}H_2 + OH^-$ at 298 K by using K_w (H_2O) = 10^{-14}, is :

(A) – 0.828 V (B) 0.828 V (C) 0 V (D) – 0.5 V

23. Given : $Hg_2^{2+} + 2e \longrightarrow 2Hg$, $E^o = 0.789$ V & $Hg^{2+} + 2e \longrightarrow Hg$, $E^o = 0.854$ V,

calculate the equilibrium constant for $Hg_2^{2+} \longrightarrow Hg + Hg^{2+}$.

(A) 3.13×10^{-3} (B) 3.13×10^{-4} (C) 6.26×10^{-3} (D) 6.26×10^{-4}

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

If H^+ concentration is decreased from 1 M to 10^{-4} M at 25ºC, where as concentration of Mn^{2+} and MnO_4^- remain 1 M.

(A) the potential decreases by 0.38 V with decrease in oxidising power

(B) the potential increases by 0.38 V with increase in oxidising power

(C) the potential decreases by 0.25 V with decrease in oxidising power

(D) the potential decreases by 0.38 V without affecting oxidising power

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

25. At equimolar concentrations of Fe^{2+} and Fe^{3+}, what must $[Ag^+]$ be so that the voltage of the galvanic cell made from the (Ag^+ | Ag) and (Fe^{3+} | Fe^{2+}) electrodes equals zero?

$$Fe^{2+} + Ag^+ \rightleftharpoons Fe^{3+} + Ag$$

$E^o_{Ag^+|Ag} = 0.7991$; $E^o_{Fe^{3+}|Fe^{2+}} = 0.771$

(A) 0.34 (B) 0.44 (C) 0.47 (D) 0.61

26. The cell Pt (H_2) (1 atm) | H^+(pH = ?) || I^- (a = 1) | AgI(s), Ag(s) | Pt has emf, $E_{298K} = 0$. The standard electrode potential for the reaction $AgI + e^- \rightarrow Ag + I^{\ominus}$ is – 0.151 volt. Calculate the pH value.

(A) 3.37 (B) 5.26 (C) 2.56 (D) 4.62

27. Using the information in the preceding problem, calculate the solubility product of AgI in water at 25°C [$E^o_{(Ag^+, Ag)} = +0.799$ volt]

(A) 1.97×10^{-17} (B) 8.43×10^{-17} (C) 1.79×10^{-17} (D) 9.17×10^{-17}

28. The solubility product of silver iodide is 8.3×10^{-17} and the standard reduction potential of Ag, Ag^+ electrode is + 0.8 volts at 25° C. The standard reduction potential of Ag,AgI/I^- electrode from these data is

(A) – 0.30 V (B) + 0.15 V (C) + 0.10 V (D) – 0.15 V

29. The efficiency of an hypothetical cell is about 84% which involves the following reaction :

$$A\,(s) + B^{2+}\,(aq) \longrightarrow A^{2+}\,(aq) + B\,(s) : \ \Delta H = -285 \text{ kJ}$$

Then, the standard electrode potential of the cell will be

(A) 1.20 (B) 2.40 V (C) 1.10 V (D) 1.24 V

30. The temperature coefficient, of the emf i.e. $\frac{dE}{dT} = -0.00065$ volt. deg^{-1} for the cell Cd | $CdCl_2$ (1M) || AgCl (s) | Ag at 25°C. Calculate the entropy changes ΔS_{298K} for the cell reaction, Cd + 2AgCl → Cd^{2+} + $2Cl^-$ + 2Ag

(A) – 105.5 JK^{-1} (B) – 150.2 JK^{-1} (C) – 75.7 JK^{-1} (D) – 125.5 JK^{-1}

31. The standard emf of the cell, Cd(s) | $CdCl_2$(aq) (0.1 M) || AgCl(s) | Ag(s) in which the cell reaction is, $Cd(s) + 2AgCl(s) \longrightarrow 2Ag(s) + Cd^{+2}\,(aq) + 2Cl^-(aq)$ is 0.6915 V at 0°C and 0.6753 V at 25°C. The ΔH^o of the reaction at 25°C is :

(A) – 176 kJ (B) – 234.7 kJ (C) + 123.5 kJ (D) – 167.26 kJ

32. The potential of the Daniell cell, $Zn \left| \begin{matrix} ZnSO_4 \\ (1\ \ M) \end{matrix} \right| \left| \begin{matrix} CuSO_4 \\ (1\ \ M) \end{matrix} \right| Cu$ was reported by Buckbee, Surdzial and Metz as $E° = 1.1028 - 0.641 \times 10^{-3}\,T + 0.72 \times 10^{-5}\,T^2$, where T is the temperature in degree celsius. Calculate $\Delta S°$ for the cell reaction at 25°C :

(A) – 45.32 EU (B) – 34.52 EU (C) – 25.43 EU (D) – 54.23 EU

33. Using the data in the preceding problem, calculate the equilibrium constant of the reaction at 25°C.

$$Zn + Cu^{2+} \rightleftharpoons Zn^{2+} + Cu, \ K = \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

(A) 8.314×10^{24} (B) 4.831×10^{31} (C) 8.314×10^{36} (D) 4.831×10^{44}

34. $\Delta G = \Delta H - T\Delta S$ and $\Delta G = \Delta H + T \left[\frac{d(\Delta G)}{dT}\right]_p$ then $\left(\frac{dE_{cell}}{dT}\right)$ is :

(A) $\frac{\Delta S}{nF}$ (B) $\frac{nE}{\Delta S}$ (C) – nFE_{cell} (D) + nEF_{cell}

35. One g equivalent of Na metal is formed from electrolysis of fused NaCl. No. of mole of Al from the fused Na_3AlF_6 with the same current passed is :

(A) 1 (B) 3 (C) 1/3 (D) 2

36. The specific conductivity of a saturated solution of AgCl is 3.40×10^{-6} ohm^{-1} cm^{-1} at 25 ºC. If Λ_{Ag^+} = 62.3 ohm^{-1} cm^2 mol^{-1} & Λ_{Cl^-} = 67.7 ohm^{-1} cm^2 mol^{-1}, the solubility of AgCl at 25 ºC is :

(A) 2.6×10^{-5} M (B) 4.5×10^{-3} M (C) 3.6×10^{-5} M (D) 3.6×10^{-3} M

37.

List-1	**List-II**
(P) Conductivity does not change much then increases	(1) NH_3 is added in C_6H_5COOH
(Q) Conductivity increases then does not change much	(2) CH_3COOH is added in NaOH
(R) Conductivity decreases then does not change much	(3) KOH is added in HCl
(S) Conductivity decreases then increases	(4) Conc. KCl is added in dilute $AgNO_3$
(T) Conductivity tends to zero at the end point	(5) $MgSO_4$ is added in $Ba(OH)_2$

	(P)	(Q)	(R)	(S)	(T)		(P)	(Q)	(R)	(S)	(T)
(A)	4	2	1	5	3	(B)	1	2	3	4	5
(C)	5	4	3	2	1	(D)	4	1	2	3	5

38. The standard reduction potentials E° of the following systems are

	System	**E°(volts)**
(i)	$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$	1.51
(ii)	$Sn^{4+} + 2e^- \longrightarrow Sn^{2+}$	0.15
(iii)	$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$	1.33
(iv)	$Ce^{4+} + e^- \longrightarrow Ce^{3+}$	1.61

The oxidising power of the various species decreases in the order

(A) $Ce^{4+} > Cr_2O_7^{2-} > Sn^{4+} > MnO_4^-$ (B) $Ce^{4+} > MnO_4^- > Cr_2O_7^{2-} > Sn^{4+}$
(C) $Cr_2O_7^{2-} > Sn^{4+} > Ce^{4+} > MnO_4^-$ (D) $MnO_4^- > Ce^{4+} > Sn^{4+} > Cr_2O_7^{2-}$

39. Consider the reaction : (T = 298 K)
$Cl_2(g) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq.)$
The emf of the cell, when $[Cl^-] = [Br_2] = [Br^-] = 0.01M$ and Cl_2 gas is at 1 atm pressure, will be :
(E° for the above reaction is = 0.29 volt)

(A) 0.54 volt (B) 0.35 volt (C) 0.24 volt (D) –0.29 volt

40. $2Ce^{4+} + Co \longrightarrow 2Ce^{3+} + Co^{2+}$, $E^o_{cell} = 1.89$ V, $E^o_{Co^{2+}/Co} = -0.277$ V hence, $E^o_{Ce^{4+}/Ce^{3+}}$ is :

(A) 0.805 V (B) 1.62 V (C) – 0.805 V (D) – 1.61 V

41. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$; $E^o = 1.51$ V ; $\Delta G_1^0 = -5 \times 1.51 \times F$

$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O$; $E^o = 1.23$ V ; $\Delta G_2^0 = -2 \times 1.23 \times F$

$E^o_{MnO_4^- | MnO_2}$ is

(A) 1.70 V (B) 0.91 V (C) 1.37 V (D) 0.548 V

42. ΔG is the available energy (energy produced) during the electrochemical reaction in galvanic cell which can be converted into useful work. In the light of second law of thermodynamics in the cell the change in electrode potential with temperature will be equal to

(A) $\frac{\Delta S}{nF}$ (B) $\frac{nF}{\Delta S}$ (C) $-2.303\ RT \log K_C$ (D) $\frac{-2.303\ RT}{nF}$

43. The reduction potential of hydrogen electrode when placed in a buffer solution is found to be – 0.413V. The pH of the buffer is -

(A) 10 (B) 4 (C) 7 (D) 12

44. A gas Cl_2 at 1 atm is bubbled through a solution containing a mixture of 1 M Br^{-1} and 1 M F^{-1} at 25ºC. If the reduction potential is F > Cl > Br, then :

(A) Cl will oxidise Br and not F (B) Cl will oxidise F and not Br.
(C) Cl will oxidise both Br and F (D) Cl will reduce both Br and F

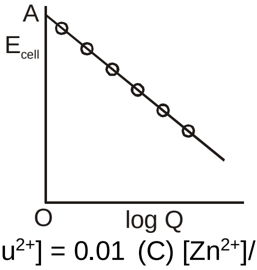
45. The oxidation potentials of Zn, Cu, Ag, H_2 and Ni are 0.76, –0.34, –0.80, 0.00, 0.25 volt, respectively. Which of the following reactions will provide maximum voltage ?

(A) $Zn + Cu^{2+} \longrightarrow Cu + Zn^{2+}$ (B) $Zn + 2Ag^+ \longrightarrow 2Ag + Zn^{2+}$
(C) $H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu$ (D) $H_2 + Ni^{2+} \longrightarrow 2H^+ + Ni$

46. The reduction potential of a half-cell consisting of a Pt electrode immersed in 1.5 M Fe^{2+} and 0.015 M Fe^{3+} solution at 25°C is $\left(E^0_{Fe^{3+}/Fe^{2+}} = 0.770\ V\right)$.

(A) 0.652 V (B) 0.88 V (C) 0.710 V (D) 0.850 V

47. $Zn + Cu^{2+}(aq) \rightleftharpoons Cu + Zn^{2+}(aq)$ Reaction quotient is $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$. $E^o_{cell} = 1.10$ V. E_{cell} will be 1.1591 V when :

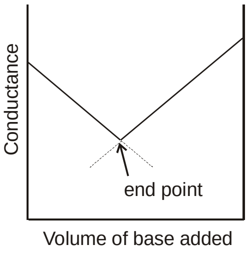


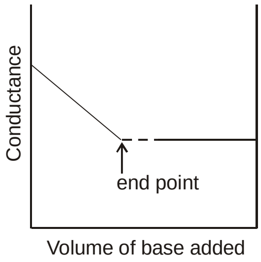
(A) $[Cu^{2+}]/[Zn^{2+}] = 0.01$ (B) $[Zn^{2+}]/[Cu^{2+}] = 0.01$ (C) $[Zn^{2+}]/[Cu^{2+}] = 0.1$ (D) $[Zn^{2+}]/[Cu^{2+}] = 1$

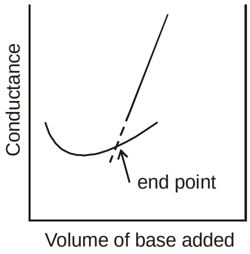
48. Pure water is saturated with pure solid AgCl, a silver rod is placed in the solution and the potential is measured against normal calomel electrode at 25°C. This experiment is then repeated with a saturated solution of AgI. If the difference in potential in the two cases is 0.177 V, what is the ratio of solubilty product (K_{sp}) of AgCl and AgI at the temperature of the experiment ? (In both cases normal calomel electrode is cathod)

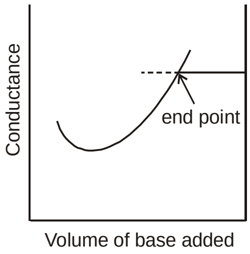
(A) 10^3 (B) 10^6 (C) 10^{-3} (D) 10^{-6}

49. Conductance measurements can be used to detect the end point of acid-base titrations. Which of the following plots correctly represent the end point of the titration of strong acid and a strong base ?

