PHYSICAL CHEMISTRY

DPP

DAILY PRACTICE PROBLEMS

NO. 01

TARGET : JEE (ADVANCED) 2015

Course : VIJETA & VIJAY (ADP & ADR) **Date : 08-04-2015**

TEST INFORMATION

DATE : 15.04.2015 **PART TEST-01 (PT-01)**

Syllabus : Mole concept, Equivalent Concept, Ionic equilibrium, Electrochemistry, Inorganic Nomenclature, Periodic table, Chemical bonding and Coordination compounds.

DPP No. # 01 (JEE-ADVANCED)

Total Marks : 169 **Max. Time : 118 min.**

Single correct Objective ('–1' negative marking) Q.1 to Q.15	**(3 marks, 2 min.)**	**[45, 30]**
One or more correct objective (no negative marking) Q.16 to Q.20	**(4 marks, 2 min.)**	**[20, 10]**
Single digit integer type ('–1' negative marking) Q.21 to Q.25	**(4 marks, 3 min.)**	**[20, 15]**
Double digit integer type (no negative marking) Q.26 to Q.29	**(4 marks, 3 min.)**	**[16, 12]**
Assertion and Reason ('–1' negative marking) Q.30 to Q.32	**(3 marks, 3 min.)**	**[09, 09]**
Comprehension ('–1' negative marking) Q.33 to Q.41	**(3 marks, 2 min.)**	**[27, 18]**
Match the Following (no negative marking) Q.42 to Q.45	**(8 marks, 6 min.)**	**[32, 24]**

1. 50 ml of 20.8% w/v $BaCl_2$ (aq) and 100 ml of 9.8% w/v H_2SO_4(aq) solution are mixed. The molarity of SO_4^{2-} in final solution is :

(A) 0.66 M (B) 0.5 M (C) 1M (D) 0.33 M

2. The minimum volume of HCl of specific gravity 1.2 and 3.65% by weight, needed to produce 1.12 L Cl_2 at 1 atm and 273 K by the following reaction :-

$$MnO_2 + HCl \rightarrow MnCl_2 + H_2O + Cl_2$$

(A) 200 ml (B) 166.7 ml (C) 333.3 ml (D) 267 ml

3. In the permaganate titration, the solution of reductant is made acidic by adding dil. H_2SO_4, rather than HCl or HNO_3 because :

(A) HCl is a reducing agent and it gets oxidised resulting into decrease in the volume of $KMnO_4$ equivalent to the reducing agent under estimation.

(B) HNO_3 is an oxidising agent and it gets reduced resulting into increase in the volume of $KMnO_4$ equivalent to the reducing agent under estimation.

(C) H_2SO_4 (dil) is neither an oxidizing agent nor a reducing agent.

(D) All of these

4. 2 litres of an acidified solution of $KMnO_4$, containing 1.58 g of $KMnO_4$ per litre, is decolourised by passing sufficient amount of SO_2 gas. If whole of the sulphur from x g of FeS_2 is converted into SO_2 to be used in above reaction, calculate the value of x :

(A) x = 1.5 (B) x = 3 (C) x = 4.5 (D) x = 6

5. A certain volume of hydroxyl amine (NH_2OH) solution was boiled with an excess of $FeCl_3$ solution to cause the reduction of Fe^{3+} ions according to the reaction :

$$Fe^{3+} + NH_2OH \longrightarrow Fe^{2+} + N_2O + H^+ + H_2O$$

The resulting solution was estimated for Fe^{2+} ions with 0.5 M $K_2Cr_2O_7$ solution in acidic medium. If the volume of $K_2Cr_2O_7$ solution and NH_2OH solution used are found to be equal, what is the molarity of NH_2OH solution:

(A) 1.5 M (B) 3 M (C) 0.75 M (D) 1 M

6. An unknown sample was dissolved in water and made to titrate with 0.1 M HCl solution initially using phenolphthalein indicator. The volume of HCl consumed was found to be V_P ml. Then to the resulting solution, methyl orange indicator was added and again titrated with same HCl solution. The volume of HCl consumed now was found to be V_M ml. If $V_P = V_M$, then the unknown sample might not contain :

(A) only Na_2CO_3

(B) equimolar mixture of NaOH, Na_2CO_3 and $NaHCO_3$

(C) equimolar mixture of NaOH and $NaHCO_3$

(D) equimolar mixture of NaOH and Na_2CO_3

7. In 1L saturated solution of CuCl, 0.1 mol AgCl is added. K_{sp} of AgCl = 1.6×10^{-10}. If the resultant concentration of Ag^+ in the solution is 1.6×10^{-7}, then K_{sp} for CuCl is :

(A) 1.6×10^{-3} (B) 10^{-3} (C) 10^{-6} (D) 1.6×10^{-6}

8. The pH of a 0.01 M acid HX is 2 and pH of 0.01 M salt ACl is also 2. What conclusions can be drawn from this information ?

(A) HX is a weak acid and AOH is strong base.

(B) HX is a strong acid and AOH is strong base.

(C) HX is a strong acid and AOH is very weak base.

(D) HX is a strong acid and A^+ undergoes partial hydrolysis.

9. 40 mL of 0.35 M NaOH solution is added to 50 mL of 0.6 N H_3PO_4 solution . The pH of the mixture would be about : (K_{a_1}, K_{a_2} and K_{a_3} are 10^{-3}, 10^{-8} and 10^{-12} respectively).

