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# CHEMISTRY today

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# CHEMISTRY MUSING

**C**hemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

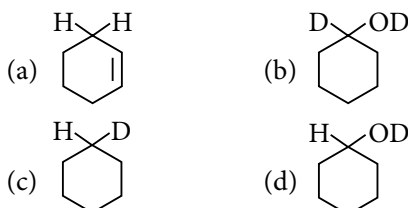
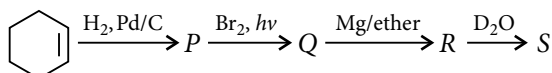
We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

## PROBLEM Set 32

### JEE MAIN/PMTs

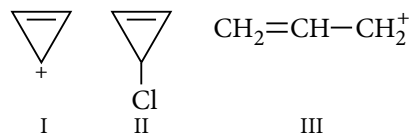
- The decreasing order of the bond moment in  $\text{NH}_3$ ,  $\text{PH}_3$ ,  $\text{AsH}_3$  and  $\text{SbH}_3$  is given by
  - $\text{NH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{SbH}_3$
  - $\text{SbH}_3 > \text{PH}_3 > \text{AsH}_3 > \text{NH}_3$
  - $\text{NH}_3 > \text{AsH}_3 > \text{PH}_3 > \text{SbH}_3$
  - $\text{NH}_3 > \text{SbH}_3 > \text{AsH}_3 > \text{PH}_3$

- In the given sequence of reactions, the compound S is



- Mole fraction of  $\text{K}_2\text{CO}_3$  in a mixture of  $\text{K}_2\text{CO}_3$  and  $\text{KHCO}_3$  is 0.5. The volume of 0.1 N HCl required to neutralize its 1.252 g mixture is
  - 100 mL
  - 152.5 mL
  - 157.8 mL
  - 102 mL
- $4\text{HNO}_3 + \text{P}_4\text{O}_{10} \longrightarrow 4\text{HPO}_3 + \text{X}$   
In the above reaction, the product X is
  - $\text{NO}_2$
  - $\text{N}_2\text{O}_3$
  - $\text{N}_2\text{O}_4$
  - $\text{N}_2\text{O}_5$

- The order of stability of the following three compounds is



- $\text{III} > \text{I} > \text{II}$
- $\text{III} > \text{II} > \text{I}$
- $\text{I} > \text{III} > \text{II}$
- $\text{I} > \text{II} > \text{III}$

### JEE ADVANCED

- What is the entropy change when 1 kg of water is heated from  $27^\circ\text{C}$  to  $200^\circ\text{C}$  forming super-heated steam under constant pressure? (Given : Specific heat of water =  $4180 \text{ J/kg}\cdot\text{K}$ , specific heat of steam =  $1670 + 0.49T \text{ J/kg}\cdot\text{K}$  (where  $T$  is absolute

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temperature) and latent heat of vaporisation =  $23 \times 10^5$  J/kg.)

- (a) 7522.4 J                      (b) 75.22 J  
(c) 7.522 J                        (d) 445.2 J

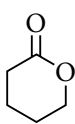
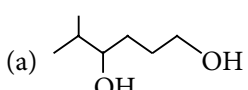
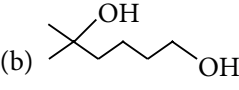
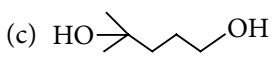
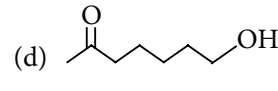
### COMPREHENSION

Amides generally in the presence of acids or bases undergo hydrolysis to form carboxylic acids and amines. The conditions required here are more extreme when compared to those for hydrolysis of esters, anhydrides or acid chlorides though the mechanism is same and the intermediates (tetrahedral) are also same.

Thus, these reactions are quite different from the alkyl substitution reactions.

7. The mechanism involved during hydrolysis of acid derivatives is  
(a) addition – elimination  
(b) nucleophilic addition – elimination

- (c) electrophilic addition – elimination  
(d) elimination – addition

8. When  is reacted with two moles of  $\text{CH}_3\text{MgI}$  followed by hydrolysis, the product obtained is
- (a)  (b)   
(c)  (d) 

### INTEGER VALUE

9.  $\text{Rn}$  (an  $\alpha$ -emitter) emits  $\alpha$ -particle having kinetic energy equal to 5.5 MeV and wavelength equal to  $2 \times 10^{-6} \text{ sec}^{-1}$ . For 1 Ci  $\text{Rn}$ , the energy released in 1 hr is  $72 \times x$ . The value of  $x$  is
10. For  $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ , the CFSE value is  $n \times 10^{-1} \Delta_0$ . The value of  $n$  is



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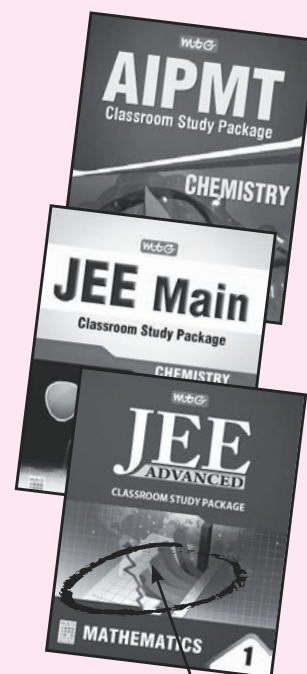
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## AIPMT

CLASS  
XI-XII

\*Dr. Sangeeta Khanna

## CLASS-XI : CHEMICAL AND IONIC EQUILIBRIUM | THERMODYNAMICS

- If  $pK_b$  for fluoride ( $F^-$ ) ion at 298 K is 10, the ionization constant of hydrofluoric (HF) acid in water at this temperature is  
(a)  $10^{-4}$  (b)  $10^{-10}$  (c)  $10^4$  (d) 10
- The solubility product of  $MgF_2$  is  $7.4 \times 10^{-11}$ . Calculate the solubility of  $MgF_2$  in 0.1 M NaF solution  
(a)  $7.4 \times 10^{-9}$  (b)  $3.7 \times 10^{-9}$   
(c)  $3.7 \times 10^{-11}$  (d)  $7.4 \times 10^{-11}$
- The aqueous solution of potash alum [ $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ ] is acidic due to  
(a) hydrolysis of  $K^+$  (b) hydrolysis of  $Al^{3+}$   
(c) hydrolysis of  $SO_4^{2-}$   
(d) presence of acid in its crystal as impurity.
- For reaction,  
 $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ ,  $K_c$  at  $427^\circ C$  is  $3 \times 10^{-6} L mol^{-1}$ . The value of  $K_p$  is nearly,  
(a)  $7.50 \times 10^{-5}$  (b)  $2.50 \times 10^{-5}$   
(c)  $2.50 \times 10^{-4}$  (d)  $1.75 \times 10^{-4}$
- Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing the volume?  
(i)  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$   
(ii)  $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s)$   
(a) (i) increase, (ii) increase  
(b) (i) decrease, (ii) decrease  
(c) (i) increase, (ii) decrease  
(d) (i) decrease (ii) increase
- At a certain temperature, the equilibrium constant  $K_c$  is 16 for the reaction,  
 $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$   
If 1.0 mol each of all the four gases is taken in a one litre container the concentration of  $NO_2$  at equilibrium would be  
(a)  $1.6 mol L^{-1}$  (b)  $0.8 mol L^{-1}$   
(c)  $0.4 mol L^{-1}$  (d)  $0.6 mol L^{-1}$
- For which of the following reactions, the degree of dissociation cannot be calculated from the vapour density data  
I.  $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$   
II.  $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$   
III.  $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$   
IV.  $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$   
(a) I and III (b) III and IV  
(c) I and II (d) II and III
- The aqueous solutions of four sodium salts NaA, NaB, NaC and NaD has pH 7.0, 9.0, 10.0 and 11.0 respectively, when each solution is 0.1 M. The strongest acid is  
(a) HA (b) HB  
(c) HC (d) HD
- In the hydrolytic equilibrium,  
 $A^- + H_2O \rightleftharpoons HA + OH^-$   
 $K_a = 1.0 \times 10^{-5}$ . The degree of hydrolysis of a 0.001 M solution of the salt is  
(a)  $10^{-2}$  (b)  $10^{-3}$   
(c)  $10^{-4}$  (d)  $10^{-5}$
- A weak acid HX has the dissociation constant  $1 \times 10^{-5} M$ . It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is  
(a) 0.0001% (b) 0.01%  
(c) 0.1% (d) 0.15%