(A) 

(B) 

(C) 

(D) 

50. Which one of the following will increase the voltage of the cell ? (T = 298 K)

$$Sn + 2Ag^+ \longrightarrow Sn^{2+} + 2Ag$$

(A) increase in the size of silver rod (B) increase in the concentration of Sn^{+2} ions
(C) increase in the concentration of Ag^+ ions (D) none of the above

51. In a $H_2 - O_2$ fuel cell, 6.72 L of hydrogen at NTP reacts in 15 minutes, the average current produced in amperes is

(A) 64.3 amp (B) 643.3 amp (C) 6.43 amp (D) 0.643 amp

52. The standard reduction potential of a silver chloride electrode is 0.2 V and that of a silver electrode is 0.79 V. The maximum amount of AgCl that can dissolve in 10^6 L of a 0.1 M $AgNO_3$ solution is

(A) 0.5 mmol (B) 1.0 mmol (C) 2.0 mmol (D) 2.5 mmol

53. A cell Cu | Cu^{++} || Ag^+ | Ag initially contains 2M Ag^+ and 2M Cu^{2+} ions in 1 L electrolyte. The change in cell potential after the passage of 10 amp current for 4825 sec during usage of cell is: (Take $\frac{2.303RT}{F} = 0.06$)

(A) – 0.009 V (B) – 1.00738 V (C) – 0.0038 V (D) –1.2 V

54. At 27ºC $\left(\frac{\partial E^o}{\partial T}\right)_P = -1.45 \times 10^{-3}\ V\ K^{-1}$ and $E^o = 1.36$ V

For the cell Pt | H_2 (g) | HCl (aq) | Cl_2 | Pt. Calculate entropy and enthalpy change in this standard state.

(A) –962.48 JK^{-1}, –346.435 KJ (B) –279.85 JK^{-1}, –346.453 KJ
(C) –1326.23 JK^{-1}, –346.435 KJ (D) –280.24 KJK^{-1}, –346.435 KJ.

55. ✍ If K_{sp} values of AgCl, AgBr & AgI at 298 K are 10^{-10}, 10^{-13} & 10^{-17} respectively,
Compare $E^o_{Cl^-/AgCl/Ag}$, $E^o_{Br^-/AgBr/Ag}$ & $E^o_{I^-/AgBr/Ag}$:

(A) $E^o_{Cl^-/AgCl/Ag}$ will have the least value and its value will be less than $E^o_{Ag^+/Ag}$

(B) $E^o_{I^-/AgBr/Ag}$ will have the least value and its value will be more than $E^o_{Ag^+/Ag}$

(C) $E^o_{Cl^-/AgCl/Ag}$ will have the least value and its value will be more than $E^o_{Ag^+/Ag}$

(D) $E^o_{I^-/AgBr/Ag}$ will have the least value and its value will be less than $E^o_{Ag^+/Ag}$

NUMERICAL VALUE QUESTIONS

56. Consider the cell Ag|AgBr(s)| Br^- || Cl^- | AgCl(s)| Ag at 25°C. The solubility product constants of AgBr & AgCl are respectively 5×10^{-13} & 1×10^{-10} . For what ratio of the concentrations of Br^- & Cl^- ions would the e.m.f. of the cell be zero ? Report as 1000 × your answer.

57. A silver coulom meter is in series with a cell electrolyzing water. In a time of 1 minute at a constant current, 1.08 g silver got deposited on the cathode of the coulometer. What total volume **(in mL)** of the gases would have produced in other cell if in this cell the anodic and cathodic efficiencies were 90% and 80% respectively. Assume STP conditions and the gases collected are dry. (Ag – 108) (Molar volume of any ideal gas at STP = 22.4 L). Report as (your answer ÷ 10)

58. During electrolysis of $CH_3COONa_{(aq)}$, the mole ratio of gases formed at anode and cathode is :

59. Calculate the emf of the cell in mV

$$Ag\ (s),\ AgIO_3\ (s)\ \Big|\ Ag^+(xM),\ \ HIO_3\ \ (1\ \ M)\ \Big|\Big|\ Zn^{+2}(1\ \ M)\Big|\ Zn(s)$$

If $K_{sp} = 3 \times 10^{-8}$ for $AgIO_3$ and $K_a = \frac{1}{6}$ for HIO_3 and E^0_{cell} for $2Ag + Zn^{+2} \longrightarrow 2Ag^+ + Zn$ is – 1.56 V.

(log 3 = 0.48) (Take $\frac{2.303\ \ RT}{F} = 0.06$) **(Write magnitude of first two digits of your answer)**

60. A saturated solution of MX is prepared K_{SP} of MX is $a \times 10^{-b}$. If 10^{-7} mol of MNO_3 are added in 1 ℓ of this solution conductivity of this solution is 55×10^{-7} S m^{-1} :

$$\overset{o}{\lambda}_{m^+} = 6 \times 10^{-3}\ S\ m^2\ mol^{-1}\ ;\ \overset{o}{\lambda}_{x^-} = 8 \times 10^{-3}\ ;\ \overset{o}{\lambda}_{NO_3^-} = 7 \times 10^{-3}$$

Find the value of (a + b) ? Given that 10 < a < 100

61. $Zn^{2+}(aq) + 4OH^-(aq) \longrightarrow Zn(OH)_4^{2-}(aq)$

Value of equilibrium constant (K_f) for above reaction is 10^x then find x:

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

$Zn(OH)_4^{2-}(aq) + 2e^- \rightarrow Zn(s) + 4OH^-(aq);\ E^o = -1.36V$

$2.303\frac{RT}{F} = 0.06$

62. A cell reaction, $Zn + 2Fe^{3+} \rightleftharpoons 2Fe^{2+} + Zn^{2+}$, works at 25ºC with the cell emf 1.2 volt and at 45ºC with the cell emf 1.718 volt. Assuming ΔS^o to be constant in this temperature range, calculate ΔS^o in kJ/K. (Give your answer in the nearest integer).

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

63. Which of the following statements is wrong about galvanic cells ?
(A) Cathode is the positive electrode
(B) Cathode is the negative electrode
(C) Electrons flow from cathode to anode in the external circuit
(D) Reduction occures at cathode

64. When a cleaned strip of zinc metal is placed in a solution of $CuSO_4$, a spontaneous reaction occurs. Which of the following observation(s) is/are made ?
(A) the mass of zinc metal decreases gradually
(B) the copper metal starts depositing on either zinc plate or settles down to the vessel
(C) the solution remains electrically neutral
(D) the temperature of the solution decreases as it is an endothermic reaction.

65. Mark out the correct statement(s)

(A) Copper metal cannot reduce iron (II) ions in acidic solutions.

(B) Sodium can be obtained by the electrolysis of aqueous solution of NaCl using Pt electrodes.

(C) The current carrying ions in an electrolytic cell are not necessarily discharged at the electrodes.

(D) Cations having more negative oxidation potential than –0.828 V are reduced in preference to water.

66. When a lead storage battery is recharged

(A) $PbSO_4$ is formed (B) Pb is formed (C) SO_2 is consumed (D) H_2SO_4 is formed

67. Which of the following statements is / are correct ?

(A) The conductance of one cm^3 (or 1 $unit^3$) of a solution is called conductivity.

(B) Specific conductance increases while molar conductivity decreases on progressive dilution.

(C) The limiting equivalent conductivity of weak electrolyte cannot be determine exactly by extraplotation of the plot of Λ_{eq} against $\sqrt{c}$.

(D) The conductance of metals is due to the movement of free electrons.

68. Peroxodisulphate salts ($Na_2S_2O_8$) are strong oxidizing agents used as bleaching agents for fats, oil etc. Given

$O_2(g) + 4H^{\oplus}(aq) + 4e^- \longrightarrow 2H_2O(\ell)$ $E^o = 1.23$ V

$S_2O_8^{-2} + 2e^- \longrightarrow 2SO_4^{-2}$ (aq) $E^o = 2.01$ V

Which of the following statements is (are) correct ?

(A) Oxygen gas can oxidize sulphate ion to per-oxo disulphate ion ($S_2O_8^{-2}$) in acidic solution.

(B) $O_2(g)$ is reduced to water

(C) Water is oxidised to O_2

(D) $S_2O_8^{-2}$ ions are reduced to SO_4^{-2} ions.

69. 0.1 molar solution of NaBr solution is electrolysed by passing 965 column charge. After electrolysis which statement is correct for resulting solution.

(A) Specific conductance increases (B) molar conductance increases

(C) No change in molar conductance. (D) Specific resistance increases.

70. A beaker contains a small amount of iron Fe(s). Which of the following aqueous solution, when added to the beaker, would dissolve the iron i.e. convert Fe(s) to Fe^{2+} (aq) ?

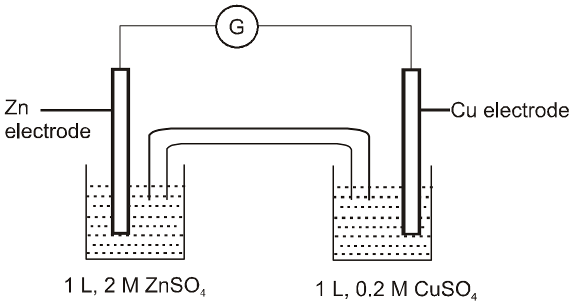
Half cells	E^o at 25°C
$Zn^{2+} + 2e^- \longrightarrow Zn$	–0.76
$Fe^{2+} + 2e^- \longrightarrow Fe$	–0.41
$Al^{3+} + 3e^- \longrightarrow Al$	–1.66
$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$	0.70
$Cr_2O_7^{2-} + 6e^- + H^+ \longrightarrow 2Cr^{3+}$	1.23
$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	1.30

(A) $Cr_2O_7^{2-}$ (acidic solution) (B) H_2O_2 (acidic solution)

(C) Al^{3+} (D) Zn^{2+}

COMPREHENSION

Comprehension # 1



Given $E^o_{Zn^{+2}|Zn} = -0.76$ V K_f $[Cu(NH_3)_4]^{+2} = 4 \times 10^{11}$

$E^o_{Cu^{+2}|Cu}$ = 0.34 V

Answer the following.

71. The emf of cell at 200 k is [Given : $\frac{2.303 \times R}{F}$ = 2×10^{-4} and assume that E° values are independent on temperature.]
(A) 1.7 V (B) 1.08 V (C) 1.09 V (D) 1.10 V

72. When 1 mole NH_3 added to cathode compartment than emf of cell is (at 298K)
(A) 0.81 V (B) 1.91 V (C) 1.1 V (D) 0.72 V

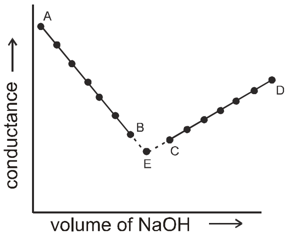
73. At what conc of Cu^{+2} emf of the cell will be zero (at 298K) and conc. of Zn^{+2} is remain same
(A) 1.19×10^{-37} (B) 1.19×10^{-20} (C) 3.78×10^{-4} (D) 0.0068

Comprehension # 2

Strong Acid Versus Strong Base

The principle of conductometric titrations is based on the fact that during the titration, one of the ions is replaced by the other and invariably these two ions differ in the ionic conductivity with the result that the conductivity of the solution varies during the course of the titration. Take, for example, the titration between a strong acid, say HCl, and a strong base, say NaOH. Before NaOH is added, the conductance of HCl solution has a high value due to the presence of highly mobile hydrogen ions. As NaOH is added, H^+ ions are replaced by relatively slower moving Na^+ ions. Consequently, the conductance of the solution decreases and this continues right upto the equivalence point where the solution contains only NaCl. Beyond the equivalence point, if more of NaOH is added, then the solution contains an excess of the fast moving OH^- ions with the result that its conductance is increased and it continues to increase as more and more of NaOH is added.

If we plot the conductance value versus the amount of NaOH added, we get a curve of the type shown in **Fig**.



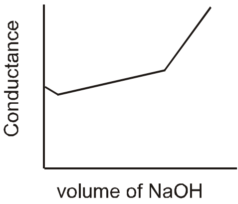
The descending portion AB represents the conductances before the euivalence point (solution contains a mixture of acid HCl and the salt NaCl) and the ascending portion CD represents the conductances after the equivalence point (solution contains the salt NaCl and the excess of NaOH). The point E which represents the minium conductance is due to the solution containing only NaCl with no free acid or alkali and thus represents the equivalence point. This point can, however, be obtained by the extrapolation of the lines AB and DC, and therefore, one is not very particular in locating this point experimentally as it is in the case of ordinary acid-base titrations involving the acid-base indicators.

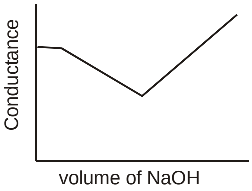
Weak Acid versus Strong Base

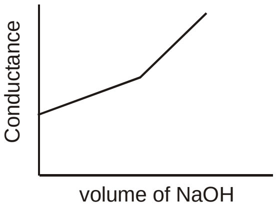
Let us take the specific example of acetic acid being titrated against NaOH. Before the addition of alkali, the solution shows poor conductance due to feeble ionization of acetic acid. Initially the addition of alkali casuse not only the replacement of H^+ by Na^+ but also suppresses the dissociation of acetic acid due to the common ion Ac^- and thus the conductance of the solution decreases in the beginning. But very soon the conductance starts increasing as addition of NaOH neutralizes the undissociated HAc to Na^+Ac^- thus causing the replacement of non-conducting HAc with strong-conducting electrolyte $Na^+ Ac^-$. The increase in conductance continunes right up to the equivalence point. Beyond this point conductance increases more rapidly with the addition of NaOH due to the highly conducting OH^- ions. The graph near the equivalence point is curved due to the hydrolysis of the salt NaAc. The actual equivalence point can, as usual, be obtained by the extrapolation method.

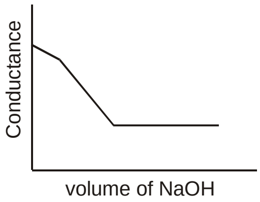
In all these graphs it has been assumed that the volume change due addition of solution from burrette is negligible, hence volume change of the solution in beaker the conductance of which is measured is almost constant throughout the measurement.