(A) 11.82 (B) 3.6 (C) 12.18 (D) 7.82

10. The solubility product of As_2O_3 is 10.8×10^{-9}. It is 50% dissociated in saturated solution. The solubility of salt is :

(A) 10^{-2} (B) 2×10^{-2} (C) 5×10^{-3} (D) 5.4×10^{-9}

11. At 298K the standard free energy of formation of $H_2O(\ell)$ is –257.20 kJ/mole while that of its ionisation into H^+ ion and hydroxyl ions is 80.35 kJ/mole, then the emf of the following cell at 298 K will be(take F = 96500 C]

H_2(g,1 bar) | H^+ (1M) || OH^- (1M) | O_2 (g, 1bar)

(A) 0.40 V (B) 0.50 V (C) 1.23 V (D) – 0.40 V

12. A galvanic cell is composed of two chlorine electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to get maximum e.m.f. (K_{sp} of $PbCl_2 = 1.2 \times 10^{-5}$, of AgCl = 1.8×10^{-10}, of $Hg_2Cl_2 = 1.4 \times 10^{-18}$)

(A) 0.1 M HCl (B) Saturated solution of $PbCl_2$ in water

(C) Saturated solution of AgCl in water (D) Saturated solution of Hg_2Cl_2 in water

13. One gm metal M^{+2} was discharged by the passage of 1.81×10^{22} electrons. What is the atomic weight of metal ?

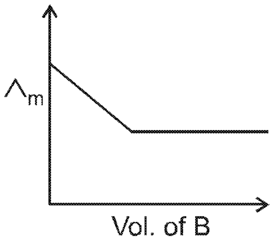
(A) 33.35 (B) 133.4 (C) 66.7 (D) 55

14. The conductivity of a solution which is 0.2M in $AgNO_3$ and 0.1M in $Ba(NO_3)_2$ is :

[$\lambda^o_{(Ag^+)} = 6 \times 10^{-3}$ Sm²mol⁻¹ , $\lambda^o_{(Ba^{2+})} = 13 \times 10^{-3}$ Sm² mol⁻¹ and $\lambda^o_{(NO_3^-)} = 7 \times 10^{-3}$ Sm²mol⁻¹]

(A) 5.3 Sm^{-1} (B) 4.3 Sm^{-1} (C) 3.3 Sm^{-1} (D) 2.3 Sm^{-1}

15. Which of the following (B) reagents when added to (A) reagent drop by drop, result in the given variation of molar conductance ?



	A		B
(A)	HCl	+	NaOH
(B)	NaCl	+	$AgNO_3$
(C)	NaOH	+	HCOOH
(D)	$BaCl_2$	+	Ag_2SO_4

16. For the reaction 'p' HNO_2 + 'q' $KMnO_4$ + 'r' H_2SO_4 $\longrightarrow$'s' HNO_3 + 't' $MnSO_4$ + 'u' K_2SO_4 + $3H_2O$
Which of the following is/are true ?
(A) H_2SO_4 is reducing agent
(B) HNO_2 is reducing agent
(C) p + q + r = 10
(D) Equivalent weight of HNO_3 in the reaction is $\frac{\text{Molar mass}}{2}$

17. The pH of 0.1 M solution of a weak base is 11. On diluting the solution, select the INCORRECT statement(s):
(A) pH increases
(B) $[OH^-]$ increases
(C) α decreases
(D) Number of H^+ ions in solution increases

18. Which is /are correct statements ?
(A) $H_2PO_2^-$ and HCO_3^- are amphiprotic species
(B) Equivalent weight of H_3PO_4 can be equal to its molar mass depending on the reaction.
(C) $KMnO_4$ has maximum equivalent weight in acidic medium
(D) Oxidation state of H in H_2 is more than that in NaH

19. On electrolysis, in which of the following , O_2 would be liberated at the anode ?
(A) dilute H_2SO_4 with Pt electrodes
(B) aqueous $AgNO_3$ solution with Pt electrodes
(C) dilute H_2SO_4 with Cu electrodes
(D) aqueous NaOH solution with Fe cathode & Pt anode

20. Mark out the correct statement(s) regarding electrolytic molar conductivity :
(A) It increases as temperature increases.
(B) It experiences resistance due to vibration of ions about mean position.
(C) Increase in concentration decreases the electrolytic molar conductivity of both strong as well as weak electrolyte.
(D) Greater the polarity of solvent, greater is the electrolytic molar conduction.

21. **(a)** 'a' moles of $K_2Cr_2O_7$ are needed in acidic medium for the oxidation of 9 moles of ethanol to acetic acid.
(b) An unknown metal chloride undergoes reduction reaction with Mg producing metal and $MgCl_2$. Experiments show that 52.4 g of metal chloride reacts with 9.6 g of Mg according to above reaction. The equivalent weight of metal in the given metal chloride is 'b'.

Report your answer as $\left(\frac{b}{a}\right)$.

22. Determine the concentration of H_3O^+ ion (in mol/L) in a solution containing 2×10^{-3} M HOCl & 2×10^{-4} M NaOCl. Given : Dissociation constant of HOCl = 1.5×10^{-4}.
Report your answer after multiplying by 10,000.

23. An organic compound contains C, H and O atoms. One molecule of the compound contains H-atoms equal to 66.67 % of total atoms and mass ratio of C to O is 3:2. If the molecular formula of the compound is $C_xH_yO_z$, what is the value of X + Y + Z. (Given vapour density of compound is 23 g/mol)

24. How many of the following statements is/are correct?

(i) The discharging of lead storage battery constitutes a galvanic cell.

(ii) During charging of lead stroage battery, anode is negatively charge.

(iii) The mass lost at anode is equal to mass gained at cathode in any galnanic cell

(iv) E_{cell} is intensive quantity and is independent of temperature

(v) The overall reaction in an electrolytic cell need not always look like a redox reaction.