\*A renowned chemistry expert, Chemistry Coaching Circle, Chandigarh, 09814129205

11. On adding 0.1 M solution each of  $\text{Ag}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$  in a  $\text{Na}_2\text{SO}_4$  solution, species first precipitated is  
 $[K_{sp}(\text{BaSO}_4) = 10^{-11}$ ,  $K_{sp}(\text{CaSO}_4) = 10^{-6}$ ,  $K_{sp}(\text{Ag}_2\text{SO}_4) = 10^{-5}]$   
 (a)  $\text{Ag}_2\text{SO}_4$  (b)  $\text{BaSO}_4$   
 (c)  $\text{CaSO}_4$  (d) all of these.
12. Calculate the buffer capacity of a solution if its pH changes from 4.745 to 4.832 on addition of 0.01 mole of  $\text{NaOH}$  to its 250 mL solution.  
 (a) 0.087 (b) 0.04  
 (c) 0.46 (d) 0.01
13.  $K_{sp}$  of  $\text{Fe}(\text{OH})_3$  in aqueous solution is  $3.8 \times 10^{-38}$  at 298 K. The concentration of  $\text{Fe}^{3+}$  will increase when  
 (a) pH is increased (b) pH is 7  
 (c) pH is decreased (d) it is exposed to air.
14. In the interaction of  $\text{B}(\text{CH}_3)_3$  with  $\text{N}(\text{CH}_3)_3$ ,  
 (a)  $\text{B}(\text{CH}_3)_3$  is a Lewis base and  $\text{N}(\text{CH}_3)_3$  is a Lewis acid  
 (b)  $\text{B}(\text{CH}_3)_3$  is a Lewis acid and  $\text{N}(\text{CH}_3)_3$  is a Lewis base  
 (c) both are Lewis acids  
 (d) both are Lewis bases.
15.  $K_{sp}(\text{BaSO}_4)$  is  $1.1 \times 10^{-10}$ . In which case is  $\text{BaSO}_4$  precipitated?  
 (a) 100 mL of  $4 \times 10^{-3}$  M  $\text{BaCl}_2$  + 300 mL of  $6.0 \times 10^{-4}$  M  $\text{Na}_2\text{SO}_4$   
 (b) 100 mL of  $4 \times 10^{-4}$  M  $\text{BaCl}_2$  + 300 mL of  $6.0 \times 10^{-8}$  M  $\text{Na}_2\text{SO}_4$   
 (c) 300 mL of  $4 \times 10^{-4}$  M  $\text{BaCl}_2$  + 100 mL of  $6.0 \times 10^{-8}$  M  $\text{Na}_2\text{SO}_4$   
 (d) In all cases
16.  $K_{sp}$  of  $\text{Mg}(\text{OH})_2$  is  $1.8 \times 10^{-11}$  at  $30^\circ\text{C}$ . Its molar solubility at  $\text{pH} = 12$  is  
 (a)  $1.8 \times 10^{-11}$  M (b)  $1.8 \times 10^{-9}$  M  
 (c)  $1.34 \times 10^{-54}$  M (d)  $1.8 \times 10^{-7}$  M
17. Select the correct statements about indicators.  
 (a) Near the equivalence point  $\text{pH} = \text{p}K_a$  for weak acid indicator and  $\text{pH} = (14 - \text{p}K_b)$  for weak base indicator.  
 (b) Most indicators have a transition range of two pH units.  
 (c) Methyl orange shows coloured form in acid solution.  
 (d) All the above statements are correct.
18. Some chemists at ISRO wished to prepare a saturated solution of a silver compound and they wanted it to have the highest concentration of silver ion possible. Which of the following compounds would they use?  
 $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$ ,  $K_{sp}(\text{AgBr}) = 5.0 \times 10^{-13}$   
 $K_{sp}(\text{Ag}_2\text{CrO}_4) = 2.4 \times 10^{-12}$   
 (a)  $\text{AgCl}$  (b)  $\text{AgBr}$   
 (c)  $\text{Ag}_2\text{CrO}_4$  (d) Any of them
19. Four solutions of  $\text{NH}_4\text{Cl}$  are taken with concentration 1 M, 0.1 M, 0.01 M and 0.001 M. Their degrees of hydrolysis are  $h_1$ ,  $h_2$ ,  $h_3$  and  $h_4$ . What is the graduation of degrees of hydrolysis?  
 (a)  $h_1 > h_2 > h_3 > h_4$  (b)  $h_1 = h_2 = h_3 = h_4$   
 (c)  $h_4 > h_3 > h_2 > h_1$  (d) None of these
20. Solubility of calcium phosphate (molecular mass,  $M$ ) in water is  $W$  g per 100 mL at  $25^\circ\text{C}$ . Its solubility product at  $25^\circ\text{C}$  will be approximately  
 (a)  $10^9 \left(\frac{W}{M}\right)^5$  (b)  $10^7 \left(\frac{W}{M}\right)^5$   
 (c)  $10^5 \left(\frac{W}{M}\right)^5$  (d)  $10^3 \left(\frac{W}{M}\right)^5$
21. When  $\text{NH}_3$  is heated in a 0.50 L flask at 700 K and 100 atm pressure, it decomposes into  $\text{N}_2$  and  $\text{H}_2$  and their equilibrium moles are given below  

$$2\text{NH}_{3(g)} \rightleftharpoons \text{N}_{2(g)} + 3\text{H}_{2(g)}$$

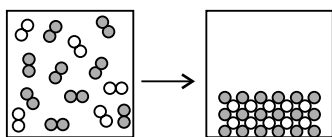
0.30	0.30	0.90
------	------	------

 Which of the pairs given represents correct value?  

Initial moles of $\text{NH}_3$	$K_c$ for $\text{NH}_3$ formation
(a) 0.80	9.72
(b) 0.90	9.72
(c) 0.80	0.103
(d) 0.90	0.103
22. Volume of the flask in which species are transferred is double of the earlier flask. In which of the following cases extent of equilibrium is affected?  
 I :  $\text{N}_{2(g)} + 3\text{H}_{2(g)} \rightleftharpoons 2\text{NH}_{3(g)}$   
 II :  $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$   
 III :  $\text{PCl}_{5(g)} \rightleftharpoons \text{PCl}_{3(g)} + \text{Cl}_{2(g)}$   
 IV :  $2\text{NO}_{(g)} \rightleftharpoons \text{N}_{2(g)} + \text{O}_{2(g)}$   
 (a) I, II (b) II, III  
 (c) I, III (d) III, IV
23. For the reaction,  $2A_{(g)} + 2B_{(g)} \rightleftharpoons 3C_{(g)}$  at a certain temperature,  $K_c$  is  $2.5 \times 10^{-2}$ . For which conditions will reaction proceed to the right at the same temperature?

[A]	[B]	[C]
(a) 0.01 M	0.10 M	0.10 M
(b) 1.0 M	1.0 M	1.0 M
(c) 1.0 M	0.10 M	0.10 M
(d) 1.0 M	1.0 M	0.10 M

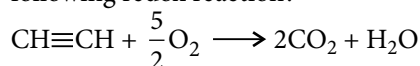
24. One mole of an ideal gas at 300 K is expanded isothermally from an initial volume of 1 litre to 10 litres.  $\Delta U$  for the process is ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )
- (a) 40 J (b) Zero  
(c) 340 J (d) 9 litre atm
25. What are the signs of  $\Delta H$ ,  $\Delta S$ , and  $\Delta G$  for the following spontaneous change?