74. The nature of curve obtained for the titration **between weak acid versus strong base as described in the above passage will be :**

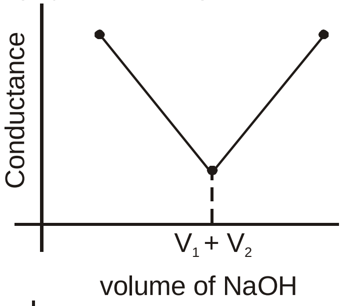
(A) 

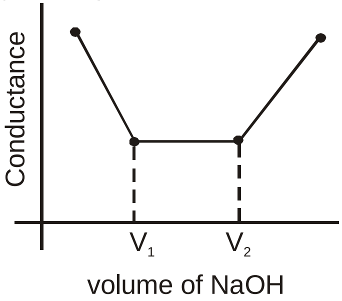
(B) 

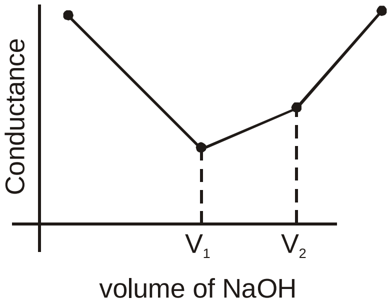
(C) 

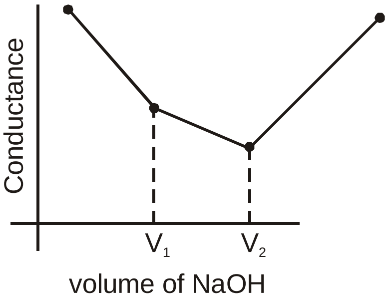
(D) 

75. The most appropriate titration curve obtained when a mixture of a strong acid (say HCl) and a weak acid (say CH_3COOH) is titrated with a strong base(say NaOH) will be

(A) 

(B) 

(C) 

(D) 

PART - V : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr. **Max. Marks : 66**

Important Instructions

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 22 questions. The maximum marks are 66.

B. Question Paper Format

3. Each part consists of five sections.
4. Section 1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section 2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section 3 contains 6 questions. The answer to each of the questions is a numerical value, ranging from 0 to 9 (both inclusive).
7. Section 4 contains 1 paragraphs each describing theory, experiment and data etc. 3 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8. Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C. Marking Scheme

9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.

10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

SECTION-1 : (Only One option correct Type)

This section contains 10 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

1.✍ An initial solution of x M, 1L Fe^{+2} was reduced to Fe(s) on passage of 1 A current for 965 seconds. If after electrolysis 0.1M, 10 ml acidified $KMnO_4$ solution was required to oxidize remaining Fe^{+2} solution then the value of 'x' is -

(A) 10^{-2} (B) 10^{-3} (C) 5×10^{-3} (D) 5×10^{-2}

2. A solution of 100 mL, 0.2 M CH_3COOH is mixed with 100 mL, 0.2 M NaOH solution. The molar conductance for 0.1 M CH_3COOH at infinite dilution is 200 S cm^2 mol^{-1} and at any concentration is 2.0 S cm^2 mol^{-1}. Then calculate pH of the solution?

(A) 7 (B) 8 (C) 5 (D) 9

3. The specific conductance of saturated solution of silver bromide is K (Ω^{-1} cm^{-1}). The limiting ionic conduction of Ag^+ and Br^- ions are a & b respectively. The solubility of AgBr in g lit^{-1} is:
(Molar mass of AgBr = 188g mol^{-1})

(A) $K \times \frac{1000}{a-b}$ (B) $\frac{K}{a+b} \times 188$ (C) $\frac{K \times 1000 \times 188}{a+b}$ (D) $\frac{a+b}{K} \times \frac{1000}{188}$

4.✍ The conductance ratio $\frac{\lambda}{\lambda^{\circ}}$ = 0.936 given this for a certain solution of KCl and λ = 122 $\Omega^{-1}cm^2$ eq^{-1} and $\frac{\lambda^{\circ}_{+}}{\lambda^{\circ}} = \frac{0.98}{1.98}$. Calculate the limiting values of Ionic conductance of $K^{\oplus}$ and Cl^- ions in $\Omega^{-1}cm^2$ eq^{-1}.

(A) 64.51, 65.83 (B) 74.60, 26.40 (C) 30.31, 69.69 (D) 70.12, 29.88

5. Osmotic pressure of 0.1 M weak acid HA is 3 atm. If molar conductance of 0.1 M HA is 30$\Omega^{-1}cm^2mol^{-1}$. than molar conductance at infinite dilution is :

(A) 150 $\Omega^{-1}cm^2$ $mole^{-1}$ (B) 300 $\Omega^{-1}cm^2$ $mole^{-1}$
(C) 100 $\Omega^{-1}cm^2$ $mole^{-1}$ (D) 200 $\Omega^{-1}cm^2$ $mole^{-1}$

6. The molar conductivity of 0.05 M solution of $MgCl_2$ in a cell with electrodes of 1.5 cm^2 surface area and 0.5cm apart and 0.15 amphere current flow when a potential difference of 5 volt is applied between two electrodes –

(A) 200Ω^{-1} cm^2 mol^{-1} (B) 195.6 Ω^{-1} cm^2 mol^{-1}
(C) 149.8 Ω^{-1} cm^2 mol^{-1} (D) 169.5 Ω^{-1} cm^2 mol^{-1}

7.✍ 5 litre solution of 0.4 M $CuSO_{4(aq)}$ is electrolyzed using Pt electrode. A current of 482.5 ampere is passed for 4 minutes. The concentration of $CuSO_4$ left in solution is (Assume volume of solution to be remained unchanged):

(A) 0.16 M (B) 0.28 M (C) 0.34 M (D) 0.40 M

8. For a concentration cell :
Pt | Ag (s) | Ag^+ (aq., C_1) || Ag^+ (aq., C_2) | Ag (s) | Pt
EMF of the cell is X volt then calculate the ratio of $\frac{C_2}{C_1}$?

(A) anti log $\left(\frac{x}{0.059}\right)$ (B) anti log $\left(\frac{x}{2 \times 0.059}\right)$ (C) anti log $\left(\frac{4x}{0.059}\right)$ (D) None of these

9.✍ A saturated solution of $Fe(OH)_3$ is present in a solution of pH = 12, what is the reduction potential of Fe^{3+}/Fe in solution ($E^0_{Fe^{3+}/Fe}$ = –0.036V, K_{sp} of $Fe(OH)_3 = 10^{-26}$), [$\frac{2.303 \times RT}{F}$ = 0.06]

(A) –0.436V (B) 0.39V (C) + 0.36V (D) – 1.2 V

10. Under which of the following condition direction of flow of current will be opposite i.e. from Zn electrode to Cu electrode at 298 K : [Given : $\frac{2.303 \times RT}{F}$ = 0.06] ; E^o_{cell} for $Zn|Zn^{2+}||Cu^{2+}|Cu$ = 1.1 V

(A) $[Zn^{2+}] > e^{84.4}\,[Cu^{2+}]$ (B) $[Zn^{2+}] < e^{84.4}\,[Cu^{2+}]$

(C) $[Zn^{2+}] = e^{84.4}\,[Cu^{2+}]$ (D) $[Cu^{2+}] = e^{84.4}\,[Zn^{2+}]$

Section-2 : (One or More than one options correct Type)

This section contains 6 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

11.✍ Two test tubes I & II contain solutions of sodium salts of halide in water. When Br_2 was added to both the solutions then following observations were noted.

Test Tube	**Observation**
I	Violet vapous emerged
II	No reaction occurred

If halides in the tubes I & II are X^- and Y^- (and their molecular forms being X_2 & Y_2 respectively) then the true options would be :

(A) SRP of Br_2 is more than the SRP of X_2 (B) SRP of Br_2 is more than the SRP of Y_2

(C) Y_2 can oxidize X^- into X_2 (D) Y_2 can oxidize Br^- into Br_2.

12. In the concentration cell

$$\mathrm{Pt}\left|\mathrm{H_2(g)}\right|\begin{matrix}\mathrm{HA}\\ \mathrm{NaA}\end{matrix}\left\|\begin{matrix}\mathrm{HA}\\ \mathrm{NaA}\end{matrix}\right|\mathrm{H_2(g)}\left|\mathrm{Pt}\right.$$

Value of cell potential will depend on –

(A) Value of pKa of HA (B) Temperature

(C) Concentration of HA in two electrodes (D) Concentration of NaA in two electrodes

13.✍ 20 millimolar solution of aq. $CuSO_4$ (500 ml) is electrolysed with sufficient amount and a total of 0.04 faraday of electricity is supplied. Then :

(A) Total volume of gases evolved at STP = 224 ml

(B) Total volume of gases evolved at STP = 448 ml

(C) Total volume of gases evolved at STP = 672 ml

(D) Resulting solution after electrolysis becomes acidic

14.✍ Emf of cell $Ag|Ag^+$ (saturated solution of Ag_2CrO_4) || $Ag^+(0.1\ M)$ | Ag is 0.164 volt at 298 K. Then

(A) K_{sp} of Ag_2CrO_4 in water is nearly 2.3×10^{-12}

(B) Given cell is a concentration cell

(C) K_{sp} of Ag_2CrO_4 can't be determined by given data.

(D) Concentration of Ag^+ ion in anode compartment when EMF is 0.164 volt is nearly 1.66×10^{-4} M

15. $E^o_{Mg^{2+}/Mg} = -2.4V$, $E^o_{Sn^{4+}/Sn^{2+}} = 0.1\ \ V$, $E^o_{MnO_4^-,\,H^+/Mn^{2+}} = 1.5\ \ V$, $E^o_{I_2/I^-} = 0.5\ \ V$

Here,

(A) MnO_4^- is the strongest Oxidizing Agent and Mg is the strongest Reducing Agent.

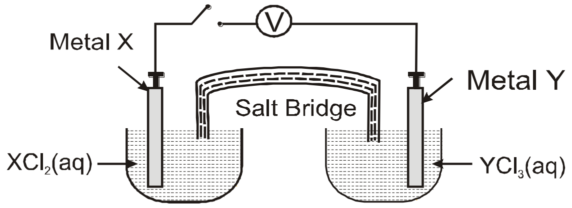
(B) $Sn^{4+} + 2I^- \longrightarrow Sn^{2+} + I_2$ is a nonspontaneous reaction.

(C) $Mg^{2+} + Sn^{2+} \longrightarrow Mg + Sn^{4+}$ is a spontaneous reaction.

(D) Here, Weakest oxidizing agent is Sn^{4+} and weakest reducing agent is Mn^{2+}

16. The following diagram shows an electrochemical cell in which the respective half cells contain aqueous 1.0 M solutions of the salts XCl_2 and YCl_3. Given that:

$3X(s) + 2Y^{3+}(aq) \longrightarrow 3X^{2+}(aq) + 2Y(s) \quad E_{cell} > 0$



Which of the following statements is correct?

(A) The electrode made from metal X has positive polarity.

(B) Electrode Y is the anode

(C) The flow of electrons is from Y to X

(D) The reaction at electrode X is an oxidation

Section-3 : (Numerical Value Questions)

This section contains 6 questions. Each question, when worked out will result in a numerical value from 0 to 9 (both inclusive)

---

17. By how many of the following actions, can the E_{cell} be increased ($\Delta S = +$ ve) for the cell reaction

$A \mid A^+ (aq) \parallel Cl^- \mid Cl_2(g) \mid Pt$

(a) By dilution of anodic solution.

(b) By dilution of cathodic soltuion.

(c) By decreasing temperature.

(d) By increasing pressure of Cl_2 in cathodic compartment.

(e) By increasing the mass of anode (A(s))

(f) By increasing temperature

18. At infinite dilution the molar conductance for CH_3COONa is 150 S cm^2 mol^{-1}, for HCl is 200 S cm^2 mol^{-1} and for NaCl is 125 S cm^2 mol^{-1}. Then calculate pH of 0.001 M CH_3COOH ?
(Given : Molar conductance of CH_3COOH at 0.001 M concentration is 2.25 S cm^2 mol^{-1}).

19. The conductivity of an aqueous solution of a weak monoprotic acid is 0.000032 $ohm^{-1}cm^{-1}$ at a concentration, 0.2 M. If at this concentration the degree of dissociation is 0.02, calculate the value of Λ_0 (ohm^{-1} cm^2 /eqt).

20. Pt, $H_2(g)$ | 2 M $CH_3COONH_4(aq)$ || 2 M NaCl(aq) | $H_2(g)$, Pt
20 atm 0.2 atm

Given $pK_a(CH_3COOH) = 4.74$ $pK_b = (NH_4OH) = 4.74$

If E is emf of the cell in volt, calculate 1000 E. [Take : $\frac{2.303 \quad RT}{F} = 0.059$]

21. EMF of the following cell is 0.634 volt at 298 K Pt | H_2 (1 atm) | H^+ (aq) || Hg_2^{2+}(aq.,1N) | Hg(ℓ). The pH of anode compartment is :

Given $E^0_{Hg_2^{2+}|Hg} = 0.28$ V and $\frac{2.303\ RT}{F} = 0.059$

SECTION-4 : Comprehension Type (Only One options correct)

This section contains 2 paragraphs, each describing theory, experiments, data etc. 6 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph For Questions 22 to 24

Consider the cell :

Pt | H_2 | NaOH (aq), NaCl (aq) | AgCl (s) | Ag
(0.01 M) (0.012 M)

at T^{o}C

E_{cell} = 1.05 V and $E^o_{AgCl/Ag}$ = 0.22 V

Using this knowledge ; and taking $\frac{RT}{F} = 0.06$ (log 1.2 = 0.08)

Answer the following questions.