(vi) If E^0_{cell} of a cell reaction is negative, then the reaction is non-spontaneous under all conditions.

25. 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 0.177V, the ratio of solubility product (K_{sp}) of AgCl and AgI at the temperature of the experiment is 10^x. Determine the value of x.

26. 200 mL of 0.1 M aqueous solution of acetic acid is mixed with equal volume of equimolar HCl solution at 27°C. If 1 g of NaOH is added to this, then the [H^+] in final solution is $x \times 10^{-y}$ (represented in scientific notation). Find x + y. K_a of acetic acid = 2×10^{-5}

27. A certain amount of Dichloroacetic acid ($CHCl_2COOH$) is oxidised to CO_2, H_2O and Cl_2 by 300 gram-equivalents of $KMnO_4$ in acidic medium. How many moles of Barium hydroxide are required to completely neutralize the same amount of acid ?

28. If the density of methanol is 0.792 kg L^{-1}, what is its volume needed for making 0.0027 m^3 of its 0.22 M solution ?

29. During the preparation of $H_2S_2O_8$ (peroxydisulphuric acid) using H_2SO_4 electrolytically, O_2 gas also releases at anode as by product. When 10.304 L of H_2 releases at cathode and 2.24 L O_2 at anode at STP, the weight of $H_2S_2O_8$ produced in gram is : (Round it off to nearest whole number)

30. **STATEMENT-1 :** If KIO_3 reacts with excess KI in acidic medium, and the produced I_2 is titrated with hypo solution, then milliequivalents of KIO_3 used and hypo used are equal.

STATEMENT-2 : According to law of equivalence, in a chemical reaction, milliequivalents of all the reactants are equal and also equal to milliequivalents of each product.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

31. **STATEMENT-1 :** The pH of a 0.003 M aqueous solution of NH_4CN can be approximately calculated using the formula : $pH = \frac{1}{2}(pK_w + pK_a - pK_b)$ Given : $K_a(HCN) = 4 \times 10^{-10}$ & $K_b(NH_3) = 2 \times 10^{-5}$

STATEMENT-2 : The degree of hydrolysis (h) of NH_4CN in its 0.003 M aqueous solution comes out to be greater than 0.1 and so, its value cannot be neglected with respect to 1 .

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

32. **Statement-1 :** $E^o_{cell} = 0$ for a chloride ion concentration cell.

Statement-2 : For this concentration cell, $E_{cell} = \frac{RT}{nF} \ln \frac{[Cl^-]_{LHS}}{[Cl^-]_{RHS}}$.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

Comprehension # 1

For a reaction : $aA + bB \longrightarrow cC + dD$

Three students stated different ways of determining limiting reagent.

Student 1 : Calculate the minimum moles of 'A' needed to completely consume 'B', and if available amount of 'A' exceeds what is needed, then 'B' is limiting reagent otherwise 'A' will be limiting reagent.

Student 2 : Calculate the ratio of the moles of the reactants initially taken, then compare it to theoretical mole ratio(according to stochiometry of the reaction). If the theoretical ratio exceeds ratio of moles actually taken, then reactant in numerator will be limiting reagent.

Student 3 : Calculate the amount of product (any one of the product) that can be obtained if each reactant is completely consumed and that reactant is limiting reagent which has produced least mass of product.

Assume that atleast one of A or B is the limiting reagent.

Now answer the following two questions :

33. Which student(s) has/have defined limiting reagent correctly ?
(A) Student-1 (B) Student-2 (C) Student-3 (D) All of these

34. If Student 1 in first experiment finds that when 1 mole of 'A' reacted with excess of reagent 'B' and in second experiment when 1 mole of 'B' reacted with excess of reagent 'A', then in the later experiment mass of the product produced was greater. Then which should be the limiting reagent :
(A) A (B) B (C) None (D) Cannot be predicted

Comprehension # 2

Zelina, a student of class XI is working in the chemistry lab of her school. She is provided with 4 containers of large capacity by the lab assistant.

Container 1 contains 2L of '2.8 V' H_2O_2.
Container 2 contains 2L of '16.8 V' H_2O_2.
Container 3 contains sufficient amount of water.
Container 4 is empty.

She has been asked by her teacher to prepare H_2O_2 solution using the components of container 1, 2 or 3 (partially or completely) and store it in container 4.

Now answer the following two questions :

35. The volume of water required by Zelina to prepare maximum volume of 2.55% (w/v) H_2O_2 solution is :
(A) 0.33 L (B) 1 L (C) 0.67 L (D) 2 L

36. Zelina prepared a 12.6 V H_2O_2 solution and mixed it with excess of KI solution and titrated the liberated I_2 with $\frac{9}{7}$ M hypo solution. Find the maximum volume (in L) of hypo solution that could have been consumed in above process :
(A) 5.44 L (B) 5 L (C) 4.67 L (D) 2.5 L

Comprehension # 3

K_{sp} of $Cr(OH)_3$, $Al(OH)_3$ and Fe $(OH)_3$ are 7×10^{-31}, 2×10^{-33} and 6.4×10^{-38} respectively.