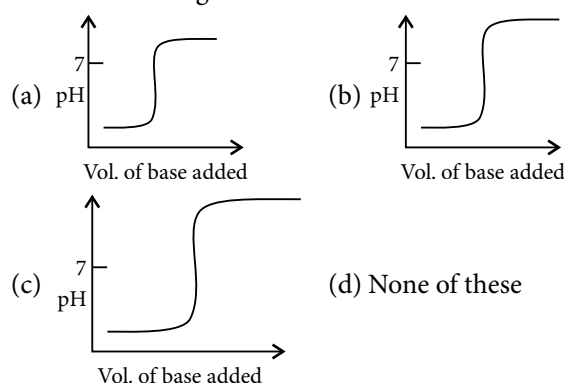
- (a)  $\Delta H = +, \Delta S = +, \Delta G = -$   
 (b)  $\Delta H = +, \Delta S = -, \Delta G = -$   
 (c)  $\Delta H = -, \Delta S = +, \Delta G = -$   
 (d)  $\Delta H = -, \Delta S = -, \Delta G = -$
26. A gas expands against a constant external pressure of 2.00 atm from an initial volume of 1.50 L to a final volume of 3.50 L. The container is well insulated so that no heat enters or leaves the system. Calculate the change in internal energy  $\Delta U$  of the gas in joules. [1 L atm = 101 J]
- (a) -404 (b) +404  
(c) 4.00 (d) 25.3
27. The standard enthalpy of formation of  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$ ,  $\text{N}_2\text{O}(\text{g})$  and  $\text{NO}_2(\text{g})$  in  $\text{kJ mol}^{-1}$  are -393, -110, +81 and 34 respectively. Calculate the standard enthalpy of reaction (in kJ) given below :
- $$2\text{NO}_2(\text{g}) + 3\text{CO}(\text{l}) \longrightarrow \text{N}_2\text{O}(\text{g}) + 3\text{CO}_2(\text{g})$$
- (a) -836 (b) +1460  
(c) +836 (d) -1170
28. A reaction mixture has concentration such that  $\Delta G$  is zero. However,  $\Delta G^\circ$  for the reaction is +10 kJ. This information means that
- (a) further reaction will take place to form more products.  
 (b) the reverse reaction will take place to form more reactants.  
 (c) the reaction mixture is at equilibrium but the concentration of products is small  
 (d) the reaction mixture is at equilibrium and the concentration of products is large.

29. Which of the following is correct order of acidic strength?
- (a)  $\text{HF} > \text{HCl} > \text{HBr}$   
 (b)  $\text{Mn}^{2+} > \text{Mn}^{3+} > \text{Mn}^{4+}$  (Lewis acid)  
 (c)  $\text{N}_2\text{O}_5 > \text{NO}_2 > \text{N}_2\text{O}_3$   
 (d)  $\text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{HClO}_4$

30. How much electrical work will be done in the following redox reaction?



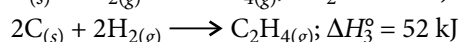
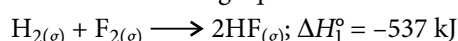
- (a)  $5FE^\circ$  (b)  $10FE^\circ$  (c)  $4FE^\circ$  (d)  $8FE^\circ$
31. Which of the following is the correct graph for titration of strong acid with weak base?



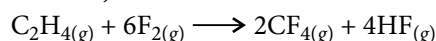
32. A sample of liquid in a thermally insulated container (a calorimeter) is stirred for 2 hr by a mechanical linkage to a motor in the surrounding, for this process

- (a)  $w < 0; q = 0; \Delta U = 0$  (b)  $w > 0; q > 0; \Delta U > 0$   
 (c)  $w < 0; q > 0; \Delta U = 0$  (d)  $w > 0; q = 0; \Delta U > 0$

33. Given the following equations and  $\Delta H^\circ$  values,

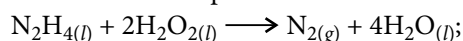


Determine the enthalpy of reaction at 298 K for the reaction,

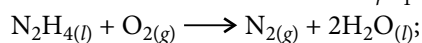


- (a) -1165 kJ (b) -2486 kJ  
(c) +1165 kJ (d) +2486 kJ

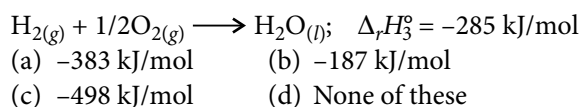
34. Determine enthalpy of formation for  $\text{H}_2\text{O}_2(\text{l})$ , using these listed enthalpies of reaction.



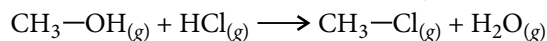
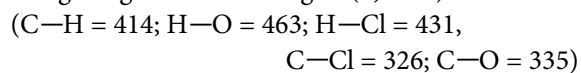
$$\Delta_r H_1^\circ = -818 \text{ kJ/mol}$$



$$\Delta_r H_2^\circ = -622 \text{ kJ/mol}$$



35. Calculate the enthalpy for the following reaction using the given bond energies (kJ/mol).



- (a) -23 kJ/mol      (b) -42 kJ/mol  
(c) -59 kJ/mol      (d) -511 kJ/mol
36. Calculate the heat produced (in kJ) when 224 g of CaO is completely converted to CaCO<sub>3</sub> by reaction with CO<sub>2</sub> at 27°C in a container of fixed volume.  
Given:  $\Delta H_f^\circ(\text{CaCO}_3, \text{s}) = -1207 \text{ kJ/mol}$ ;  
 $\Delta H_f^\circ(\text{CaO}, \text{s}) = -635 \text{ kJ/mol}$ ;  
 $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -394 \text{ kJ/mol}$ ;

$$[\text{Use } R = 8.3 \text{ K}^{-1} \text{ mol}^{-1}]$$

- (a) 702.04 kJ      (b) 721.96 kJ  
(c) 712 kJ      (d) 721 kJ
37. For the reaction,  
 $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$ ,  
 $\Delta H_r = -170.8 \text{ kJ mol}^{-1}$ . Which of the following statements is not true?  
(a) The reaction is exothermic.  
(b) At equilibrium, the concentration of CO<sub>2</sub>(g) and H<sub>2</sub>O(l) are not equal.  
(c) The equilibrium constant for the reaction is given by  $K_P = \frac{[\text{CO}_2]}{[\text{CH}_4][\text{O}_2]^2}$ .  
(d) Addition of CH<sub>4</sub>(g) or O<sub>2</sub>(g) at equilibrium will cause a shift to the right.

38. The pH of solution of both ammonium acetate and sodium chloride is 7 due to  
(a) hydrolysis in both cases  
(b) cationic and anionic hydrolysis of the former and not the latter.  
(c) no hydrolysis in both  
(d) hydrolysis of the latter but not the former.

39. Which of the following solutions on mixing will show maximum increase in temperature on neutralization?  
(a) 50 mL HCl + 40 mL NaOH of 0.01 Normality  
(b) 10 mL HCl + 10 mL NaOH of 0.01 Normality  
(c) 400 mL HCl (0.01N) + 100 mL NaOH (0.01N)  
(d) 500 mL HCl (0.01 N) + 600 mL NaOH (0.01N)

40. What will be the pH of a solution obtained by mixing 800 mL of 0.05 N sodium hydroxide and 200 mL of 0.1 N hydrochloric acid assuming complete ionization of the acid and base?