22. Which of the following is overall cell reaction for the given reaction ?

(A) $\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Cl^-(aq) + Ag$

(B) $H_2(g) + 2OH^-(aq) + 2AgCl(s) \longrightarrow 2H_2O + 2Ag(s) + 2Cl^-(aq)$

(C) $H_2 + 2Ag^+ \longrightarrow 2H^+ + Ag$

(D) $H_2 + 2OH^- + 2Ag^+ \longrightarrow 2Ag + 2H_2O$

23. Find the value of pK_w of water at T^{o}C.

(A) 14.91 (B) 12.91 (C) 13.91 (D) 14.15

24. What can be said about the temperature T^{o}C ?

(A) It is greater than 25^{o}C
(B) It is smaller than 25^{o}C
(C) It is equal to 25^{o}C
(D) Nothing can be said from given information

Paragraph For Questions 25 to 27

The specific conductance of 0.001 M Na_2SO_4 solution is $2.6 \times 10^{-2}\ \Omega^{-1}m^{-1}$ and it increases to $7\times10^{-2}\ \Omega^{-1}m^{-1}$ when the solution becomes also saturated with $CaSO_4$. The limiting molar conductance of Na^+ & Ca^{2+} are 0.005 $\Omega^{-1}\ m^2\ mol^{-1}$ and 0.006 $\Omega^{-1}\ m^2\ mol^{-1}$.

25. Limiting molar conductivity of SO_4^{2-} is -

(A) 0.006 $\Omega^{-1}m^2\ mol^{-1}$ (B) 0.016 $\Omega^{-1}m^2\ mol^{-1}$ (C) 0.012 $\Omega^{-1}m^2\ mol^{-1}$ (D) 0.01 $\Omega^{-1}m^2\ mol^{-1}$

26. Concentration of SO_4^{2-} & Ca^{2+} in the given solutions is -

(A) $[SO_4^{2-}]$ = 0.002 mol/lt, $[Ca^{2+}]$ = 0.002 mol/lt
(B) $[SO_4^{2-}]$ = 0.001 mol/lt, $[Ca^{2+}]$ = 0.002 mol/lt
(C) $[SO_4^{2-}]$ = 0.003 mol/lt, $[Ca^{2+}]$ = 0.002 mol/lt
(D) $[SO_4^{2-}]$ = 0.001 mol/lt, $[Ca^{2+}]$ = 0.001 mol/lt

27. Solubility product of $CaSO_4$ is -

(A) 6×10^{-6} (B) 4×10^{-6} (C) 2×10^{-6} (D) 10^{-6}

SECTION-5 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

28.

List-I			**List-II**
(P)	Molar conductivity	(1)	$\frac{\text{Conductivity}}{\text{Molarity}}$
(Q)	Conductivity	(2)	$\frac{\text{Conductivity}}{\text{Limiting molar conductivity}}$
(R)	Degree of dissociation	(3)	$\frac{\text{Molar conductivity}}{\text{Limiting molar conductivity}}$
(S)	Solubility of sparingly soluble salt	(4)	Decreases with dilution

Codes :

	P	Q	R	S		P	Q	R	S
(A)	4	1	2	3	(B)	2	3	4	1
(C)	1	2	3	4	(D)	1	4	3	2

Practice Test-2 (IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.										
Que.	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
Ans.										
Que.	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**28**		
Ans.										

APSP Answers

PART - I

1.	(1)	**2.**	(4)	**3.**	(3)	**4.**	(2)	**5.**	(4)
6.	(3)	**7.**	(3)	**8.**	(3)	**9.**	(2)	**10.**	(3)
11.	(1)	**12.**	(4)	**13.**	(4)	**14.**	(2)	**15.**	(1)
16.	(2)	**17.**	(1)	**18.**	(3)	**19.**	(2)	**20.**	(3)
21.	6	**22.**	3 (I, II, III)	**23.**	2	**24.**	13	**25.**	50

PART - II

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

PART - III

1.	(B)	**2.**	(B)	**3.**	(C)	**4.**	(C)	**5.**	(A)
6.	(C)	**7.**	(B)	**8.**	(C)	**9.**	(C)	**10.**	(D)
11.	(B)	**12.**	(A)	**13.**	(C)	**14.**	(B)	**15.**	(A)
16.	(C)	**17.**	(B)	**18.**	(D)	**19.**	(B)	**20.**	(D)
21.	(A)	**22.**	(B)	**23.**	(D)	**24.**	(A)	**25.**	(C)
26.	(B)	**27.**	(D)	**28.**	(A)	**29.**	(C)	**30.**	(C)
31.	(A)	**32.**	(C)	**33.**	(B)	**34.**	(B)	**35.**	(B)
36.	(B)	**37.**	(A)	**38.**	(A)	**39.**	(B)	**40.**	(A)
41.	(B)	**42.**	(C)	**43.**	(B)	**44.**	(B)	**45.**	(B)
46.	(D)	**47.**	(D)	**48.**	(B)	**49.**	()	**50.**	(B)
51.	(B)	**52.**	(A)	**53.**	(C)	**54.**	(B)	**55.**	(C)
56.	(C)	**57.**	(C)	**58.**	(B)	**59.**	(B)	**60.**	(C)
61.	(C)	**62.**	(C)	**63.**	(D)	**64.**	(B)	**65.**	(A)
66.	(A)	**67.**	(C)	**68.**	(A)	**69.**	(C)	**70.**	(B)
71.	(B)	**72.**	(A)						

PART - IV

1. (a) $0.34 < E° < 0.8$; (b) $-0.44 < E° < 0$ **2.** –0.8825 volt

3. 0.836 volt, 1.1937 volt **4.** 0.936V

5. n = 3, Since mass of Sn increasing, Sn - electrode is working as cathode and X - metal electrode anode and electrons are flowing from X-electrode to Sn-electrode in the external circuit.

6. E = 0.059 V **7.** E = 0.395 V **9.** –0.042 V **10.** $K_{SP} = 10^{-5}$ **11.** –0.16V

12. $\Delta G = -196.5$ kJ ; $\Delta H = 198.8$ kJ ; $\Delta S = -7.72$ J d_{eg-1} **13.** 3.389×10^{-4} volt deg^{-1}

14. $\Delta S^o = -24.125$ kJ K^{-1} ; $\Delta G^o = -7179.6$ J ; $\Delta H^o = -7196.43$ kJ

15. $\Delta S^o = -30.88$ JK^{-1} $\Delta H^o = -77.23$ kJ $\Delta G^o = -68.03$ kJ

16. A = 114, Q = 5926.8C. **17.** V = 1.763 L **18.** 43.456 g

19. $[Cu^{2+}] = 10^{-4}$ M. **20.** 2×10^{-16} mole / litre.

21. (a) $E^o = 0.59$ V, $\log_{10}K_{sp} = -10$; (b) 52.88, 10^{-6} mole.

22. (A) **23.** (C) **24.** (A) **25.** (A) **26.** (C)

27. (B) **28.** (D) **29.** (D) **30.** (D) **31.** (D)

32. (D) **33.** (C) **34.** (A) **35.** (C) **36.** (A)

37. (D) **38.** (B) **39.** (B) **40.** (B) **41.** (A)

42. (A) **43.** (C) **44.** (A) **45.** (B) **46.** (A)

47. (B) **48.** (B) **49.** (A) **50.** (C) **51.** (A)

52. (B) **53.** (A) **54.** (B) **55.** (D) **56.** 5

57. 14 **58.** 3 **59.** 11 **60.** 26 **61.** 20

62. 5 **63.** (BC) **64.** (ABC) **65.** (ACD) **66.** (BD)

67. (ACD) **68.** (CD) **69.** (AB) **70.** (AB) **71.** (B)

72. (A) **73.** (A) **74.** (A) **75.** (C)

PART - V

1. (A) **2.** (D) **3.** (C) **4.** (A) **5.** (A)

6. (A) **7.** (B) **8.** (A) **9.** (A) **10.** (A)

11. (ACD) **12.** (BCD) **13.** (BD) **14.** (AD) **15.** (AB)

16. (D) **17.** 4 (a, b, d, f) **18.** 5 **19.** 8 **20.** 59

21. 6 **22.** (B) **23.** (C) **24.** (A) **25.** (B)

26. (C) **27.** (A) **28.** (D)

APSP Solutions

PART - I

1. $E_{cell} \Rightarrow E^0_{Sn^{4+}/Sn^{2+}} + E^0_{Fe^{2+}/Fe^{3+}}$ $\Rightarrow$ $0.15 — 0.77 = -0.62$ V

2. $2Cu^{+1} \longrightarrow Cu + Cu^{+2}$

$2Cu^{+1} + 2e \longrightarrow 2Cu$

$Cu - 2e \longrightarrow Cu^{+2}$

$2Cu^{+1} \longrightarrow Cu^{+2} + Cu$

$$\therefore \quad E° = \frac{2 \times 0.521 + 2(-0.337)}{2} = 0.184$$

3. $\frac{W_1}{E_1} = \frac{W_2}{E_2}$; $\frac{4}{12} = \frac{W_{Ag}}{108}$; $W_{Ag} = 36$

4. $Cu^{2+} + 1e^- \rightarrow Cu^+$ $\qquad E^0_1 = 0.15$ v $\Delta G^0_1 = -\, n_1\, E^0_1 F$

$Cu^+ + 1e^- \rightarrow Cu$ $\qquad E^0_2 = 0.50$ v $\Delta G^0_2 = -\, n_2\, E^0_2 F$

$Cu^{2+} + 2e^- \rightarrow Cu$ $\qquad \Delta G^o = \Delta G^o_1 + \Delta G^o_2$

$(-1)\, n\, E^o F = (-1)\, n_1\, E^0_1 F + (-1)\, n_2 E^0_2 F$

$$E^o = \frac{n_1E^0_1 + n_2E^0_2}{n} = \frac{0.15 \times 1 + 0.50 \times 1}{2} = 0.325V$$

5. $H^+ + e^- \longrightarrow \frac{1}{2} H_2$. $\qquad E = 0 - \frac{.0591}{1} \log_{10} \frac{1}{[H^+]} = +\,0.0591 \log_{10}[H^+]$.

$E_1 = 0$ {pH = 0}.

$E_2 = +\,0.0591\log_{10}[10^{-7}] = -\,.0591 \times 7$ {at pH = 7} = $-\,0.41$ V.

6. $E_{cell} = E^o_{cell} - \frac{0.0591}{1}\log_{10}[H^+]\,[Cl^-]$ and $E'_{cell} = E^o_{cell} - \frac{0.0591}{1} \log_{10} 100[H^+]\,[Cl^-]$.

$E'_{cell} - E_{cell} = -\,2 \times 0.0591 = -\,0.1182$.

8. Cell notation is anode || cathode.

9. $0.34 = \frac{0.06}{2} \log K_{eq}$

$\log K_{eq} = 11.3$ or $K_{eq} = 2 \times 10^{11}$

10. Number of moles of Cu^{2+} produced from anode = number of moles of Cu^{2+} deposited at cathode.

11. For same charge passed mole of H_2 produced = 2 × moles of O_2 produced.

13. $\frac{W}{E} = \frac{it}{96500}$ $\Rightarrow$ $\frac{3}{E} = \frac{9.95 \times 10 \times 60}{96500} \Rightarrow$ E = 48.5

14. $K = \frac{1}{R}\left(\frac{\ell}{a}\right) \Rightarrow 0.0112 = \frac{1}{55}\left(\frac{\ell}{a}\right) \Rightarrow \frac{\ell}{a} = 0.616$

15. $\lambda_{eq} = \frac{\left(\frac{1}{R} \times G^*\right) \times 10^{-3}}{N}$ $\qquad \therefore 10^{-2} = \frac{\left(\frac{1}{50} \times G^*\right) \times 10^{-3}}{1/10}$ $\qquad \therefore G^* = 50\ m^{-1}$

16. Λ_m(NaCl), $\lambda_m(Na^+)$, $\lambda_m(Cl^-)$ keep on increasing as concentration decreases but κ keeps on decreasing with dilution.

17. **(i)** $K_2SO_4 . Al_2(SO_4) . 24\ H_2O \Rightarrow 2\ K^{+}_{aq} + 2\ Al^{+3}_{aq} + 4\,SO^{-2}_{aq}$.

$$\lambda^{\alpha}_{m(\text{Potash alum})} = 2\,\lambda^{\alpha}_{m(K^{+})} + 2\ \lambda^{\alpha}_{m(Al^{+3})} + 4\,\lambda^{\alpha}_{m(SO_4^{-2})}$$

$= 2 \times 73.5 + 2 \times 189 + 4 \times 160$

$= 1165\ r^{-}.cm^{2}.mol^{-1}$

V.F. for Potash alum = 8 . (total Positive charge)

$$\lambda^{\alpha}_{eq(\text{Potash alum})} = \frac{\lambda^{\alpha}_{eq(\text{Potash alum})}}{8} = \frac{1165}{8} = 145.6\ \Omega^{-}\ cm^{2}\ eq^{-1}$$

$$\frac{\lambda^{\alpha}_{m(\text{Potash alume})}}{\lambda^{\alpha}_{eq(\text{Potash alume})}} = \frac{1165}{145.6} = 8 : 1$$

(ii) $\dfrac{\lambda^{\alpha}_{m}}{\lambda^{\alpha}_{eq}}$ = V.F. of Compound, V.F. of Potash alume = 8.

18. $\underset{(SA)}{HCl} \rightarrow H^{\oplus} + Cl^{-}$ $\underset{(SASB)}{NaCl} \rightarrow Na^{\oplus} + Cl^{-}$

H^{+} have highest mobility in comparison with $Na^{\oplus}$, both compound 100% dissociate.
because Molar mass of H^{+} is less than $Na^{\oplus}$ ion and NH_4OH is weak basic.

19. Equivalent conductance in different cell is equal :

$\lambda_{eq} = \dfrac{K \times 1000}{N}$ K and N are constant

20. $CH_3COOH + NaOH \longrightarrow Na^{+} + CH_3COO^{-} + H_2O$ Conductance I^st increases slowly since no. of ions increases. After end point it increases sharply due to OH^{-} ions.