37. What is the equilibrium constant of the following reaction ?

$$Fe^{3+}(aq) + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H^+(aq)$$

(A) 6.4×10^4 (B) $\frac{10^{-4}}{6.4}$ (C) $\frac{10^{38}}{6.4}$ (D) $\frac{10^{24}}{6.4}$

38. What will happen when $FeCl_3$ is added to a suspension of $Al(OH)_3$?

(A) Colour of suspension remains same

(B) Colour of suspension changes to reddish brown

(C) Precipitate of $AlCl_3$ will produce

(D) $FeCl_3$ will not show any reaction

39. What is the maximum moles of $Fe_2(SO_4)_3$ that can be added in 2L water without precipitating $Fe(OH)_3$?

(A) 6.4×10^{-17} (B) 1.28×10^{-17} (C) 3.2×10^{-17} (D) 1.28×10^{-10}

Comprehension # 4

The cell potential for the unbalanced chemical reaction :

$$Hg_2^{2+} + NO_3^- + H_3O^+ \longrightarrow Hg^{2+} + HNO_2 + H_2O$$

under standard state conditions is $E^\circ_{cell} = 0.02$ V

Given : $NO_3^- + 3H_3O^+ + 2e^- \longrightarrow HNO_2 + 4H_2O$, $E^\circ = 0.94$ V and $\frac{2.303RT}{F} = 0.06$.

Now answer the following two questions :

40. At what pH will the cell potential be zero if the concentration of other components are equal to one ?

(A) $\frac{1}{6}$ (B) $\frac{1}{3}$ (C) $\frac{2}{3}$ (D) $\frac{2}{9}$

41. How many moles of electrons pass through the circuit when 0.6 mole of Hg^{2+} and 0.30 mole of HNO_2 are produced in the cell that contains 0.5 mole of Hg_2^{2+} and 0.40 mole of NO_3^- at the beginning of the reaction

(A) 0.6 mole (B) 0.8 mole (C) 0.3 mole (D) 1 mole

42. **Match the following :**

Column (I)	**Column (II)**
(A) 50 mL of 3M HCl solution + 150 mL of 1M $ZnCl_2$ solution	(p) 4.17 m
(B) An aqueous solution of NaCl with mole fraction of NaCl as 0.1	(q) $[Cl^-] = 3$ M
(C) 20% (w/w) propanol (C_3H_7OH) solution	(r) $[H^+] = 0.75$ M
(D) 10.95% (w/v) HCl solution	(s) 6.1 m

43. Given that :

K_a (CH_3COOH) = 2×10^{-5} , K_a (C_2H_5COOH) = 8×10^{-6} , K_a (ROH) = 3×10^{-13}

K_1 (H_2CO_3) = 4×10^{-7} , K_2 (H_2CO_3) = 4×10^{-11}, log 2 = 0.3 ; $\sqrt{1.12} = 1.06$

Match the entries in Column-I with Column-II

Column-I (Solution)	Column-II
(A) 0.1 M CH_3COONa and 0.1 M $(C_2H_5COO)_2Ba$	(p) $4 < pH < 6$
(B) 0.1 M $NaHCO_3$	(q) $6 < pH < 10$
(C) 0.1 M aq. ROH	(r) acidic solution
(D) 10^{-3} M aq. RONa	(s) Basic solution

44.

Column I	**Column II**
(A) AgBr	(p) Solubility in water is more than expectation.
(B) AgCN	(q) Solubility in acidic solution is more than that in pure water.
(C) $Fe(OH)_3$	(r) Solubility in strongly basic solution is more than that in pure water.
(D) $Zn(OH)_2$	(s) Solubility decreases in presence of common anion.

45. Match the following electrochemical cells at 25ºC in Column-I with their characteristics in Column-II :

Given : $E^0_{Zn^{2+}/Zn} = -0.76$ V, $E^0_{Ag/Ag^+} = -0.81$ V, $E^0_{D^+/D_2} = -0.01$ V

K_{sp} (AgCl) = 10^{-10}, K_{sp} (AgBr) = 5×10^{-13}

	Column-I		**Column-II**
(A)	$Pt(s) \mid H_2(g) \mid KOH(aq) \parallel HCl(aq) \mid H_2(g) \mid Pt(s)$ (1atm) (0.01M) (0.01M) (1atm)	(p)	Concentration cell
(B)	$Zn(s) \mid Zn^{2+}(aq) \parallel Ag^+(aq) \mid Ag(s)$ (0.1M) (0.1M)	(q)	$E_{cell} > 0$
(C)	$Pt(s) \mid D_2(g) \mid D^+(aq) \parallel H^+(aq) \mid H_2(g) \mid Pt(s)$ (0.1atm) (0.1M) (0.01M) (0.001atm)	(r)	Cell reaction is at equilibrium
(D)	$Ag(s) \mid AgBr(s) \mid Br^-(aq) \parallel Cl^-(aq) \mid AgCl(s) \mid Ag(s)$ (5×10^{-4}M) (0.1M)	(s)	Cell will have the same emf as the one made up of standard electrodes.
		(t)	Diluting each electrode solution to double volume would not affect the emf of cell (for gases involved, assume no change in partial pressures).

Solution of DPP # 1

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CHEMISTRY

1. $n_{BaCl_2} = \frac{20.8}{100} \times \frac{50}{208} = \frac{1}{20} = 0.05$; $n_{H_2SO_4} = \frac{9.8}{100} \times \frac{100}{98} = 0.1$

	$BaCl_2$ +	$H_2SO_4 \rightarrow$	$BaSO_4(s)$ +	2HCl
Moles	0.05	01		
After reaction	0	0.05	0.05	0.1

$\Rightarrow$ $n_{SO_4^{2-}}$ remaining = 0.05 $\Rightarrow$ $[SO_4^{2-}] = \frac{0.05}{150} \times 1000 = \frac{1}{3} = 0.33$

2. $MnO_2 + 4HCl \longrightarrow MnCl_2 + 2H_2O + Cl_2$

$n_{Cl_2} = \frac{1.12}{22.4} = \frac{1}{20}$ $\Rightarrow$ $n_{HCl} = 4 \times \frac{1}{20} = \frac{1}{5}$

$\Rightarrow$ $m_{HCl} = \frac{1}{5} \times 36.5 = V \times 1.2 \times \frac{3.65}{100}$ $\Rightarrow$ V = 166.7 ml

3. In case of HCl, greater volume of $KMnO_4$ is used while in case of HNO_3, lesser volume of $KMnO_4$ is used, than appropriate.