- (a) 12.3010      (b) 2.699  
(c) 10.546      (d) 11.4771

41. If  $K_{sp}(\text{PbSO}_4) = 1.8 \times 10^{-8}$  and  $K_a(\text{HSO}_4^-) = 1.0 \times 10^{-2}$ . The equilibrium constant for the reaction,  
 $\text{PbSO}_4(\text{s}) + \text{H}^+(\text{aq}) \rightleftharpoons \text{HSO}_4^-(\text{aq}) + \text{Pb}^{2+}(\text{aq})$  is

- (a)  $1.8 \times 10^{-6}$       (b)  $1.8 \times 10^{-10}$   
(c)  $2.8 \times 10^{-10}$       (d)  $1.0 \times 10^{-2}$

42. For a reaction,  $A(\text{g}) + 3B(\text{g}) \longrightarrow 2C(\text{g})$ ;  $\Delta H^\circ = -24 \text{ kJ}$ . The value of  $\Delta G^\circ$  is -9 kJ. The standard entropy change of reaction is

- (a)  $5 \text{ J K}^{-1}$       (b)  $50 \text{ J K}^{-1}$   
(c)  $500 \text{ J K}^{-1}$       (d)  $0.5 \text{ J K}^{-1}$

43. Match the following :

List I	List II
(P) Heat capacity	1. $\Delta H$ is positive
(Q) Standard Gibbs free energy changes	2. $\Delta G$ is negative
(R) Endothermic process	3. $-2.303RT \log K$
(S) Spontaneous process	4. $\frac{dQ}{dt}$
	5. $\Delta H = \Delta n gRT$

Codes :

	P	Q	R	S
(a)	5	4	2	1
(b)	4	3	1	2
(c)	4	3	2	1
(d)	5	3	2	1

44. Match the following :

List I	List II
(P) van't Hoff equation	1. Variation of enthalpy of a reaction with temperature
(Q) Kirchhoff equation	2. Variation of equilibrium constant with temperature.
(R) Second law of thermodynamics	3. Entropy of an isolated system tends to increase and reach a thermodynamics maximum value.
(S) Hess's law of constant summation	4. Enthalpy change in a reaction is always constant and independent of the manner in which the reaction occurs.



## Codes :

	P	Q	R	S
(a)	1	2	3	4
(b)	1	3	2	4
(c)	2	1	3	4
(d)	1	2	4	3

45. For which of the following processes  $\Delta S_{\text{total}} < 0$ ?
- Melting of ice below  $-4^{\circ}\text{C}$  at 1 atm
  - Intermixing of gases
  - Burning of  $\text{H}_2$  in oxygen
  - Evaporation of water above  $100^{\circ}\text{C}$

CLASS-XII : COORDINATION CHEMISTRY | *p*-BLOCK ELEMENTS

- Which one of the following arrangements does not truly represent the property indicated against it?
  - $\text{Br}_2 < \text{Cl}_2 < \text{F}_2$  : Oxidising power
  - $\text{Br} < \text{Cl} < \text{F}$  : Electronegativity
  - $\text{Br} < \text{F} < \text{Cl}$  : Electron affinity
  - $\text{Br}_2 < \text{Cl}_2 < \text{F}_2$  : Bond energy
- Which of the following species have undistorted octahedral structure?
  - $\text{SF}_6$
  - $\text{PF}_6^-$
  - $\text{SiF}_6^{2-}$
  - $\text{XeF}_6$
 The correct answer is
  - 1,2 and 4
  - 1, 2 and 3
  - 1,3 and 4
  - 2,3 and 4
- Hydrolysis of one mole of peroxodisulphuric acid produces
  - one mole of sulphuric acid and one mole of peroxomonosulphuric acid
  - one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide
  - two moles of sulphuric acid
  - two moles of peroxomonosulphuric acid.
- When chlorine water is added to a solution of  $\text{KBr}$ , the solution immediately turns orange red, because
  - chlorine is reduced to chloride ion
  - of the formation of  $\text{Br}_3^-$
  - of the formation of  $\text{BrCl}$
  - bromide ion is oxidised to bromine.
- Copper sulphate solution reacts with  $\text{KCN}$  to give
  - $\text{Cu}(\text{CN})_2$
  - $\text{CuCN}$
  - $\text{K}_2[\text{Cu}(\text{CN})_4]$
  - $\text{K}_3[\text{Cu}(\text{CN})_4]$
- Which of the following is tetrabasic acid?
  - Orthophosphoric acid
  - Pyrophosphoric acid
  - Metaphosphoric acid
  - Pyrophosphoric acid
- Calcium cyanamide on treatment with steam under pressure gives  $\text{NH}_3$  and
  - $\text{CaCO}_3$
  - $\text{Ca}(\text{OH})_2$
  - $\text{CaO}$
  - $\text{CaHCO}_3$
- Nitrogen combines with metals to form
  - nitrites
  - nitrate
  - nitrides
  - nitrosyl chloride.
- $\text{SO}_2$  oxidises
  - $\text{Mg}$
  - $\text{KMnO}_4$
  - $\text{K}_2\text{Cr}_2\text{O}_7$
  - all of these.
- Iodine is formed when  $\text{KI}$  reacts with a solution of
  - $\text{ZnSO}_4$
  - $\text{CuSO}_4$
  - $\text{FeSO}_4$
  - $(\text{NH}_4)_2\text{SO}_4$
- Tin reacts with conc.  $\text{HNO}_3$  to form
  - metastannic acid
  - stannic nitrate
  - stannous nitrate
  - tin stone.
- Which of the following statements regarding the manufacture of  $\text{H}_2\text{SO}_4$  by Contact process is not true?
  - S is burnt in air to form  $\text{SO}_2$ .
  - $\text{SO}_2$  is oxidized to  $\text{SO}_3$  in presence of  $\text{V}_2\text{O}_5$  as catalyst (or finely divided spongy platinum as catalyst) at a pressure of 2 atm and a temperature of about 700 K
  - $\text{SO}_3$  is dissolved in  $\text{H}_2\text{O}$  to get 100%  $\text{H}_2\text{SO}_4$ .
  - $\text{H}_2\text{SO}_4$  obtained by contact process is of higher purity than that obtained by lead chamber process.
- Which of the following statements is not true about trimethyl and trisilyl amine?
  - Trimethyl amine has a pyramidal shape while trisilyl amine has a planar shape.
  - Nitrogen atom in both trimethyl and trisilyl amines is in a state of  $sp^3$  and  $sp^2$  hybridization respectively.
  - Lone pair of electrons present in *p*-orbitals of nitrogen in trisilyl amine form  $p\pi-d\pi$  bond with the vacant *d*-orbitals of silicon atom.
  - Trisilyl amine is more basic in comparison to trimethyl amine because of the availability of the lone pair of electrons on nitrogen atom.