21.

$$\begin{array}{ll}
ClO_3^{-} + 2H_2O + 4e \longrightarrow ClO^{-} + 4OH^{-} & ;\ \Delta G_1^{\circ} \\
ClO^{-} + H_2O + e \longrightarrow \frac{1}{2}\ Cl_2 + 2OH^{-} & ;\ \Delta G_2^{\circ} \\
\frac{1}{2}\ Cl_2 + e \longrightarrow Cl^{-} & ;\ \Delta G_3^{\circ} \\
\hline
ClO_3^{-} + 3H_2O + 3e \longrightarrow Cl^{-} + 6OH^{-} & ;\ \Delta G^{\circ} \\
\hline
\end{array}$$

$\therefore$ $\Delta G^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ} + \Delta G_3^{\circ}$

$-\ 6FE^{\circ} = -\ 4F \times 0.54 - 1F \times 0.45 - 1F \times 1.07$

$\therefore$ $E^{\circ} = +\dfrac{3.68}{6} = +\ 0.61\ V$

22. $Zn + Ni^{+2} \longrightarrow Zn^{+2} + Ni$

$E^{o} = E^{o}_{Ni^{+2}/Ni} - E^{o}_{Zn^{+2}/Zn}$

$= -0.23 - (-0.76) = +\ 0.53\ V$

Positive value shows that the process is spontaneous.
Rest of all (I) (II) (III) combination have negative E^{o} value.

(I) $E^{o} = -0.44 - (-0.23) = -0.21\ V$

(II) $E^{o} = -0.76 - (-0.23) = -0.53\ V$

(III) $E^{o} = -0.76 - (-0.44) = -0.32\ V$

23. $\dfrac{m_X}{m_Y} = \dfrac{\dfrac{A_X}{2}\times Q}{\dfrac{A_Y}{1}\times Q} \Rightarrow \quad \dfrac{m_X}{m_Y} = 1 \quad \because \quad A_X = 2A_Y$

24. Let wt of metal deposited for x, y, z is 3a, 2a, a respectively & let moles of e^- passing for x, y, z be 1, 2 and 3 respectively then the wt of x, y, z deposited is E_x, $2E_y$, $3E_z$ (where E_x, E_y, E_z are equivalent wt. of x, y, z)

$\therefore \quad E_x = 3a$

$2E_y = 2a \Rightarrow E_y = a \qquad \& \qquad 3E_z = a \Rightarrow \qquad E_z = \dfrac{a}{3}$

$\therefore \quad E_x : E_y : E_z$

$= \quad 3a : a :$

$= \quad 9 : 3 : 1$

25. $R = \dfrac{1}{k}\ \dfrac{\ell}{A}$

Dilution upto twice of initial volume just complete submerge of electrodes, k becomes half and A becomes double. Hence R remains 50 Ω.

PART - II

1. The E° of cell will be zero.

2. Here Cr^{3+} is oxidised to $C_2O_7^{2-}$

3. At LHS (oxidation) $2 \times (Ag \longrightarrow Ag^+ + e^-)$ $\qquad E^o_{ox} = -x$

At RHS (reduction) $Cu^{2+} + 2e^- \longrightarrow Cu$ $\qquad E^o_{red} = +\,y$

$2Ag + Cu^{2+} \longrightarrow \ Cu + \ 2Ag^+,$ $\qquad E^o_{red} = (y - x)$

4. $0 = 0.295 - \dfrac{0.059}{2}\ \log K \quad ; \quad \log K = 10 \quad ; \quad K = 10^{10}.$

5.

	A	B	C
E^o_{red}	+0.5 V	–3.0 V	–1.2 V

The reducing power follows the following order: B > C > A.

6. $E^o_{cell} = 0.77 + 0.14 = 0.91$ volt.

7. $\overset{0}{\Lambda}_{NaBr} = 126 + 152 - 150 = 128\ S\ cm^2\ mol^{-1}.$

8. $Zn + 2H^+_{(aq)} \longrightarrow Zn^{2+}\,(aq) + H_2\,(g)$

$$E = E^o - \frac{0.0591}{2}\log\frac{[Zn^{2+}]\ \ pH_2}{[H^+]^2}$$

Adding H_2SO_4 means increasing H^+ and therefore E_{cell} will increase and reaction will shift to forward direction.

9. $Cr^{2+} \,|\, Cr^{3+} = +0.41V$ $\qquad Mn^{2+} \,|\, Mn^{3+} = -1.57V$

$Fe^{2+} \,|\, Fe^{3+} = -0.77V$ $\qquad Co^{2+} \,|\, Co^{3+} = -1.97V$

As Cr will have maximum oxidation potential value, therefore its oxidation will be easiest.

10. $Al^{3+} + 3e^- \longrightarrow Al.$

$\dfrac{5.12 \times 10^3}{27} = 189.62$ mol.

Charge = $189.62 \times 3 \times 96500 = 5.489 \times 10^7$ coulomb.

11. $CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$ From the reaction,

$\Lambda^0_{CH_3COONa} + \Lambda^o_{HCl} = \Lambda^0_{CH_3COOH} + \Lambda^o_{NaCl}$ or $\Lambda^0_{CH_3COOH} = \Lambda^0_{CH_3COONa} + \Lambda^o_{HCl} - \Lambda^o_{NaCl}$

Thus to calculate the value of one should know the value of Λ^o_{NaCl} along with and Λ^o_{HCl}.

12. $0.152 = -0.8 - \dfrac{0.059}{1} \log K_{SP}$; $\log K_{SP} = -16.11$.

13. $C = 0.1$ M, $R = 100\ \Omega$

$K = 1.29\ Sm^{-1} = \dfrac{1}{100} \times \dfrac{\ell}{A}$.

$C = 0.02$ M, $R = 520\ \Omega$.

$K = \dfrac{1}{520} \times 129 \Rightarrow \text{Å}_M = \dfrac{\frac{1}{520} \times 129}{1000 \times 0.02} = 124 \times 10^{-4}\ Sm^2mol^{-1}$.

14. According to Kohlrausch's law the molar conductivity at infinite dilution (Λ^o) for weak electrolyte CH_3COOH is

$\Lambda^o_{CH3COOH} = \Lambda^o_{CH3COONa} + \Lambda^o_{HCl} - \Lambda^o_{NaCl}$

So for calculating the value of $\Lambda^o_{CH3COOH}$, value of Λ^o_{NaCl} should also be known.

15. $0 = +1.1 - \dfrac{0.0591}{2} \log \dfrac{[Zn^{2+}]}{[Cu^{2+}]}$; $\log \dfrac{[Zn^{2+}]}{[Cu^{2+}]} = 37.3$. ; $\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ **$= 10^{37.3}$ Ans.**

16. $E_{cell} = E^0_{cell} - \dfrac{0.059}{6} \log \dfrac{[Cr^{+3}]^2}{[Fe^{+2}]^3} = 0.3 - \dfrac{0.056}{6} \log \dfrac{(0.1)^2}{(0.01)^3} = 0.3 - 0.04 = 0.26$ V

17. $Fe^{3+} + 3e^- \longrightarrow Fe$ $\Delta G_1 = -3 \times F \times E^0_{Fe^{3+}/Fe}$

$Fe^{2+} \longrightarrow Fe$ $\Delta G_2 = -2 \times F \times E^0_{Fe^{2+}/Fe}$

$Fe^{3+} + e^- \longrightarrow Fe^{2+}$ $\Delta G = \Delta G_1 - \Delta G_2$

$\Delta G = 3 \times 0.036F - 2 \times 0.439 \times F = -1 \times E^0 (Fe^{3+}/Fe^{+2}) \times F$

$E^0 (Fe^{3+}/Fe^{+2}) = 2 \times 0.439 - 3 \times 0.036 = 0.878 - 0.108 = 0.770$ V

18. $\dfrac{2}{3} Al_2O_3 \longrightarrow \dfrac{4}{3} Al + O_2$

$\Delta_rG = +966\ kJ\ mol^{-1} = 966 \times 10^3\ J\ mol^{-1}$

$\Delta G = -nFE_{cell}$

$966 \times 10^3 = -4 \times 96500 \times E_{cell}$

$E_{cell} = 2.5$ V

19. $2H^+ (aq) + 2e^- \longrightarrow H_2 (g)$

$E_{red} = E^o_{red} - \dfrac{0.0591}{n} \log \dfrac{P_{H_2}}{(H^+)^2}$; $E_{red} = 0 - \dfrac{0.0591}{2} \log \dfrac{2}{(1)^2}$; $E_{red} = -\dfrac{0.0591}{2} \log 2$

$\therefore$ E_{red} is forund to be negative for (3) option.

20. $X + Y^{2+} \longrightarrow X^{2+} + Y$

For reaction to be spontaneous E^o must be positive.

$E^o_{Zn/Zn+2} + E^o_{Ni2+/Ni} = 0.76 + (-0.23) = +0.53$ (positive)

21. Higher the SRP, better is oxidising agent

Hence MnO_4^- is strongest oxidising agent

22. x = 1.4 S/m.

$R = 50\ \Omega$

M = 0.2

$K = \frac{1}{R} \times \frac{\ell}{A} \quad \Rightarrow \frac{\ell}{A} = 1.4 \times 50\ m^{-1}$.

Now, new soltuion has M = 0.5, R = 280 Ω

$$\Rightarrow K = \frac{1}{R} \times \frac{\ell}{A} = \frac{1}{280} \times 1.4 \times 50 = \frac{1}{4} \Rightarrow \Lambda_M = \frac{K}{1000 \times M} = \frac{\frac{1}{4}}{1000 \times 0.5} = \frac{1}{2000} = 5 \times 10^{-4}$$

23. $\lambda_c = \lambda_\infty - B\sqrt{C}$ (Debye Huckel onsagn equation)

24. **Reason:** Higher the position of element in the electrochemical series, more difficult is the reduction of its cations.

If Ca^{2+} (aq) is electrolysed, water is reduced in preference to it. Hence it cannot be reduced electrolytically from an aqueous solutions.

25. $Mn^{2+} \xrightarrow{E_1^0 = 1.51V} Mn^{2+} \xrightarrow{E_2^0 = -1.18V} Mn$

∴ for Mn^{2+} disproportionation, $E^0 = -1.51\ V - 1.18\ V$

$= -2.69\ V < 0$

Reaction is non-spontaneous.

26. $Cu^{2+} + 2e^- \longrightarrow Cu$

2F 1 mole

= 63.5 g.

27. Galvanization is applying a coating of Zn.

28. For strongest reducing agent E°_{OP} should be maximum.

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

Whereas,

$E^\circ_{OP\ Mn^{2+}/MnO_4^-} = -1.51\ V \quad \Rightarrow \quad E^\circ_{OP\ Cr^{3+}/Cr_2O_7^{-2}} = -1.33\ V \quad \Rightarrow \quad E^\circ_{OP\ Cl^-/Cl_2} = -1.36\ V$

29. $B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O$

1 mol 3 mol

3 mol O_2 is required for Burning 1 mol B_2H_6

$H_2O \xrightarrow{\text{Electrolysis}} H_2 + \frac{1}{2}O_2$ (V.F. of O_2 = 4)

$\frac{\text{Equivalent of } O_2}{\text{V.F. of } O_2} = \text{mol of } O_2 = 3$

$\left[\frac{(100A) \times t\,\text{sec.}}{96500}\right] \times \frac{1}{4} = 3 \quad \Rightarrow \quad \therefore\ t = \frac{3 \times 96500 \times 4}{100 \times 3600}\text{hr.} = 3.22\text{hrs.}$

PART - IV

1. (a) Metal should below hydrogen and Cu^{2+} but should above Ag^+ in series.

(b) Metal should above hydrogen but should below from Zn^{2+} and Fe^{2+} both.

2. $TiO^{2+} + 2H^+ + e^- \longrightarrow Ti^{3+} + H_2O$, 0.1 V $\Delta G_1^o = -2 \times F \times 0.1$

$Ti^{3+} + 3e^- \longrightarrow Ti$ – 1.21 V $\Delta G_2^o = -3 \times (-1.21) \times F$

$TiO^{2+} + 2H^+ + 4e^- \longrightarrow Ti + H_2O$

$-4 \times E^o \times F = -1 \times 0.1 \times F + -3 \times (-1.21) \times F$

$E^o = \frac{0.1 - 3.63}{4} = -0.8825$ volt.

3. $E_{oxidation} = -0.78 - \frac{0.0591}{2}\log 9^2 \qquad = -0.78 - \frac{0.0591}{2} \times 2 \times \log 9 \; = -0.836$ volt

$E_{reduction} = -E_{oxidation} = 0.836$ volt

In neutral medium,

$E_{Oxidation} = -0.78 - \frac{0.0591}{2}\log (10^{-7})^2 \quad = -1.1937$ volt

4. $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2\,Cr^{3+} + 7\,H_2O$, 1.33 volt

$$E = 1.33 - \frac{0.0591}{6}\log\frac{(0.01)^2}{(0.01)\times(10.^{-3})^{14}} = 1.33 - \frac{0.0591}{6}\log 10^{-2}\times 10^{42}$$

$$= 1.33 - \frac{0.0591}{6}\times \log 10^{40} = 1.33 - \frac{0.0591}{6}\times 40 = 0.936 \text{ volt}$$

5. $0.65 = E_{oxid} + E_{red} = \left\{0.78 - \frac{0.0591}{n}\log(0.1)\right\} + \left\{0 - 0.14 - \frac{0.0591}{2}\log\frac{1}{0.5}\right\}$

$0.01 = -\frac{0.0591}{n}\times(-1) - \frac{0.0591}{2}\times 0.301 = 0.0591\left(\frac{1}{n} - \frac{0.301}{2}\right)$ n = 3

Electrons flow from X electrode to Zn electrode.