4. From law of equivalence,

Eq of $KMnO_4$ (v.f. = 5) = Eq. of SO_2 (v.f. = 2)

$\frac{1.58}{158} \times 5 \times 2 = n_{SO_2} \times 2$

$\therefore$ $n_{SO_2} = 0.05$ moles ; Whole of S from FeS_2 is converted into SO_2

$\therefore$ Applying POAC on S:

$2 \times n_{FeS_2} = 1 \times n_{SO_2}$

$\therefore$ $2 \times \frac{m_{FeS_2}}{120} = 1 \times 0.05$ $\therefore$ $m_{FeS_2} = 3$ g = x $\therefore$ x = 3

5. meq. of NH_2OH = meq. of $K_2Cr_2O_7$

$\therefore$ $V \times M \times 2 = V \times 6 \times 0.5$ $\therefore$ M = 1.5

6. If the unknown sample contains equimolar mixture of NaOH and Na_2CO_3 , then $V_P = 2V_M$.

7. It is logical to see that out of 0.1 mol AgCl, only 1.6×10^{-7} moles passed into the solution.

Hence, $AgCl(s) \rightleftharpoons Ag^+ + Cl^-$

1.6×10^{-7} $\quad 1.6 \times 10^{-7} + x$

$(1.6 \times 10^{-7})(1.6 \times 10^{-7} + x) = 1.6 \times 10^{-10}$

$1.6 \times 10^{-7} + x = 10^{-3}$

$x \approx 10^{-3}$

x is the concentration of Cl^- due to CuCl.

$CuCl_{(s)} \rightleftharpoons Cu^+ + Cl^-$

10^{-3} $\quad 10^{-3}$

$K_{sp} = 10^{-6}$

8. pH = 2 $\Rightarrow [H^+] = 0.01$ M

$$HX \longrightarrow H^+ \quad + \quad X^-$$

0.01

finally ≈ 0 0.01 0.01

Hence, HX is strong acid.

$[A^+] = 0.01$

$$A^+ \quad + \quad H_2O \rightleftharpoons AOH \quad + \quad H^+$$

t = 0 0.0.

final ≈ 0 0.01 0.01

A^+ is almost completely hydrolysed, acting as very strong acid, with $K_h > 1$

$$\Rightarrow \quad \frac{10^{-14}}{K_b} > 1 \qquad \Rightarrow \quad K_b < 10^{-14}$$

10. $10.8 \times 10^{-9} = (0.5S \times 2)^2\,(0.5S)$ $\quad \Rightarrow \quad S^3 = \dfrac{10.8 \times 10^{-9}}{0.25 \times 0.5}$

11. Cell reaction

Cathode: $H_2O(\ell) + \frac{1}{2}O_2(g) + 2e^- \longrightarrow 2OH^-(aq.)$

Anode : $H_2(g) \longrightarrow 2H^+\,(aq.) + 2e^-$

$$H_2O(\ell) + \frac{1}{2}O_2(g) + H_2(g) \longrightarrow 2H^+(aq.) + 2OH^-(aq.)$$

Also we have

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$ $\qquad \Delta G^\circ_f = -257.2$ kJ/mole

$H_2O(\ell) \longrightarrow H^+(aq.) + OH^-\,(aq.)$ $\qquad \Delta G^\circ = 80.35$ kJ/mole

Hence for cell reaction

$\Delta G^\circ = -96.50$ kJ/mole $\qquad$ So , $E^\circ = -\dfrac{\Delta G^\circ}{nF} = \dfrac{96500}{2 \times 96500} = 0.50$ V

12. The cell is concentration cell So, $\quad E_{cell} = \dfrac{-0.059}{1} \log \dfrac{[Cl^-]_{cathode}}{[Cl^-]_{anode}}$

more is the difference in concentration of Cl^- in the electrodes, larger is the value of E_{cell} . Hg_2Cl_2 provides least concentration of Cl^-.

15. Accroding to this graph, $\wedge_m$ first decreases, and after point , $\wedge_m$ is nearly constant.

This happens when HCOOH is added to NaOH, OH^- are removed from solution and $HCOO^-$ replace them. But conductivity of OH^- is very high. Hence conductance keeps on decreasing till the end point.
After the endpoint, solution already contain $HCOO^-$. Hence HCOOH, being weak acid sees common ion effect and do not dissociate much to increase $\wedge_m$.

17. $BOH \rightleftharpoons B^+ + OH^-$
as $V \uparrow \propto \uparrow$ so $[OH^-]$ will decrease pOH $\uparrow \Rightarrow$ pH $\downarrow$.