14.  $P_2O_5$  reacts with  $H_2SO_4$  to give  $SO_3$  and  $HPO_3$ . Which property of  $P_2O_5$  is depicted in this reaction?
- It acts as a strong dehydrating agent.
  - It is a white powder.
  - It sublimes on heating.
  - It is acidic in nature.
15. A greenish yellow gas reacts with an alkali metal hydroxide to form a halate, which can be used in fire works and safety matches. The gas and halate respectively are
- $Br_2$ ,  $KBrO_3$
  - $Cl_2$ ,  $KClO_3$
  - $I_2$ ,  $NaIO_3$
  - $Cl_2$ ,  $NaClO_3$
16. 20 V  $H_2O_2$  means that
- 20 mL of this  $H_2O_2$  evolves 20 mL of  $O_2$  at NTP
  - 10 mL of this  $H_2O_2$  evolves 20 mL of  $O_2$  at NTP
  - 1 mL of this  $H_2O_2$  evolves 20 mL of  $O_2$  gas at NTP
  - all of the above.
17. Pure nitrogen gas is obtained by heating
- $NH_3 + NaNO_2$
  - $NH_4Cl + NaNO_2$
  - $N_2O + Cu$
  - $(NH_4)_2Cr_2O_7$
18. Which one of the following oxides of nitrogen reacts with ferrous sulphate to form a dark brown compound used in the detection of nitrate?
- $N_2O$
  - $NO$
  - $NO_2$
  - $N_2O_5$
19. Which one of the following statements about  $H_2S$  is not correct?
- It is a covalent compound.
  - It is a gas at room temperature.
  - It is a much stronger reducing agent than water.
  - It is a weak base in aqueous solution.
20. Which of the following reactions depicts oxidizing property of  $SO_2$ ?
- $SO_2 + H_2O \longrightarrow H_2SO_3$
  - $2H_2S + SO_2 \longrightarrow 3S + 2H_2O$
  - $Cl_2 + SO_2 \longrightarrow SO_2Cl_2$
  - $2MnO_4 + 5SO_2 + 2H_2O \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$
21. Which of the following orders is not correct?
- Decrease in basic strength,  $NH_3 > PH_3 > AsH_3 > SbH_3$
  - Increase in bond angle,  $SbH_3 < AsH_3 < PH_3 < NH_3$
  - Decrease in bond angle,  $NH_3 > PH_3 > AsH_3 > SbH_3$ .
  - Increase in boiling point,  $PH_3 < SbH_3 < BiH_3 < NH_3$
22. A yellow metallic powder is burnt in a stream of fluorine to obtain a colourless gas  $X$  which is thermally stable and chemically inert. Its molecule has octahedral geometry. Another colourless gas  $Y$  with same constituent atoms as that of  $X$  is obtained when sulphur dichloride is heated with sodium fluoride. Its molecule has trigonal pyramidal structure.  $X$  and  $Y$  are respectively.
- $SF_4$  and  $S_2F_2$
  - $SF_6$  and  $SF_4$
  - $NaF$  and  $NaCl$
  - $SF_4$  and  $SF_6$
23. Sometimes a yellow turbidity appears while passing  $H_2S$  gas even in the absence of group II radicals. This is because
- sulphur is present in the mixture as impurity
  - group IV radicals are precipitated as sulphides
  - of the oxidation of  $H_2S$  gas by some acid radicals
  - group III radicals are precipitated as hydroxides.
24. The oxidation states of sulphur in the anions  $SO_3^{2-}$ ,  $S_2O_4^{2-}$  and  $S_2O_6^{2-}$  follow the order :
- $S_2O_4^{2-} < SO_3^{2-} < S_2O_6^{2-}$
  - $SO_3^{2-} < S_2O_4^{2-} < S_2O_6^{2-}$
  - $S_2O_4^{2-} < S_2O_6^{2-} < SO_3^{2-}$
  - $S_2O_6^{2-} < S_2O_4^{2-} < SO_3^{2-}$
25. For making  $H_2O_2$  in the laboratory
- $MnO_2$  is added to diluted cold  $H_2SO_4$
  - $BaO_2$  is added to  $CO_2$  bubbling through cold water
  - $PbO_2$  is added to an acidified water
  - $Na_2O_2$  is added to an acidified solution of  $KMnO_4$ .
26. Which of the following statements is not true about ozone?
- It is a pale blue gas at room temperature.
  - It oxidises sulphur and phosphorus evolving oxygen gas.
  - It oxidises  $SnCl_2$  and  $SO_2$  evolving oxygen gas.
  - It convert  $BaO_2$  to  $BaO$  and  $H_2O_2$  to  $H_2O$ .

27. An element (X) forms compounds of the formula  $XCl_3$ ,  $X_2O_5$  and  $Ca_3X_2$  but does not form  $XCl_5$ . Which of the following is the element X?  
(a) B (b) Al (c) N (d) P
28. The products of the reaction between  $HNO_3$  and  $P_4O_{10}$  are  
(a)  $H_3PO_4$  and  $N_2O_5$  (b)  $H_3PO_4$ ,  $NO_2$  and  $O_2$   
(c)  $HPO_3$ ,  $NO_2$  and  $O_2$  (d)  $HPO_3$  and  $N_2O_5$
29. There is a little difference in acid strength in the series  $H_3PO_4$ ,  $H_3PO_3$  and  $H_3PO_2$  because  
(a) phosphorus in these acids exists in different oxidation states  
(b) number of unprotonated oxygen atoms responsible for increase of acidity due to the inductive effect remains the same  
(c) phosphorus is not a highly electronegative element  
(d) phosphorus oxides are less basic.
30. Which of the following bonds has the highest energy?  
(a) Se—Se (b) Te—Te  
(c) S—S (d) O—O
31. Correct order of O—O bond length (increasing) in  $O_2$ ,  $H_2O_2$  and  $O_3$  is  
(a)  $H_2O_2 < O_3 < O_2$  (b)  $O_2 < O_3 < H_2O_2$   
(c)  $O_3 < O_2 < H_2O_2$  (d)  $O_3 < H_2O_2 < O_2$
32. Among  $Al_2O_3$ ,  $SiO_2$ ,  $P_2O_3$  and  $SO_2$ , the correct order of acid strength is  
(a)  $SO_2 < P_2O_3 < SiO_2 < Al_2O_3$   
(b)  $SiO_2 < SO_2 > Al_2O_3 < P_2O_3$   
(c)  $Al_2O_3 < SiO_2 < SO_2 < P_2O_3$   
(d)  $Al_2O_3 < SiO_2 < P_2O_3 < SO_2$
33. Of the following sets which one does not contain isoelectronic species?  
(a)  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $ClO_4^-$  (b)  $CN^-$ ,  $N_2$ ,  $C_2^{2-}$   
(c)  $SO_3^{2-}$ ,  $CO_3^{2-}$ ,  $NO_3^-$  (d)  $BO_3^{3-}$ ,  $CO_3^{2-}$ ,  $NO_3^-$
34. Bromine can be easily prepared by  
(a) heating any bromide with conc.  $H_2SO_4$   
(b) heating any bromide with HCl  
(c) passing iodine vapour through bromide solution  
(d) heating any bromide with dilute  $H_2SO_4$ .
35. HI cannot be prepared by the action of conc.  $H_2SO_4$  on KI because  
(a) HI is stronger acid than  $H_2SO_4$   
(b) HI is more volatile than  $H_2SO_4$   
(c)  $H_2SO_4$  also oxidizes HI so formed, to  $I_2$   
(d)  $H_2SO_4$  form complex with HI.
36. Which among the following elements of 3<sup>rd</sup> period shows maximum tendency of forming  $d\pi-p\pi$  bond?  
(a) Chlorine (b) Silicon  
(c) Phosphorus (d) Sulphur
37. Correct statements about the hydrogen halides include that  
I. they are all coloured  
II. their thermal stability decreases with increasing atomic number of the halogen  
III. they all form soluble silver salts  
IV. they all donate protons to water.  
(a) I, II, III are correct (b) I, III are correct  
(c) II, IV are correct (d) IV is correct
38. The compound(s) or ion(s), in which iodine is the central atom, isoelectronic with  $XeO_4$ ,  $XeF_2$  and  $XeF_6$  respectively are  
(a)  $IF_6^-$ ,  $IF_2^-$ ,  $IO_4^-$  (b)  $IO_4^-$ ,  $IF_2^-$ ,  $IF_6^-$   
(c)  $IF_2^-$ ,  $IO_4^-$ ,  $IF_6^-$  (d)  $IF_2^-$ ,  $IF_6^-$ ,  $IO_4^-$
39. Which of the following is a low-spin (spin-paired) complex?  
(a)  $[Co(H_2O)_6]^{2+}$  (b)  $[Fe(CN)_6]^{3-}$   
(c)  $[Ni(NH_3)_6]^{2+}$  (d)  $[FeF_6]^{3-}$
40. Which one of the following pairs of isomers and types of isomerism are correctly matched?  
1.  $[Co(NH_3)_5(NO_2)]Cl_2$  and  $[Co(NH_3)_5(ONO)]Cl_2$ ; Linkage  
2.  $[Cu(NH_3)_4][PtCl_4]$  and  $[Pt(NH_3)_4][CuCl_4]$ ; Coordination  
3.  $[Pt(NH_3)_4Cl_2]Br_2$  and  $[Pt(NH_3)_4Br_2]Cl_2$ ; Ionization
- Select the correct answer using the codes given below :  
(a) 2 and 3 (b) 1, 2 and 3  
(c) 1 and 3 (d) 1 and 2
41. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect?  
(a) Carboxypeptidase-A, is an enzyme and contains iron  
(b) Haemoglobin is the red pigment of blood and contains iron.  
(c) Cyanocobalamin is  $B_{12}$  and contains cobalt.  
(d) *cis*-platin is an anticancer medicine.