6. $Pt / H_2O / H^+ (HA) // H^+ (HB) / H_2 / Pt$

$H_2 \longrightarrow 2H^+ + 2e^-$

$2H^+ + 2e^- \longrightarrow H_2$

$2H^+_{(HB)} \longrightarrow 2H^+_{HA} \qquad E^o = 0$

$E = 0 - \frac{0.0591}{2}\log\frac{[H^+]^2_{HA}}{[H^+]^2_{HB}} \qquad$ But $Ka = \frac{[H^+]^2}{C}$

$= -\frac{0.0591}{2}\log\frac{10^{-3}\times C}{10^{-5}\times C} \qquad = -0.0591$

the cell is constructed in reversed direction.

$E_{cell} = 0.0591$ volt.

7. $Pt / H_2 / H^+ (C_6H_5NH_{2(C)} // H^+_{(HCl)} / H_2 / Pt$

$H_2 \longrightarrow 2H^+_{(10-8M)} + 2e^-$, $\qquad C_6H_5NH_2 + H_2O \longrightarrow C_6H_5NH_3^+ + OH^-$

$2H^+ + 2e^- \longrightarrow H_2 \qquad K_b = \frac{(OH^-)^2}{\frac{5\times10^{-4}}{0.5}}$

$2H^+_{(5\times10-2)} \longrightarrow 2H^+_{(10-8)}$

$E = 0 - \frac{0.0591}{2}\log\frac{(10^{-8})^2}{(5\times10^{-2})^2} = -\frac{0.0591}{2}\log 10^{-14}\times 4 = \frac{0.0591}{2}.[\log 4 - 14] = 0.396$ volt

8. (A) $Hg_2Cl_2(s) + Cu(s) \longrightarrow Cu^{2+}(aq) + 2Cl^-(aq) + 2Hg(l)$

(B) $2Ag_{(s)} + 2IO_3^- + Zn^{2+} \longrightarrow 2AgIO_{3(g)} + Zn_{(s)}$

(C) $Mn_{(s)} + 2OH^- + Cu^{2+} \longrightarrow Mn(OH)_{2(s)} + Cu_{(s)}$

9. $E = 0 - \frac{.06}{1}\log\frac{10^{-10}/0.2}{10^{-13}/10^{-3}} = -0.042$ V

10. $E^0_{cell} = \frac{.06}{2}\log\frac{1}{K_{SP}} \quad\Rightarrow\quad -0.12 + 0.27 = .03\log\frac{1}{K_{SP}} \quad\Rightarrow\quad K_{SP} = 10^{-5}$

11. $E^0_{Cell} = 0.06(-\log K_{SP}) \quad\Rightarrow\quad 0.8 - E^0_{I^-/AgI/Ag} = 0.96 \quad\Rightarrow\quad E^0_{I^-/AgI/Ag} = 0.16V$

12. Cd (12.5%) in Hg / 3Cd SO_4, $8H_2O$ (solid) / satd sol of $CdSO_4$ || $Hg_2SO_{4(s)}$ | Hg, E = 1.018 volt

$\left(\frac{dE}{dT}\right)_P = -4 \times 10^{-5}$ volt $d_{eg-1.}$

$\Delta G = -nEF = -2\ 1.018 \times 96500 = -196.474$ kJ

$\Delta S = nF.\left(\frac{dE}{dT}\right)_P = 2 \times 96500 \times (-4 \times 10^{-5}) = -7.72\ JK^{-1}$.

$\Delta G = \Delta H - T\Delta S$

$\Delta H = -196.474 + \frac{298 \times (-7.72)}{1000} = -196.474 - 2.3 = 198.774$ kJ

13. $Ag(s) + \frac{1}{2}Hg_2Cl_2(s) \longrightarrow AgCl_{(s)} + Hg(l)$, $\Delta H = 1280$ cal.

E = 0.0455 volt

$\Delta H = -nEF + nF.T.\frac{dE}{dT}$

$1280 \times 4.18 = -1 \times 0.0455 \times 96500 + 1 \times 96500 \times 298 \times \frac{dE}{dT}$. $\Rightarrow$ $\frac{dE}{dT} = 3.387 \times 10^{-4}$ volt deg^{-1}.

14. $\frac{dE}{dT} = -0.125\ VK^{-1}$. $E^o = 0.0372$ volt

$\Delta G^o = -nEF = -2 \times 0.0372 \times 96500 = -7.1796$ kJ.

$\Delta S^o = nF \times \left(\frac{dE}{dT}\right)_P = 2 \times 96500 \times (-0.125) = -24.125$ kJ K^{-1}.

$\Delta H^o = \Delta G^o + T\,\Delta\,S^o = -7.1796 - 298 \times 24.125 = -7196.43$ kJ

15. $E^0_{25^oC} = 0.3525$ volt $E^0_{20^oC} = 0.3533$ volt n = 2

$\frac{dE}{dT} = \left(\frac{E^0_{25^oC} - E^0_{20^oC}}{T_2 - T_1}\right) = \frac{0.3525 - 0.3533}{25 - 20} = -1.6 \times 10^{-4}$ volt deg^{-1}.

$\Delta G^o_{25} = \Delta H^o_{25} - 298 \times \Delta S^o_{25} = -2 \times 0.3525 \times 96500 = -68.03$ kJ

$\Delta S^o = 2 \times 96500 \times (-1.6 \times 10^{-4}) = -30.88$ Jk.

$\Delta H^o = \Delta G^o + T\Delta S^o = -68.03 - 298 \times \frac{30.88}{1000} = -77.23$ kJ

16. v.f. of metal = 2.

w = Zit.

$1.95 = \frac{E}{96500}$ it $= \frac{M \times it}{v.f. \times 96500}$ $\Rightarrow$ M = 114 g.

अब Cu के लिए, $w = \frac{63.5 \times (it)}{2 \times 96500}$ $\Rightarrow$ $1.95 = \frac{63.5 \times (it)}{2 \times 96500}$ $\Rightarrow$ it = 5926.77 C.

17. $2CH_3COONa \xrightarrow{\text{Electrolysis}} \frac{C_2H_6 + 2CO_2}{\text{at anode}} + \frac{H_2}{\text{Cathode}}$

Electric supplied $= \frac{0.965 \times 60 \times 60}{96500} = 3.6 \times 10^{-3}$ F

$V_{H2} = \frac{3.6 \times 10^{-3}}{2} \times \frac{0.0821 \times 298}{1} = 0.44$ lit ; $V_{total} = V_{C_2H_4} + V_{CO_2} + V_{H2} = 4 \times 0.44 = 1.76$ lit.

18. Reaction at anode $2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H^+ + 2e^-$

$H_2S_2O_8$, O_2 are the product at anode.

$2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

Reaction at cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

Eq. of H_2 = Eq. of O_2 + Eq. of $H_2S_2O_8$

$\frac{9.722}{22.4} \times 2 = \frac{2.35}{22.4} \times 4 + x \times 2$ ⇒ $x = 0.244$ mole ⇒ $W_{H_2S_2O_8} = 43.49$ g.

19. E^o $Bi^{3+}/Bi = 0.226$ volt E^o $Cu^{2+}/Cu = 0.344$ volt

$0.226 = 0.344 \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$ ⇒ $-\log [Cu^{2+}] = 4$ $[Cu^{2+}] = 10^{-4}$ M.

20. $K = 5.8 \times 10^{-8}$ Scm^{-1}, $\Lambda^o_{H^+} = 350$ Scm^2 $\Lambda^o_{OH^-} = 198$ Scm^2

$\Lambda_{H_2O} = \frac{1000 \times 5.8 \times 10^{-8}}{55.5}$; $\alpha = \frac{\Lambda_{H_2O}}{\Lambda^o_{H_2O}} = \frac{(1000 \times 5.8 \times 10^{-8})}{55.5 \times (350 + 198)} = 0.1907 \times 10^{-8} = 1.907 \times 10^{-9}$

$K_a = C\alpha^2 = 55.55 \times (1.907)^2 \times 10^{-18} = 2.02 \times 10^{-16}$.

21. **(a)** $\Delta G^o_r = -109 + 129 - 77 = -57$ kJ/mol

Cell representation : Ag | AgCl | | Cl^-| Ag^+ | Ag.

$-1 \times 96500 \times E^o = -57 \times 10^3$.

E^o = 0.59 volt.

$0 = 0.59 - \frac{0.059}{1} \log \frac{1}{K_{SP}}$.

log K_{SP} = **– 10.**

(b) $Zn \longrightarrow Zn^{2+} + 2e^-$, 0.76 volt.

$2Ag^+ + 2e^- \longrightarrow 2Ag$, 0.80 volt.

$Zn + 2Ag^+ \longrightarrow Zn^{2+} + 2Ag$, $E^o_{cell} = 1.56$ volt.

$n_{Zn} = \frac{6.539 \times 10^{-2}}{65.39} = 10^{-3}$ mol, $[Ag^+] = \sqrt{K_{sp}} = 10^{-5}$ M.

$0 = 1.56 - \frac{0.059}{2} \log K$ $n_{Ag+} = 10^{-5} \times 0.1 = 10^{-6}$ M.

$n_{Ag} = 10^{-6}$ mol. ⇒ **log K = 52.8.**

22. $H^+ + e^- \longrightarrow \frac{1}{2} H_2$, $E° = 0$, $\Delta G° = 0$

$H_2O \rightleftharpoons H^+ + OH^-$, $\Delta G° = -8.314 \times 298 \ln 10^{-14}$

$H_2O + e^- \longrightarrow \frac{1}{2} H_2 + OH^-$, $-1 \times E° \times 96500 = -8.314 \times 298 \ln 10^{-14}$

$E° = -0.828$ Volt.

23. $Hg_2^{2+} + 2e^- \longrightarrow 2Hg$, 0.789 Volt

$Hg \longrightarrow Hg^{2+} + 2e^-$, –0.854 Volt

$Hg_2^{2+} \longrightarrow Hg + Hg^{2+}$, –0.065 Volt

$\Delta G = -2 \times (-0.065) \times 96500 = -8.314 \times 298 \ln K_{eq.}$; $K_{eq.} = 6.3 \times 10^{-3}$

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

$$E_1 = E° - \frac{0.0591}{5}\log \frac{[Mn^{2+}]}{[MnO_4^-] \times 1^8}$$

$$E_2 = E° - \frac{0.0591}{5}\log \frac{[Mn^{2+}]}{[MnO_4^-] \times \left(10^{-4}\right)^8} = -\frac{0.0591}{5} \times 32 = -0.37824 \qquad E_1 - E_2 = 0.38 \text{ Volt.}$$

25. $0 = (-0.771 + 0.7991) - \frac{0.0591}{1}\log\frac{1}{x} \quad \Rightarrow \quad 0 = 0.0281 + 0.0591 \log x$

$\log x = -\frac{0.0281}{0.0591} \quad \Rightarrow \quad x = 0.335$ M

26. $0 = (-0.151 - 0) - \frac{0.0591}{1}\log [H^+]$.

$0.0591 \times \log[H^+] = -0.151 \quad ; \quad pH = \frac{0.151}{0.0591} = 2.56$

27. $E^0_{Ag\,|\,Ag\,I\,|\,I^-} = E^0_{Ag^+|Ag} - \frac{0.0591}{1}\log\frac{1}{K_{SP}}$

$-0.151 = 0.799 - \frac{0.0591}{1}\log\frac{1}{K_{sp}}$

$0.0591 \log K_{sp} = -0.151 - 0.799$

$\log K_{sp} = -16.074$

$K_{sp} = 8.43 \times 10^{-17}$

28. $E_{I^-/AgI/Ag} = 0.8 - \frac{0.0591}{1}\log\frac{1}{K_{sp}}$

$= 0.8 + 0.0591 \times \log 8.3 \times 10^{-17} = -0.15$ Volt

or

$E^o{}_{Ag/AgI/I^-} = E^o{}_{Ag/Ag^+ + \frac{RT}{F}} . \ln\frac{1}{k_{sp}} = -0.8 - \frac{8.31 \times 298 \times 2.303}{96500}\log k_{sp}$

$= -0.8 - 0.0591. \log 8.3 \times 10^{-17} = -0.8 + 0.095 = 0.15$ V.

29. $A_{(s)} + B^{2+}_{aq.} \longrightarrow A^{2+}_{aq.} + B_{(s)}$, $\Delta H° = -285$ KJ

Assuming Δs to negligible , $\Delta G° = \Delta H° = -285 \times 10^3 \times 0.84 \quad = \quad -2 \times E° \times 96500$

$E° = 1.24$ Volt

30. $\frac{d\varepsilon}{dt} = -0.00065$ Vol deg^{-1}

$\Delta S_{298} = n.F. \frac{dE}{dT} \qquad = 2 \times 96500 \times (-0.00065) = -125.5$ J/K.

31. $\frac{dE}{dT} = \frac{(0.6753 - 0.6915)}{(25 - 0)} = -6.48 \times 10^{-4}$ V deg^{-1}

$\Delta H_{298} = -neF + nFT\frac{dE}{dT} = -2 \times 0.6753 \times 96500 + 2 \times 96500 \times 298 \times (-6.48 \times 10^{-4})$

$= 2 \times 96500 (-0.6753 - 0.1931) = -167.6$ KJ.