19. (A) Anode $\qquad 2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

(B) Anode $\qquad 2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

(C) Anode $\qquad Cu \longrightarrow Cu^{2+} + 2e^-$

(D) Anode $\qquad 2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$

20. Resistance of cell is not due to vibrations of ion but actually it is due to collisons of ions.

21. **(a)** $H_2O + C_2H_6O \longrightarrow C_2O_2H_4 + 4H^{\oplus} + 4e^-$
'a' = 6
(b) Metal chloride + Mg $\longrightarrow$ Metal + $MgCl_2$
From reaction, 24g of Mg metal produces 95g of $MgCl_2$

$\therefore$ 9.6g of Mg metal produces $\frac{9.6 \times 95}{24}$ = 38g of $MgCl_2$

Mass of Cl in $MgCl_2$ = Mass of Cl in metal chloride = 38–9.6 = 28.4g
Mass of metal in metal chloride = 52.4 – 28.4 = 24g
Now, 28.4g of chlorine combines with 24g of metal
& 35.5g of chlorine combines with Eq Wt of metal (by definition)

$\therefore$ Eq wt. of metal = $\frac{35.5 \times 24}{28.4}$ = 30 = 'b'.

22. $$\begin{array}{lll} HOCl \rightleftharpoons & H^+ + & OCl^- \\ 2 \times 10^{-3} - x & x & 2\times10^{-4} + x \end{array}$$

$1.5 \times 10^{-4} = \frac{x(2 \times 10^{-4} + x)}{(2 \times 10^{-3} - x)}$; $3 \times 10^{-7} - 1.5 \times 10^{-4}x = 2\times10^{-4}x + x^2$

$x^2 + 3.5 \times 10^{-4}x - 3\times10^{-7} = 0$; $x = \frac{-3.5 \times 10^{-4} + \sqrt{(3.5 \times 10^{-4})^2 + 12 \times 10^{-7}}}{2} = 4\times10^{-4}$

23. Let $m_c = 3x$ and $m_o = 2x$ $\Rightarrow$ $n_c = \frac{3x}{12}$ and $n_o = \frac{2x}{16}$

$= \frac{x}{4}$ $= \frac{x}{8}$

$\Rightarrow$ $n_c ; n_o = \frac{x}{4} : \frac{x}{8} = 2 : 1$

Let the empirical formula be C_2H_xO

$x = \frac{66.67}{100}(2 + 1 + x)$; $x = \frac{2}{3}(3 + x)$; $3x = 6 + 2x$

x = 6
Hence EF = C_2H_6O
Molar mass = 2 × 23
= 46
E. F. mass = 24 + 6 +16 = 46 $\Rightarrow$ Molecular formula = C_2H_6O
Hence, total number of atoms = 2 + 6 +1 = 9

24. **(i)** On discharging, it generates electricity and hence works as galvanic cell.
(ii) Anode is positively charged during charging
(iii) It depends on the species getting oxidised and reduced.
(iv) E_{cell} depends on temperature
(v) This is true. Example $Ag^+ + Cl^- \longrightarrow AgCl$, is the overall reaction occuring in the cell
$Ag \mid AgCl \mid Cl^-(aq) \parallel Ag^+ \mid Ag$
(v) It is E_{cell} which determines spontanity

25. Ag | AgCl(s) || Calomel E_1

Saturated solution

Ag | AgI(s) || Calomel E_2

Saturated solution

$E_2 - E_1 = E_{AgCl\,|\,Ag} - E_{AgI\,|\,Ag} = 0.177$; This can be understood as

Ag | AgI(s) || AgCl(s) | Ag

Or

Ag | Ag^+(aq.) || Ag^+(aq.) | Ag

$\left(\sqrt{K_{sp}(AgI)}\right)$ $\left(\sqrt{K_{sp}(AgCl)}\right)$

$\Rightarrow$ $0.177 = \dfrac{-0.059}{1} \log \dfrac{[Ag^+]_a}{[Ag^+]_c}$ $\Rightarrow$ $0.177 = 0.059 \log \dfrac{\sqrt{K_{sp}(AgCl)}}{\sqrt{K_{sp}(AgI)}}$; $\dfrac{K_{sp}(AgCl)}{K_{sp}(AgI)} = 10^6$

26. $n_{CH_3COOH} = 0.2 \times 0.1 = 0.02$; $n_{HCl} = 0.2 \times 0.1 = 0.2$; $n_{NaOH} = \dfrac{1}{40} = 0.025$

$\Rightarrow$ $HCl + NaOH \longrightarrow NaCl + H_2O$; 0.02 mole HCl consumes 0.02 mole NaOH.

$\Rightarrow$ 0.005 mole NaOH is left to react with CH_3COOH.

$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

	CH_3COOH	NaOH	CH_3COONa
	0.02	0.005	
left	0.015	0	0.005

The final solution is a buffer.

$\Rightarrow$ $K_a = \dfrac{[H^+] \times [CH_3COO^-]}{[CH_3COOH]}$ $\Rightarrow$ $[H^+] = \dfrac{K_a \times [CH_3COOH]}{[CH_3COO^-]} = \dfrac{2 \times 10^{-5} \times 0.015}{0.005} = 6 \times 10^{-5}$

x = 6

y = 5 $\Rightarrow$ x + y = 11

27. $CHCl_2COOH \longrightarrow CO_2 + H_2O + Cl_2$

v.f. = 6

$\Rightarrow$ moles of $CHCl_2COOH \times 6 = 300$ $\Rightarrow$ moles of $CHCl_2COOH = 50$

$\Rightarrow$ $2CHCl_2COOH + Ba(OH)_2 \rightarrow Ba(CHCl_2COO)_2 + 2H_2O$ $\Rightarrow$ $n_{Ba(OH)_2} = \dfrac{50}{2} = 25$

28. Molar mass of methanol (CH_3OH) = 32 g mol^{-1} = 0.032 kg mol^{-1}

Molarity of the given solution = $\dfrac{0.793\,kg\,L^{-1}}{0.032\,kg\,mol^{-1}} = 24.78\,mol\,L^{-1}$