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42. Nickel ( $Z = 28$ ) combines with a uninegative monodentate ligand  $X$  to form a paramagnetic complex  $[\text{NiX}_4]^{2-}$ . The number of unpaired electron(s) in the nickel and geometry of this complex ion, respectively are  
 (a) one, tetrahedral (b) two, tetrahedral  
 (c) one, square planar (d) two, square planar.
43. Among the following metal carbonyls, the C—O bond order is lowest in  
 (a)  $[\text{Mn}(\text{CO})_6]^+$  (b)  $[\text{Fe}(\text{CO})_5]$   
 (c)  $[\text{Cr}(\text{CO})_6]$  (d)  $[\text{Co}(\text{CO})_5]^+$
44. The correct order of magnetic moments (spin values in B.M.) of the complexes is  
 (Atomic no. Mn = 25, Fe = 26, Co = 27)  
 (a)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$   
 (b)  $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$   
 (c)  $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$   
 (d)  $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$
45. Ammonia forms the complex  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with copper ions in alkaline solutions but not in acidic solution because  
 (a) in alkaline solution  $\text{Cu}(\text{OH})_2$  is precipitated which is soluble in excess of alkali  
 (b) copper hydroxide is an amphoteric substance  
 (c) in acidic solution hydration protects  $\text{Cu}^{2+}$  ions  
 (d) in acidic solution protons coordinate with ammonia molecule forming ions and  $\text{NH}_3$  molecules are not available.

## ANSWER KEYS

### CLASS-XI

1. (a) 2. (a) 3. (b) 4. (d) 5. (c)  
 6. (c) 7. (a) 8. (a) 9. (b) 10. (b)  
 11. (b) 12. (c) 13. (c) 14. (b) 15. (a)  
 16. (d) 17. (d) 18. (c) 19. (c) 20. (b)  
 21. (d) 22. (c) 23. (d) 24. (b) 25. (d)  
 26. (a) 27. (a) 28. (c) 29. (c) 30. (b)  
 31. (a) 32. (d) 33. (b) 34. (b) 35. (a)  
 36. (a) 37. (c) 38. (b) 39. (d) 40. (a)  
 41. (a) 42. (b) 43. (b) 44. (c) 45. (a)

### CLASS-XII

1. (d) 2. (b) 3. (a) 4. (d) 5. (d)  
 6. (d) 7. (a) 8. (c) 9. (a) 10. (b)  
 11. (a) 12. (c) 13. (d) 14. (a) 15. (b)  
 16. (c) 17. (b) 18. (b) 19. (d) 20. (b)

21. (d) 22. (b) 23. (c) 24. (a) 25. (b)  
 26. (c) 27. (c) 28. (d) 29. (b) 30. (c)  
 31. (b) 32. (d) 33. (c) 34. (a) 35. (c)  
 36. (a) 37. (c) 38. (b) 39. (b) 40. (b)  
 41. (a) 42. (b) 43. (b) 44. (d) 45. (d)

## SOLUTIONS

### CLASS-XI

2. (a):  $\text{MgF}_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{F}^-$   

$$K_{sp} = x(2x + 0.1)^2$$

$$K_{sp} \text{ of } \text{MgF}_2 = [\text{Mg}^{2+}][\text{F}^-]^2$$

$$K_{sp} = x(2x + 0.1)^2$$

$$K_{sp} = x(4x^2 + 0.01 + 0.4x)$$

$$K_{sp} = 4x^3 + 0.01x + 0.4x^2$$
 $x^3$  and  $x^2$  are negligible in comparison to  $x$   
 so,  $x = \frac{K_{sp}}{0.01} = \frac{7.4 \times 10^{-11}}{0.01} = 7.4 \times 10^{-9}$
3. (b):  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \xrightarrow{\text{H}_2\text{O}}$   
 $\text{KOH} + \text{H}_2\text{SO}_4 + \text{Al}(\text{OH})_3 + \text{H}_2\text{SO}_4$   
 Here, hydrolysis is cationic because  $\text{Al}^{3+}$  only reacts with water.
4. (d):  $\Delta n = 3 - 2 = 1$   

$$K_p = K_c (RT)^{\Delta n} = 3 \times 10^{-6} \times (0.0821 \times 700)$$

$$= 1.72 \times 10^{-4}$$
6. (c):  $\text{SO}_{2(g)} + \text{NO}_{2(g)} \rightleftharpoons \text{SO}_{3(g)} + \text{NO}_{(g)}$   
 Initial conc. 1 1 1 1  
 At equilibrium  $1-x$   $1-x$   $1+x$   $1+x$   

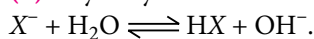
$$K = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = \frac{(1+x)(1+x)}{(1-x)(1-x)}$$

$$16 = \frac{(1+x)^2}{(1-x)^2} \Rightarrow \frac{(1+x)}{(1-x)} = 4$$
  
 or  $x = 0.6$   
 $[\text{NO}_2] = 1 - x = 1 - 0.6 = 0.4 \text{ mol L}^{-1}$
7. (a): The degree of dissociation cannot be calculated from the vapour density data if the number of moles remain unchanged before and after reaching equilibrium.
8. (a): Aqueous solution of NaA has pH 7.0 (lowest value). Hence, HA is the strongest acid.
9. (b): Degree of hydrolysis,  $h = \sqrt{\frac{K_w}{K_a \cdot c}}$   

$$= \sqrt{\frac{1 \times 10^{-14}}{1 \times 10^{-5} \times 0.001}}$$

$$= \sqrt{\frac{1 \times 10^{-14}}{1 \times 10^{-5} \times 1 \times 10^{-3}}} \\ = \sqrt{10^{-6}} = 10^{-3}$$

10. (b): Hydrolysis reaction is



For a salt of weak acid with strong base,

$$K_h = \frac{K_w}{K_a} = ch^2 \quad \therefore \frac{10^{-14}}{10^{-5}} = 0.1 \times h^2$$

$$\text{or } h^2 = 10^{-8} \quad \text{or } h = 10^{-4}$$

$$\% \text{ hydrolysis} = 10^{-4} \times 100 = 10^{-2} = 0.01$$

11. (b): For  $Ag_2SO_4$ ;  $K_{sp} = [Ag^+]^2 [SO_4^{2-}]$

$$[SO_4^{2-}] \text{ needed for precipitation of } Ag_2SO_4 > \frac{K_{sp}}{[Ag^+]^2} \\ = \frac{10^{-5}}{0.1 \times 0.1} = 10^{-3} M$$

For  $CaSO_4$ ;  $K_{sp} = [Ca^{2+}] [SO_4^{2-}]$

$\therefore [SO_4^{2-}]$  needed for precipitation of

$$CaSO_4 > \frac{K_{sp}}{[Ca^{2+}]} = \frac{10^{-6}}{0.1} = 10^{-5} M$$

$$BaSO_4 > \frac{10^{-11}}{0.1}$$

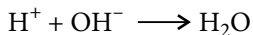
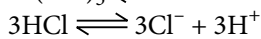
$$SO_4^{2-} > 10^{-10} M$$

Thus, minimum  $[SO_4^{2-}]$  is required for precipitation of  $BaSO_4$  and hence it is precipitated out first.