32. $E° = 1.1028 – 0.641 \times 10^{–3}\ T + 0.72 \times 10^{–5}\ T^2$

$\left(\frac{dE^o}{dT}\right)_{2S} = –0.641 \times 10^{–3} + 2 \times 0.72 \times 10^{–5}\,T \qquad = (–0.641 + 0.36) \times 10^{–3} = –0.281 \times 10^{–3}$

$\Delta S° = nF\,\frac{dE^o}{dT} = 2 \times 96500 \times (–281 \times 10^{–3}) \ = – 54.23$ EU

33. $E^{\circ}_{298} = 1.1028 – 0.641 \times 10^{–3} \times 25 + 0.72 \times 10^{–5} \times (25)^2 = 1.091275$ Volt

$= –8.314 \times 298 \ln K = – 2 \times 1.091275 \times 96500$

$K = 10^{36.91} = 8.128 \times 10^{36}$**.**

34. $\Delta S = – \left\{\frac{d}{dT}(\Delta G)\right\}_p \quad = + nF\left(\frac{dE}{dT}\right)_p$

$\left(\frac{dE}{dT}\right)_p = \frac{\Delta S}{nF}$

35. $Na^+ \ + \ e^- \ \longrightarrow \ Na(s)$

1mole 1 Faraday

$Al^{3+} + 3e^- \longrightarrow Al(s)$

1 Faraday

No. of mole of Al = $\frac{1}{3}$ mole.

36. $\Lambda_{Ag^+} = 62.3\ Scm^2\ mol^{–1},\ \Lambda_{Cl^-} = 67.7\ Scm^2\ mole^{–1}$

$K_{Agcl} = 3.4 \times 10^{–6}\ Scm^{–1}$

$\Lambda^{\infty}_{AgCl} = (62.3 + 67.5) = \frac{1000 \times 3.4 \times 10^{-6}}{S}$

$S = \frac{3.4 \times 10^{-3}}{(62.3 + 67.5)} = 2.6 \times 10^{–5}\ M$

38. Higher the std. reduction potential, higher is the oxidising power.

39. $E_{cell} = 0.29 – \frac{0.059}{2} \log \frac{0.01 \times (0.01)^2}{(0.01)^2 \times 1}$ or $E_{cell} = 0.35$ volt

40. $E^o_{cell} = 1.89$; $E^o_{Ce4+/Ce3+} + E^o_{Co/Co2+} = E + 0.277 \Rightarrow E = 1.62\ V$

41. $E^o_{MnO_4^- / MnO_2} = \frac{5 \times 1.5 – 2 \times 1.23}{3} = 1.7$ volt

42. $\Delta S = \frac{nFd\ \ E_{cell}}{d\ \ t}$ or $\frac{d\ \ E_{cell}}{d\ \ t} = \frac{\Delta\ \ S}{n\ \ F}$

43. $– 0.413 = 0 – 0\ .059 \log \frac{1}{[H^+]}$ or $\frac{0.414}{0.059} = – \log\ H^+ = pH$ or $pH = 7$

44. Z > Y > X (Non metals like $F_2 > Cl_2 > Br_2$)

So, Y will oxidise $X^–$ but not $Z^–$

Z will oxidise both $X^–$ and $Y^–$

X can't oxidise $Y^–$ or $Z^–$.

45. $E^o_{cell} = 0.8 – (– 0.76) = 1.56\ V$

46. $E_{cell} = 0.77 - \frac{0.059}{1}\log\frac{1.5}{0.015} = 0.652$ V

47. $1.1591 = 1.1 - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$ or $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{-2} = 0.01$

48. $Ag \longrightarrow Ag^+ + e^-$

$E_1 = E_{oxid} + E_{calomel}$

$= E' - \frac{0.0591}{1}\log\sqrt{K_{sp_1}} + E_{calomel}$

$E_2 = E' - \frac{0.0591}{1}\log\sqrt{K_{sp_2}} + E_{calomel}$ ⇒ $E_2 - E_1 = 0.177 = 0.0591\log\sqrt{\frac{K_{sp_1}}{K_{sp_2}}}$

$\frac{K_{sp_1}}{K_{sp_2}} = 10^6.$

49. $H^+ + Cl^- + NaOH \longrightarrow Na^+ + Cl^- + H_2O$ to conductance Ist decreases since no. of ions decreases after end point it inceases.

50. $E_{cell} = E^o_{cell} - \frac{0.059}{2}\log\frac{[Sn^{2+}]}{[Ag^+]^2}$ Ag^+ increase, E_{cell} increase.

51. $\frac{i \times 15 \times 60}{96500} = \frac{6.72}{22.4} \times 2$ ⇒ i = 64.3 amp.

52. $AgCl + e^- \longrightarrow Ag + Cl^-$ E° = 0.2 V

$Ag \longrightarrow Ag^+ + e^-$ E° = – 0.79 V

$AgCl \xrightarrow{e^-} Ag^+ + Cl^-$ E° = – 0.59 V

$E^\circ = \frac{0.059}{n}\log K$ ⇒ $-0.59 = \frac{0.059}{1}\log K_{SP}$ ⇒ $K_{SP} = 10^{-10}$

Now solubility of AgCl in 0.1 M $AgNO_3$

$S(S + 0.1) = 10^{-10}$ ⇒ $S = 10^{-9}$ mol/L

Hence 1 mole dissolves in 10^9 L solution

hence in 10^6 L amount that dissolves in 1 m mol.

53. Q = 10 × 4825 = 48250 C

no. of faraday $= \frac{48250}{96500} = 0.5$

$$\begin{array}{lllll} Ag & + & \frac{1}{2}Cu^{++} \longrightarrow & Ag^+ & + \quad \frac{1}{2}Cu \\ & & 2.00 & 2.00 & \\ & & 2-0.25 & 2 + 0.50 & \end{array}$$

$E_{cell} = E^o_{Cell} - \frac{0.0591}{1}\log\frac{[Ag^+]}{[Cu^{++}]^{1/2}}$

$E_1 = E^o_{Cell} - \frac{0.0591}{1}\log\frac{2.00}{(2.00)^{1/2}}$

$E_2 = E^o_{Cell} - \frac{0.0591}{1}\log\frac{2.50}{(1.75)^{1/2}}$

$$\Delta E = E_2 - E_1 = \frac{0.0591}{1}\left[\log\sqrt{2} - \log\frac{2.50}{\sqrt{1.75}}\right] = \frac{0.0591}{1}\ [\log 1.41 - \log 1.88]$$

$$= \frac{0.0591}{1}\ [0.1492 - 0.2742] = -\frac{0.0591}{1} \times 0.125 = -\ 0.00738\ \text{V}.$$

54. $nF\left(\frac{\partial E^o}{\partial T}\right) = \Delta S^o = -2 \times 96500 \times 1.45 \times 10^{-3} = -279.85\ JK^{-1}$

$\Delta G^o = -nFE^o = -2 \times 1.36 \times 96500 = -262.48$ KJ.

$\Delta H^o = \Delta G^o + T\Delta S^o$

$= -262.48 \times 10^3 - 300 \times 279.85$

$= -262480 - 83955 = -346.435$ KJ

55. $E^o_{X^-/AgX/Ag} = E^o_{Ag^+/Ag} + \frac{0.059}{1}\log_{10} K_{sp}\ (AgX)$

Thus, salt having least value of K_{sp} will have least value of $E^o_{X^-/AgX/Ag}$ and all values will be less than $E^o_{Ag^+/Ag}$ (since 2nd term will always have a negative values).

56. If cell is taken to be conc cell, $E^o_{cell} = 0$

Anode : $Ag \longrightarrow Ag^+_a + e^-$

Cathode : $Ag^+_c + e^- \longrightarrow Ag$

$Ag_c^+ \rightleftharpoons Ag_a^+$

From Nernst eq,

$E_{cell} = E^o_{cell} - \frac{0.059}{1}\log\frac{[Ag^+]_a}{[Ag^+]_c}$ $\Rightarrow$ $0 = 0 - \frac{0.059}{1}\log\frac{[Ag^+]_a}{[Ag^+]_c}$

$\therefore [Ag^+]_a = [Ag^+]_c \Rightarrow \frac{K_{sp}\text{ of AgBr}}{[Br^-]} = \frac{K_{sp}\text{ of AgCl}}{[Cl^-]}$ or , $\frac{5 \times 10^{-13}}{10^{-10}} = \frac{[Br^-]}{[Cl^-]} = \frac{[Br^-]}{[Cl^-]} = \frac{1}{200}$.

57. Charge passed = 0.01 Faraday

At the anode $\left(H_2O \longrightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-\right)$ with 90 % efficientcy 0.01 × 0.9 F have been used and will produce $\frac{1}{4}$ × 0.01 × 0.9 mole of O_2 i.e. 0.00225 mol O_2 .

At the cathode $2H_2O \xrightarrow{+2e^-} H_2 + 2OH^-$

moles of H_2 produced = $\frac{0.01 \times 0.8}{2}$ mol = 0.004 mol

Total moles produced of gases = 0.004 + 0.00225 = 0.00625 mol

vol. at STP = 0.00625 × 22400 mL = 140 mL

59. $K_a = \frac{C\ \ \alpha^2}{1-\alpha}$ $\Rightarrow$ $\frac{1}{6} = \frac{\alpha^2}{1-\alpha}$

$\Rightarrow$ $\alpha = \frac{-1 \pm \sqrt{(1)^2 + 4 \times 6 \times 1}}{12} = \frac{-1 \pm \sqrt{1+24}}{12} = \frac{1}{3}$

$\therefore$ $[IO_3^-] = 1 \times \frac{1}{3} = \frac{1}{3}$ M

$\Rightarrow \quad [Ag^+] = \dfrac{3\times10^{-8}}{\frac{1}{3}} = 9 \times 10^{-8}$ M

Now $2Ag + Zn^{+2} \xrightarrow{2e^-} 2Ag^+ + Zn$

Gives: $E = -1.56 + \dfrac{0.06}{2}\log\dfrac{1}{(9\times10^{-8})^2} = -1.1376$ V

Ans. 11

60. $MX \rightleftharpoons M^+ + X^-$

$a + 10^{-7} \qquad a$

$K_{SP} = (a + 10^{-7})\, a$

$\dfrac{55\times10^{-7}}{1000} = (6 \times 10^{-3} (a + 10^{-7}) + 8 \times 10^{-3} a + 7 \times 10^{-3} \times 10^{-7})$

$55 \times 10^{-10} = 6 \times 10^{-3} a + 6 \times 10^{-10} + 8 \times 10^{-3} a + 7 \times 10^{-10}$

$42 \times 10^{-10} = 14 \times 10^{-3} a$

$a = 3 \times 10^{-7}$

$K_{SP} = 12 \times 10^{-14}$

61. $E^o_{cell} = E^o_{RP(RHS)} - E^o_{RP(LHS)}$

$= -0.76 - (-1.36) = 0.6$

$\Delta_r G^o = -RT \ln K_{eq}$;

or $\log K_{eq} = \dfrac{nFE^o}{RT \times 2.303} = \dfrac{2\times0.6}{0.06} = 20 \quad \Rightarrow \quad \dfrac{2\times0.6}{0.06} \Rightarrow 20;\ K_f = 10^{20}$

62. $\Delta S^o = nF\dfrac{dE}{dt} = 2 \times 96500 \times \dfrac{1.718 - 1.2}{20} = 5000$ Joule/K.

63. Reduction and electronation take place at cathode elctrode, so it become positive electrode.

64. (A, B, C) Reduction Potential of Ce is higher than that of Zn.

65. (A) because $E^o_{Cu^{2+}/Cu} > E^o_{Fe^{2+}/Fe}$.

66. Recharging reaction: $2PbSO_4 (s) + 2H_2O. \longrightarrow Pb(s) + PbO_2(s) + 2H_2SO_4 (aq)$

67. On dilution specific conductance decreases while molar conductivity increases.

68. Create a cell with required cell reaction

$O_2 + SO_4^{-2} \longrightarrow S_2O_8^{-2} + H_2O \qquad E^o_{cell} = 1.23 - 2.01 < 0$

$\Rightarrow$ Nonspontaneous cell reaction

69. Electrolysis of NaBr Solution

At Anode $\quad 2Br^- \longrightarrow Br_2 + 2e^-$

at cathode $\quad 2H_2O \xrightarrow{+2e^-} H_2 + 2OH^-$

It is clear that Br^- ion are replaced by OH^-.

Hence molar conductance & specific conductance increases.

70. (A) For $Cr_2O_7^{2-}$ (acidic solution)

$E^o = 1.23$ which is greater than $E^o_{(Fe^{2+}/Fe)}$ hence it can oxidize Fe

(B) $H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^-$ $E^o = -0.70$ V

$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ $E^o = 1.30$ V

$H_2O_2 + 2H^+ \longrightarrow 2H_2O$ $E^o = \dfrac{(-0.70\times 2)+(4\times 1.30)}{2} = 1.9$

Here E^o is grater than $E^o_{(Fe^{2+}/Fe)}$ hence H_2O_2 in acidic medium can oxides Fe.

71. $E_{cell} = E^o_{cell} - \dfrac{2.303\ \ RT}{nF}\log\dfrac{(Zn^{+2})}{(Cu^{+2})} = 0.76 + 0.34 - \dfrac{2.303\times 8.31\times 200}{2\times 96500}\log\dfrac{2}{0.2} = 1.08$ volt.

72. $Cu^{+2} + 4\,NH_3 \rightleftharpoons [Cu\,(CH_3)_4]^{+2}$

0.2 1 0

x 1–0.8 0.2

$k_f = 4.0\times 10^{11} = \dfrac{0.2}{x\times(0.2)^4} = \dfrac{1}{x\times(0.2)^3}$

$x = \dfrac{10^{-11}}{(0.2)^3\times 4} \Rightarrow x = 3.125\times 10^{-10}$ $[Cu^{+2}] = 3.125\times 10^{-10}$

$E_{cell} = 0.75 + 0.34 - \dfrac{0.0591}{2}\log\dfrac{2}{3.125\times 10^{-10}}$

$= 1.1 - \dfrac{0.0591}{2}(10 - 0.194) = 1.1 - 0.29 = 0.81$ volt

73. $E_{cell} = 1.1 - \dfrac{0.0591}{2}\log\dfrac{[2]}{[Cu^{+2}]} = 0$

$\log\dfrac{[2]}{[Cu^{+2}]} = \dfrac{1.1\times 2}{0.0591} = 37.23 \Rightarrow \dfrac{2}{[Cu^{+2}]} = 1.68\times 10^{37} \Rightarrow [Cu^{+2}] = 1.19\times 10^{-37}$

74. First conductance decreases due to nutralisation of free H^+ ions of weak acid, then it increases due to formation of salt and after equivalence point it increases more fastly due to increasing of OH^- ions.