Applying

$M_1 \times V_1 = M_2V_2$

(Given solution) (solution to be prepared) ; $24.78 \times V_1 = 0.22 \times 2.7$ L

or $V_1 = 0.024$ L = 24 mL

29. At cathode : $2H^+ + 2e^- \to H_2$

At anode : $2H_2O \to O_2 + 4H^+ + 4e^-$

$2SO_4^{2-} \to S_2O_8^{2-} + 2e^-$

Equivalents at cathode = Equivalents at anode

$$\Rightarrow \quad \frac{10.304}{22.4} \times 2 = \frac{2.24}{22.4} \times 4 + n_{S_2O_8^{2-}} \times 2$$

$$\Rightarrow \quad \frac{10.304}{22.4} = \frac{2.24}{22.4} + n_{S_2O_8^{2-}} \quad \Rightarrow \quad n_{S_2O_8^{2-}} = 0.46 - 0.2 = 0.26$$

$$\Rightarrow \quad m_{S_2O_8^{2-}} = 0.26 \times 194 = 50.44$$

$$\approx 50$$

30. Since v.f. of I_2 in both reactions is different, so modification should be applied while applying law of equivalence.

32. Pt, Cl_2 | Cl^-(aq) || Cl^- (aq) | Cl_2 (g), Pt.

Anode : $2Cl^- \longrightarrow Cl_2 + 2e^-$ (R.H.S.) ; Cathode : $Cl_2 + 2e^- \longrightarrow 2Cl^-$ (L.H.S.)

$$E_{cell} = 0 - \frac{RT}{nF} \ln \frac{[Cl^-]_{L.H.S}}{[Cl^-]_{R.H.S}} \quad ; \quad E_{cell} = \frac{RT}{nF} \ln \frac{[Cl^-]_{R.H.S}}{[Cl^-]_{L.H.S}}$$

35. $N_1V_1 + N_2V_2 = N_3V_3$

$$\frac{2.8}{5.6} \times 2 + \frac{16.8}{5.6} \times 2 = \frac{2.55}{34} \times 2 \times V_3 \times 10 \quad \therefore \; V_3 = \frac{14}{3} \quad \therefore \quad V_w = \frac{14}{3} - 4 = \frac{2}{3} = 0.67\text{L}.$$

36. If max. volume of hypo solution is to be consumed, max. amount of I_2 should be liberated for which the amount of 12.6 V H_2O_2 solution prepared should be maximum.
Now, max. volume of 12.6 V H_2O_2 solution can be prepared by using 16.8 V H_2O_2 solution completely (2 L) and 2.8 V H_2O_2 solution partially (< 2 L).

$$\therefore \quad M_1V_1 + M_2V_2 = M_fV_f \qquad \therefore \quad \left(\frac{16.8}{11.2} \times 2\right) + \left(\frac{2.8}{11.2} \times V\right) = \frac{12.6}{11.2} \times (2 + V)$$

Upon solving, $V = \frac{6}{7}$ L.

$\therefore$ Max. volume of 12.6 V H_2O_2 sol = $2 + V = \frac{20}{7}$ L.

Now, $eq_{H_2O_2} = eq_{Hypo}$

$$\left(\frac{12.6}{5.6} \times \frac{20}{7}\right) = \frac{9}{7} \times V_{Hypo} \qquad \therefore \quad V_{Hypo} = 5\text{ L}.$$

37. $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$ 6.4×10^{-38} ....(1)

$H_2O \rightleftharpoons H^+ + OH^-$ 10^{-14} ....(2)

Doing 3 × – 1

$$Fe^{3+}_{(aq)} + 3H_2O \rightleftharpoons 3H^+_{(aq)} + Fe(OH)_3(s) \quad ; \quad K_{eq} = \frac{(10^{-14})^3}{6.4 \times 10^{-38}} = \frac{10^{-4}}{6.4}$$

38. $Fe^{3+} + Al(OH)_3(s) \rightleftharpoons Fe(OH)_3(s) + Al^{3+}$

$$K_{eq} = \frac{2 \times 10^{-33}}{6.4 \times 10^{-38}} = \frac{1 \times 10^5}{3.2}$$

; The large K_{eq} suggest, red particles of $Fe(OH)_3$ will precipitate

39. Water already contains $[OH^-] = 10^{-7}$ which exert common ion effect on solubility of $Fe(OH)_3$.

To avoid precipitation ;

$Q_{SP} = K_{sp}$

Let $[Fe_2(SO_4)_3] = x$

$\Rightarrow$ $[Fe^{3+}] = 2x$ $\Rightarrow$ $2x \times (10^{-7})^3 = 6.4 \times 10^{-38}$ $\Rightarrow$ $2x \times 10^{-21} = 6.4 \times 10^{-38}$

$\Rightarrow$ $x = 3.2 \times 10^{-17}$ $\Rightarrow$ $n_{Fe_2(SO_4)_3}$ in 2 L water $= 6.4 \times 10^{-17}$

40. Cathode : $NO_3^- + 3H_3O^+ + 2e^- \longrightarrow HNO_2 + 4H_2O$; $E^o = 0.94$ V

Anode : $2Hg^{2+} + 2e^- \longrightarrow Hg_2^{2+}$; $E^o = 0.92$ V

Overall balanced cell reaction :

$NO_3^- + 3H_3O^+ + Hg_2^{2+} \longrightarrow 2Hg^{2+} + HNO_2 + 4H_2O$; $E^o = 0.02$ V

$$E = E^o_{cell} - \frac{0.06}{2} \log \frac{[Hg^{2+}]^2[HNO_2]}{[NO_3^-][H_3O^+]^3[Hg_2^{2+}]}$$

$$E = E^o_{cell} - \frac{0.06}{2} \log \frac{1}{[H_3O^+]^3}$$

$$0 = 0.02 - 0.03 \log \frac{1}{[H_3O^+]^3}$$

$$0 = 0.02 - 0.03 \times 3\,(pH)$$

$$pH = \frac{0.02}{0.03 \times 3} = \left(\frac{2}{9}\right).$$

41.