12. (c): Buffer capacity

$$= \frac{\text{Moles of acid or base added per litre of buffer}}{\text{Change in pH}} \\ = \frac{0.01/0.25}{0.087} = 0.46$$

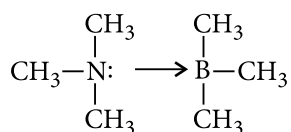
13. (c):  $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$



On adding acid (decrease in pH), the equilibrium shifts in the forward direction.

$\therefore [Fe^{3+}]$  increases.

14. (b):  $N(CH_3)_3$  has vacant lone-pair on N-atom which can be donated to electron-deficient B-atom of  $B(CH_3)_3$ .



15. (a): Considering dilution factor due to mixing,  $BaSO_4$  is precipitated if

$$[Ba^{2+}] [SO_4^{2-}] > K_{sp}$$

$$(a) [Ba^{2+}]_{\text{mix}} = \frac{4 \times 10^{-3}}{4} = 10^{-3} M$$

$$[SO_4^{2-}]_{\text{mix}} = \frac{4 \times 6 \times 10^{-4}}{3} = 4.5 \times 10^{-4} M$$

$$[Ba^{2+}][SO_4^{2-}] = 4.5 \times 10^{-7} > K_{sp}$$

16. (d):  $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

$$pH = 12$$

$$pOH = 2$$

$$\therefore [OH^-] = 10^{-2} M$$

$$K_{sp} = [Mg^{2+}][OH^-]^2$$

$$1.8 \times 10^{-11} = (s)(10^{-2})^2$$

$$\therefore s = 1.8 \times 10^{-7} M$$

20. (b):  $s = \frac{10W}{M}$  mol litre

$$K_{sp} \text{ of } Ca_3(PO_4)_2 = 108 s^5 = 108 \left( \frac{10W}{M} \right)^5 \\ = 10^7 \left( \frac{W}{M} \right)^5 \quad (\text{approx.})$$

21. (d):  $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$

Initial	a	0	0
Equil.	(a - 2x)	x	3x

$$x = 0.30$$

$$\therefore a - 2x = 0.30$$

$$\therefore a = 0.90$$

Thus, initial moles of  $NH_3 = 0.90$  mol

$$K_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{\left( \frac{0.30}{0.50} \right) \left( \frac{0.90}{0.50} \right)^3}{\left( \frac{0.30}{0.50} \right)^2} = 9.72$$

$$\text{Thus, } K_c \text{ for } NH_3 \text{ formation} = \frac{1}{9.72} = 0.103$$

22. (c): Equilibrium is affected when  $\Delta n_g \neq 0$  thus, I and III.

23. (d):  $Q = \frac{[C]^3}{[A]^2 [B]^2}$

$$(a) = 1000 \gg K_c$$

$$(b) = 1 > K_c$$

$$(c) = 0.1 > K_c$$

$$(d) = 1 \times 10^{-3} < K_c$$

Reaction proceeds to right when  $Q < K_c$

24. (b):  $\Delta U = 0, \Delta T = 0$  ( $\because$  it is isothermal) and the gas is ideal. If the gas is non ideal or it is some chemical reaction then  $\Delta U \neq 0$ .

25. (d):  $\Delta S = -ve$ , as molecules are arranged; reaction is spontaneous  $\Delta G = -ve$  and one of favourable factors is  $-\Delta H$ .

26. (a):  $P_{\text{external}} = \text{constant}; W_{\text{irr}} = \Delta U$   
 $W_{\text{irr}} = -P\Delta V$  as  $q = 0$

30. (b): No. of electrons exchanged by 5 oxygen atoms = 10

$$W_{\text{(Electrical)}} = nFE_{\text{cell}}^{\circ}$$

31. (a): At end point, medium should be acidic.

33. (b):  $\Delta H^{\circ} = 2 \times \Delta H_1^{\circ} + 2 \times \Delta H_2^{\circ} - \Delta H_3^{\circ}$

34. (b): For  $\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}_2(\text{l})$

$$\Delta_f H^{\circ}(\text{H}_2\text{O}_2, \text{l}) = \Delta_r H_3^{\circ} + \frac{\Delta_r H_2^{\circ}}{2} - \frac{\Delta_r H_1^{\circ}}{2}$$

35. (a)

36. (a):  $\text{CaO}(\text{s}) + \text{CO}_2(\text{g}) \longrightarrow \text{CaCO}_3(\text{s})$

$$\Delta_f H_f^{\circ} = \Delta_f H_f^{\circ}(\text{CaCO}_3) - \Delta_f H_f^{\circ}(\text{CaO}) - \Delta_f H_f^{\circ}(\text{CO}_2)$$

$$= -1207 - (-635) - (-394) = -178 \text{ kJ/mol}$$

$$\therefore \Delta U = \Delta H - \Delta n_g RT$$

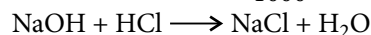
$$\Delta U = -178 - \frac{(-1) \times 8.3 \times 300}{1000} = -175.51 \text{ kJ}$$

$$n_{\text{CaO}} = \frac{224}{56} = 4$$

$$\therefore q_v = n \cdot \Delta_r U = 4 \times (-175.51) = -702.04 \text{ kJ}$$

40. (a): Moles of NaOH ( $n = 1$ ) =  $\frac{800 \times 0.05}{1000} = 0.04$

$$\text{Moles of HCl } (n = 1) = \frac{200 \times 0.1}{1000} = 0.02$$



$$\begin{array}{cccc} 0.04 & 0.02 & 0 & 0 \\ 0.02 & 0 & 0.02 & 0.02 \end{array}$$

$$\text{Total volume of solution} = 800 + 200 = 1000 \text{ ml} = 1 \text{ L}$$

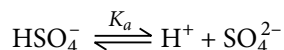
$$[\text{OH}^-] = \frac{0.02}{1} = 0.02$$

$$\text{pOH} = -\log(2 \times 10^{-2})$$

$$\text{pOH} = 1.699$$

$$\text{pH} = 14 - 1.699 = 12.301$$

41. (a):  $\text{PbSO}_4 \xrightleftharpoons{K_{sp}} \text{Pb}^{2+} + \text{SO}_4^{2-}$



For  $\text{PbSO}_4 + \text{H}^+_{(\text{aq})} \rightleftharpoons \text{HSO}_4^-_{(\text{aq})} + \text{Pb}^{2+}_{(\text{aq})}$

$$K = \frac{K_{sp}}{K_a} = \frac{1.8 \times 10^{-8}}{10^{-2}}$$

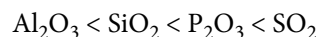
42. (b):  $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$

### CLASS-XII

28. (d):  $2\text{HNO}_3 + \text{P}_2\text{O}_5 \longrightarrow 2\text{HPO}_3 + \text{N}_2\text{O}_5$

$\text{P}_2\text{O}_5$  is a strong dehydrating agent.

32. (d): With decrease in size from Al to S the basic nature of oxide decreases and acidic nature increases.



$\text{Al}_2\text{O}_3$  is amphoteric,  $\text{SiO}_2$  is slightly acidic,  $\text{P}_2\text{O}_3$  and  $\text{SO}_2$  are anhydride of the acids  $\text{H}_3\text{PO}_3$  and  $\text{H}_2\text{SO}_3$ ,  $\text{H}_2\text{SO}_3$  is a stronger acid than  $\text{H}_3\text{PO}_3$ .

33. (c):  $\text{SO}_3^{2-}$  (42 electrons),  $\text{CO}_3^{2-}$  (32 electrons) and  $\text{NO}_3^-$  (32 electrons) are not isoelectronic.