75. First conductance decreases due to nutralisation of strong acid H^+ ion then after it increases due to nutralisation of weak acid and after equivalence point it increases more fastly.

PART - V

1. $Fe^{+2} + 2e^- \longrightarrow Fe$

Number of milimoles of e^- passed = $\dfrac{(965)(1)}{96500}\times 1000 = 10$

∴ Milimoles of Fe^{+2} reduced = 5

∴ Milimoles of Fe^{+2} left = 1000 x – 5

∴ By equating mili equivalent = (1000x – 5) × 1 = (0.1)(10)(5) ⇒ $x = 10^{-2}$

2.

	CH_3COOH	+	NaOH	$\rightleftharpoons$	CH_3COONa	+	H_2O
milli moles	100×0.2		100×0.2		–		–
	0		0		100×0.2		

Then,

$$[CH_3COONa] = \frac{100 \times 0.2 \times 10^{-3}}{200} \times 1000 = 0.1 \Rightarrow \text{D.O.D } (\alpha) \text{ for } CH_3COOH = \frac{\Lambda_m}{\Lambda_m^0} = \frac{2.0}{200} = 10^{-2}$$

Then, K_a of $CH_3COOH = C\alpha^2 = 0.1 \times (10^{-2})^2 = 10^{-5}$

$\Rightarrow$ pKa = 5 for CH_3COOH.

So, pH of CH_3COONa salt is :

$$pH = 7 + \frac{1}{2}\, pKa + \frac{1}{2}\log C. \qquad = 7 + \frac{1}{2} \times 5 + \frac{1}{2}\log 0.1 = 9.$$

3. $\Lambda_m^{\infty} = \Lambda_{Ag^+}^{\infty} + \Lambda_{Br^-}^{\infty}$

$= a + b$

$$\Lambda_m^{\infty} = K \times \frac{1000}{S} \Rightarrow S = \frac{K}{\Lambda_m^{\infty}} \times 1000 \Rightarrow S\,(g/lit) = \frac{K}{a+b} \times 1000 \times 188$$

4. $\frac{\lambda}{\lambda^{\circ}} = \frac{122}{\lambda^{\circ}} = 0.936$

$\lambda^{\circ} = 130.34\ \Omega^{-1}cm^2\ eq^{-1}$

$$\frac{\lambda_+^{\circ}}{\lambda^{\circ}} = \frac{0.98}{1.98} \Rightarrow \frac{\lambda_+^{\circ}}{130.34} = \frac{0.98}{1.98}$$

$\lambda_{K+}^{\circ} = \lambda_+^{\circ} = 64.51\ \Omega^{-1}cm^2\ eq^{-1}$

And

$$\frac{\lambda_-^{\circ}}{\lambda^{\circ}} = 1 - \frac{\lambda_+^{\circ}}{\lambda^{\circ}} \Rightarrow \frac{\lambda_+^{\circ}}{\lambda^{\circ}} = 1 - \frac{0.98}{1.98}$$

$$\frac{\lambda_-^{\circ}}{130.34} = \frac{1}{1.98} \Rightarrow \lambda_-^{\circ} = \frac{130.34}{1.98} = 65.83\ \Omega^{-1}cm^2\ eq^{-1}$$

5. $\Pi = iCRT$

$3 = i \times 0.1 \times \frac{1}{12} \times 300$

$i = 1.2$

$i = 1 + \alpha(n-1)$

$1.2 = 1 + \alpha(2-1) = 0.2$

$$0.2 = \frac{30}{\lambda_m^{\infty}} \Rightarrow \lambda_m^{\infty} = 150\ \Omega^{-1}cm^2\ mol^{-1}$$

6. $V = iR \qquad R = \frac{V}{i} = \frac{5}{0.15} = \frac{100}{3}\,\Omega$

$K = \frac{1}{R} \times \frac{\ell}{a} = \frac{3}{100} \times \frac{0.5}{1.5} = 10^{-2}$

$\Lambda_M = \frac{K \times 1000}{M} = 10^{-2} \times \frac{1000}{0.05} = 200\Omega^{-1}\ cm^2\ mol^{-1}$

7. $Cu^{2+} \quad + \quad 2e^- \quad \rightarrow \quad Cu$

$2mol \qquad \frac{482.5 \times 4 \times 60}{96500}$ mol

$= 1.2$ mol electrons

2 mole electrons then Cu^{+2} reacted = 1 mole

When 1.2 mole electrons then Cu^{+2} reacted = $\frac{1}{2} \times 1.2 = 0.6$

so, remaining Cu^{+2} moles = 2 – 0.6 = 1.4 moles

Remaining $[CuSO_4] = \frac{1.4}{5} = 0.28$ M.

8. For concentration cell $E^o_{cell} = 0$

$$Ag\,(s) \longrightarrow Ag^+\,(C_1) + e^-$$
$$Ag^+\,(C_2) + e^- \longrightarrow Ag\,(s)$$

$$Ag^+\,(C_2) \longrightarrow Ag^+\,(C_1)$$

Then, $E_{cell} = X = 0 - 0.059 \log\left(\frac{C_1}{C_2}\right)$

$$\Rightarrow \log\left(\frac{C_2}{C_1}\right) = \frac{X}{0.059}$$

$$\Rightarrow \frac{C_2}{C_1} = \text{anti log}\left(\frac{x}{0.059}\right)$$

9. $Fe(OH)_3 \rightleftharpoons Fe^{+3} + 3OH^-$; $[Fe^{+3}] = \frac{K_{sp}}{[OH^-]^3} = \frac{10^{-26}}{(10^{-2})^3} = 10^{-20}$

$$E_{Fe^{+3}/Fe} = E^0_{Fe^{+3}/Fe} - \frac{0.06}{3}\log\frac{1}{[Fe^{+3}]} = -0.036 - \frac{0.06}{3} \times 20 = -0.036 - 0.4 = -0.436$$

10. For cell reaction to take place in opposite direction. E_{cell} must be negative.

$$E_{cell} < 0$$
$$E^o_{cell} - \frac{0.06}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} < 0$$
$$1.1 - \frac{0.06}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} < 0$$
$$\frac{0.06}{2}\log\frac{[Zn^{2+}]}{[Cu^{2+}]} > 1.1$$
$$\log\frac{[Zn^{2+}]}{[Cu^{2+}]} > 36.67$$
$$\ell n\frac{[Zn^{2+}]}{[Cu^{2+}]} > 84.4$$
$$[Zn^{2+}] > [Cu^{2+}]e^{84.4}$$

11. X^- is I^-

Y^- is Cl^-

SRP $Cl_2 > Br_2 > I_2$

12. $$E_{cell} = -\frac{RT}{nF}\,\ell n\,\frac{[H^+]_{anode}}{[H^+]_{cathode}} = -\frac{RT}{nF}\,\ell n\,\frac{\frac{K_a[HA]_{anode}}{[NaA]_{anode}}}{\frac{K_a[HA]_{cathode}}{[NaA]_{cathode}}}$$

13. Anode : $2H_2O \longrightarrow O_2\uparrow + 4OH^- + 4e^-$

0.01 mol $\quad 0.04$ F

Cathode : $Cu^{2+} + \quad 2e^- \quad \longrightarrow \quad Cu(s)$

$20\times10^{-3}\times0.5 \quad 0.04$ faraday

$= 10^{-2}$ mol $\quad -0.02$

$= 0.01$ mol $\quad = 0.02$ F

$2H_2O + 2e^- \longrightarrow H_2(g) + 2OH^-$

$0.02F \quad 0.01$ mol

Total volume of gases evolved at STP = (0.01 + 0.01) × 22.4 = 448 ml

14. $0.164 = 0 + \dfrac{0.0591}{1}\log_{10}\dfrac{0.1}{[Ag^+]_{anode}}$

$\Rightarrow \quad [Ag^+]_{anode} = 1.66 \times 10^{-4}$ M.

$K_{sp} = [Ag^+]^2 \times [CrO_4^{2-}] = 1.66 \times 10^{-4} \times \left(\dfrac{1.66\times10^{-4}}{2}\right)$

15. **Hint:** Reverse of (B) & (C) is spontaneous; weakest Oxidizing Agent here is Mg^{2+}]

17. (a, b, d, f) $E = E^o - \dfrac{0.6}{n}\log\dfrac{[A^+][Cl^-]}{P_{Cl_2}}$

18. $\Lambda^o_{CH3COOH} = \Lambda^o_{CH3COONa} + \Lambda^o_{HCl} - \Lambda^o_{NaCl}$

$= 150 + 200 - 125 = 225\ S\ cm^2\ mol^{-1}$.

$\Lambda^c_{CH3COOH} = 2.25\ S\ cm^2\ mol^{-1}$.

$$\alpha = \frac{\Lambda^c_{CH_3COOH}}{\Lambda^0_{CH_3COOH}} = \frac{2.25}{225} = 10^{-2}$$

Then $[H^+]$ for $CH_3COOH = C\alpha = 0.001 \times 10^{-2} = 10^{-5}$

$\Rightarrow \quad pH = -\log[H^+] = -\log(10^{-5}) = 5$

19. $K = 3.2 \times 10^{-5}\ \Omega^{-1}.cm^{-1}$

$$\Lambda = \frac{10^3 K}{C}$$

$$\Lambda = \frac{3.2\times10^{-2}}{0.2} = 16 \times 10^{-2}$$

$$\alpha = \frac{\Lambda}{\Lambda_\infty}$$

$$\therefore \quad \Lambda_\infty = \frac{\Lambda}{\alpha} = \frac{16\times10^{-2}}{0.02} = 8$$

20. $E = E^o_{cell} - \dfrac{0.059}{2} . \log Q$

$Q = \dfrac{(10^{-7})^2}{20} \times \dfrac{0.2}{(10^{-7})^2} = \dfrac{1}{100}$

$E = 0 - \dfrac{0.059}{2} . \log \dfrac{1}{100} = \dfrac{0.059}{2} \times 2 = 0.059$

$\Rightarrow \quad 1000E = 1000 \times 0.059 = 59$

21. At cathode : $\dfrac{1}{2} Hg_2^{2+} + e^- \longrightarrow Hg(l)$

At anode : $\dfrac{1}{2} H_2(g) \longrightarrow H^+(aq) + e^-$

$\dfrac{1}{2} Hg_2^{2+} + \dfrac{1}{2} H_2(g) \longrightarrow Hg(l) + H^+(aq)$

$E_{cell} = E^0_{cell} - \dfrac{0.059}{1} \log [H^+]$

or $\quad 0.634 = (0.28 - 0) + 0.059\ pH$

or $\quad pH = \dfrac{0.634 - 0.28}{0.059} = 6$

22. Overall reaction should be the one which is written in term of species present in the given electrode/cell.

Hence at anode $\quad H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$

At cathode $\quad 2AgCl + 2e^- \longrightarrow 2Ag + Cl^-$

23. We can assume the given cell to be:

$Pt \mid H_2 \mid H^+ (aq), Cl^- (aq) \mid AgCl (s) \mid Ag$

With this assumption, $E^o_{cell} = E^o_{AgCl/Ag^-} - E^o_{SHE}$

$= 0.22\ V$

And cell reaction is :

$\dfrac{1}{2} H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Ag(s) + Cl^-(aq)$

$\Rightarrow \quad E_{cell} = E^o_{cell} - \dfrac{0.06}{1} \log (H^+) (Cl^-)$

$1.05 = 0.22 - 0.06 \log \dfrac{K_w}{(OH^-)} (Cl^-)$

$0.83 = 0.06 \left(-\log K_w - \log \dfrac{(Cl^-)}{(OH^-)} \right)$

$\dfrac{83}{6} = pK_w - \log \dfrac{0.012}{0.01}$

$\dfrac{83}{6} = pK_w - \log(1.2)$

$\Rightarrow \quad pK_w = \dfrac{83}{6} + \log(1.2) = 13.91$

24. $pK_w = 13.91$

i.e. $K_w > 10^{-14}$

Hence T is greater than 25ºC.

25. For the solution of Na_2SO_4

$$\wedge = \frac{K}{C} = \frac{2.6 \times 10^{-2}}{1}$$

$$2\lambda^o_{Na^+} + \lambda^o_{SO_4^{2-}} = 0.026$$

$$\lambda^o_{SO_4^{2-}} = 0.026 - 0.01 = 0.016\ \Omega^{-1}\ m^2\ mol^{-1}$$

26. For the Na_2SO_4 solution saturated with $CaSO_4$ (Let x $\frac{mol}{m^3}$ be the solubility of $CaSO_4$)

$$K_{solution} = K_{Na^+} + K_{SO_4^{2-}} + K_{Ca^{2+}}$$

$$0.07 = (\lambda^o_{Na^+} \times [Na^+]) + (\lambda^o_{SO_4^{2-}} \times [SO_4^{2-}]) + (\lambda^o_{Ca^{2+}} \times [Ca^{2+}])$$

$$= (0.005 \times 2) + 0.016(1 + x) + (0.006x)$$

$$0.07 = 0.01 + 0.016 + 0.016x + 0.006x$$

$$X = 2\ mol/m^3$$

$\therefore$ $[Ca^{2+}] = 0.002$ mol/lt, $[SO_4^{2-}] = 0.003$ mol/lt

27. Solubility product of $CaSO_4 = [Ca^{2+}][SO_4^{2-}] = 0.002 \times 0.003 = 6 \times 10^{-6}$