	NO_3^-	+	$3H_3O^+$	+	Hg_2^{2+}	$\longrightarrow$	$2Hg^{2+}$	+	HNO_2	+	$4H_2O$
t = 0	0.4		–		0.5		–		–		–
t = t	0.1mole		–		0.2mole		0.6mole		0.3mole		–

Cathode : NO_3^-	+ $3H_3O^+$	+ $2e^-$	$\longrightarrow$	HNO_2	+	$4H_2O$
		0.6mole		0.3mole		

42. (A) $[Cl^-] = \frac{50 \times 3 + 150 \times 1 \times 3}{200} = \frac{600}{200} = 3\ M$

(B) molality = $\frac{0.1}{0.9 \times 18} \times 1000 = 6.17\ m$

(C) Molality = $\frac{10 \times 1000}{60 \times 90} = 1.85\ m.$

(D) Molarity of HCl = $\frac{\frac{10.95}{36.5}}{100} \times 1000 = 3\ M$

43. A→ given in qn 9

B→ $pH = \frac{pK_1 + pK_2}{2} = \frac{7 - \log 4 + 11 - \log 4}{2} = 9 - 2\log 2$

$= 9 - 0.6$

$= 8.4$

C → $[H^+] = \sqrt{K_1 \times C + K_w}$

$= \sqrt{3 \times 10^{-13} \times 0.1 + 10^{-14}} = 2 \times 10^{-7}$

pH = 7–log 2 = 6.7

B→ $RONa \rightarrow RO^- + Na^+$

$RO^- + H_2O \longrightarrow ROH + OH^-$ $\qquad K = \frac{10^{-14}}{3 \times 10^{-13}} = \frac{1}{30}$

$10^{-3}\ M$

At eq. $10^{-3} - x \qquad x \qquad x$

$\frac{x^2}{10^{-3} - x} = \frac{1}{30} \Rightarrow x = 10^{-3} \Rightarrow H^+ = 10^{-11}$, pH = 11

vf = 3 vf = 6

44. (A) For AgBr, $K_{sp} = [Ag^+][Br^-]$

so on increase in $[Br^-]$, solubility of AgBr decreases.

(B) For AgCN, $K_{sp} = [Ag^+][CN^-]$

CN^- undergoes hydrolysis so solubility in water is more than expectation.

In acidic solution, CN^- gets protonated so solubility of AgCN increases.

AgCN forms complex $Ag(CN)_2^-$ with excess of CN^-.

(C) For $Fe(OH)_3$, $K_{sp} = [Fe^{3+}][OH^-]^3$.

In acidic solution OH^- decreases so solubility increases.

Solubility decreases in presence of OH^-.

(D) For $Zn(OH)_2$, $K_{sp} = [Zn^{2+}][OH^-]^2$

$Zn(OH)_2$ is amphoteric in nature so its solubility increases in both acidic as well as strongly basic solution.

45. (A) Both cathode and anode are Hydrogen electrodes. So, given cell is a concentration cell.

Now, $[OH^-]_a = 0.01$ M

$\therefore$ $[H^+]_a = 10^{-12}$ M and $[H^+]_c = 10^{-2}$ M

So, $E_{cell} = -\frac{0.059}{1}\log_{10}\frac{[H^+]_a}{[H^+]_c} = -0.059 \times (-10) = 0.59\text{ V } (> 0)$

(B) $E_{cell} = [E^o_{Ag^+/Ag} - E^o_{Zn^{2+}/Zn}] - \frac{0.059}{2}\log_{10}\frac{[Zn^{2+}]}{[Ag^+]^2}$

$= 1.57 - \frac{0.059}{2}\log_{10} 10\ (> 0)$

(C) $E_{cell} = [E^o_{H^+/H_2} - E^o_{D^+/D_2}] - \frac{0.059}{2}\log_{10}\left(\frac{[D^+]^2 \times p_{H_2}}{[H^+]^2 \times p_{D_2}}\right)$

$= 0 - (-0.01) - \frac{0.059}{2}\log_{10}\left(\frac{(0.1)^2 \times 0.001}{(0.01)^2 \times 0.1}\right)$

$= 0.01\text{ V } (> 0)$

Since the expression of log upon solving has value 1, so, $E_{cell} = E^o_{cell}$ and it can be said that Cell will have the same emf as the one made up of standard electrodes.

Also the expression of log will have the same value even after diluting each electrode solution to double volume. So, it would not affect emf of cell.

(D) $E_{cell} = E^o_{cell} - \frac{0.059}{1}\log_{10}\frac{[Cl^-]}{[Br^-]}$

$= \frac{0.059}{1}\log_{10}\frac{K_{sp}[AgCl]}{K_{sp}[AgBr]} - \frac{0.059}{1}\log_{10}\frac{[Cl^-]}{[Br^-]}$

$= \frac{0.059}{1}\log_{10}\frac{(10^{-10})}{(5\times10^{-13})} - \frac{0.059}{1}\log_{10}\frac{(0.1)}{(5\times10^{-4})}$

$= 0$

So, cell reaction is at equilibrium.

Also, upon diluting the electrode solutions to double volume, both E^o_{cell} and expression of log will remain unchanged. So, E_{cell} will remain zero and thus, no change in emf of cell would occur.