34. (a):  $2\text{KBr} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O}$

35. (c):  $2\text{HI} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{H}_2\text{O} + \text{I}_2 + \text{SO}_2$

36. (a): Among the given elements, Cl has maximum tendency of  $d\pi-p\pi$  bonding. On moving across the period, nuclear charge increases and more  $s, p$  electrons are added. The atomic size and so the size of  $3d$ -orbitals decreases from  $\text{Si} \rightarrow \text{P} \rightarrow \text{S} \rightarrow \text{Cl}$ .

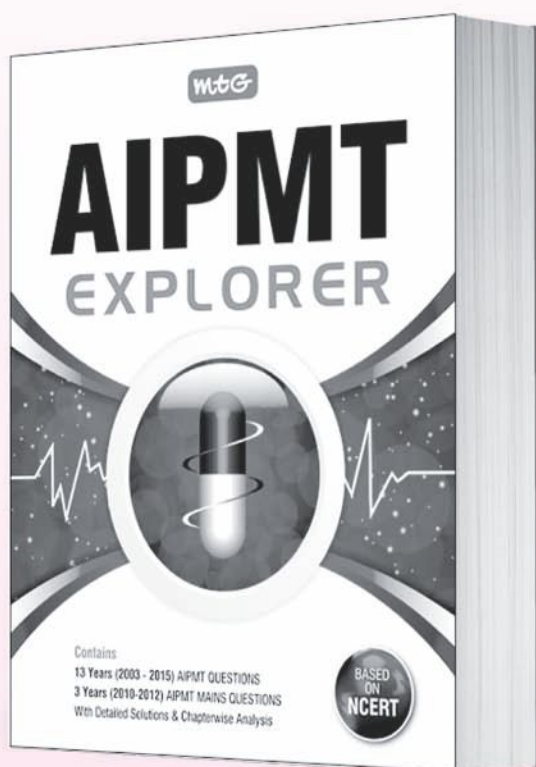


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# ADVANCED CHEMISTRY BLOC

(CHEMICAL BONDING)

Mukul C. Ray, Odisha

## OVERPOWERING THE LIMITATIONS OF ELECTRONIC THEORY-INTRODUCING VALENCE BOND THEORY

No theory is perfect. It is modified from time to time. The bond pair in a covalent bond as per electronic theory is exactly placed in between the atoms. Heisenberg's uncertainty principle, however, objects this idea that the position of an electron pair can be described with accuracy. Similarly, electronic theory hardly sees difference between the bond lengths in hydrogen and fluorine molecules. Also it has no idea to distinguish the bond strengths of the two bonds of oxygen molecule.

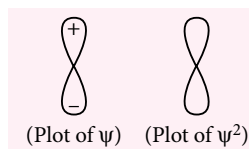
Consider Schrodinger's wave equation. For a  $2p$ -orbital say, there are two parts in the wave function, radial and angular parts. The angular part, for example, for the  $2p_x$ -orbital is :

$$\phi(2p_x) = \left( \frac{3}{\sqrt{4\pi}} \right) \sin\theta \cos\phi$$

This angular part when multiplied with radial part gives the total wave function. Generally, it is drawn, as  $p$ -orbital is the graph of the angular part of the wave function and present it like the graph of  $\psi$ , the total wave function. Now depending on whether presenting  $\psi$  or  $\psi^2$ , signs of wave functions appear in the lobes. In the squared wave function, both the lobes become positive.

The valence bond theory uses the plot of  $\psi^2$  to show orbital overlaps. Pauling's Valence Bond Theory visualizes a bond as the result of overlap of half-filled orbitals. During overlap :

- Orbitals with similar size overlap more effectively than orbitals of mis-matched sizes.
- Orbitals with nearly identical energy overlap effectively as compared to orbitals which are widely different in energies.

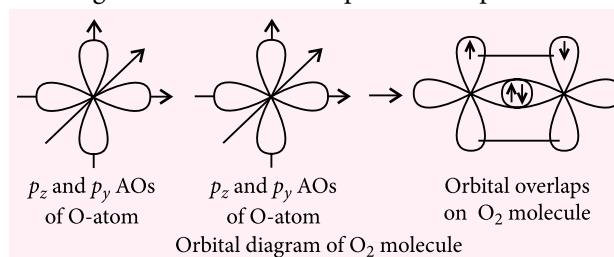


Both these points are illustrated by the decreasing stability of LiH, NaH, KH. In these compounds while hydrogen uses  $1s$ -orbital, lithium uses  $2s$ , sodium  $3s$  and potassium  $4s$ . These orbitals are increasingly larger in size and higher in energy hence give poor overlap.

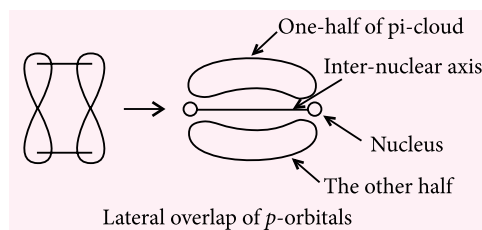
## Head-on and Lateral Overlaps

In molecules like HF,  $F_2$  overlappings found are  $s-p$ ,  $p-p$  respectively. Considering  $z$ -axis as the molecular axis, these can better be represented as  $s-p_z$  and  $p_z-p_z$ . It is known that  $s$ -orbitals are spherical in shape; means the electron density is not concentrated along any particular direction. On the other hand, they are projected along an axis,  $x$ ,  $y$  or  $z$  in  $p$ -orbitals. Such projected lobes give better overlaps. Therefore, bond strengths decrease in the order:  $p-p > s-p > s-s$ . These are all head-on overlaps giving rise to what is called as sigma bond.

In oxygen atom there are two half-filled atomic orbitals. When two such atoms overlap, there can be one head-on and another lateral overlaps. When  $z$ -axis is the molecular axis,  $p_z-p_z$  is the head-on overlap and  $p_x-p_x$  or  $p_y-p_y$  are the possible lateral overlaps. The covalent bonding due to lateral overlaps is called pi-bond.



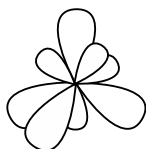
In a pi-bond one-half of the cloud lies above and the other half lies below the inter-nuclear axis.



Sigma bonds have electron density along the axis whereas in pi-bonds; one-half lies above and the other half lies below the axis. The stronger counterpart sigma bond determines the bond axis and also allows free rotation. The weaker one only shortens the bond length and prevents free rotation around the bond axis.

### An improvisation in the form of inter-mixing of orbitals was needed :

Methane, a household fuel, in the form of natural gas is a symmetric molecule with all bond lengths identical and bond angles  $109.5^\circ$ . In the excited state the carbon atom has the configuration  $2s^1, 2p_x^1, 2p_y^1, 2p_z^1$ . Involvement of these orbitals directly in bonding would have produced two types of bonds and bond angles surely other than  $109.5^\circ$ . Here comes the need of hybridisation—the inter-mixing of orbitals of the central atom before bonding takes place. The four half-filled orbitals of carbon atom inter-mix to produce four  $sp^3$ -hybrid orbitals, which subsequently overlap with s-orbital of hydrogen atom.



Four  $sp^3$ -hybrid orbitals

Methane is tetrahedral not because of  $sp^3$ -hybridisation but because of the fact that in tetrahedral configuration it is most stable.

About the hybrid orbitals, few points are notable like they form stronger bonds than pure orbitals and they never form pi-bonds.

### THE EXACT NATURE OF HYBRIDISATION DEPENDS ON HYBRIDISATION ENERGY, ELECTRON REPULSION ENERGY AND BOND ENERGY

The central oxygen atom in water molecule is  $sp^3$ -hybridised. The lone pairs are now in hybrid orbitals that involve some  $p$ -character, which is higher in energy than  $s$ -orbital. By the way the energy of the system has increased. However, the lone pair repulsion has decreased because of increase in bond angles and bond strength has increased. This makes a profitable business for the oxygen atom.

In  $H_2S$ , the original lone pair repulsion is decreased considerably because of large size of the atom. Now the system prefers to enter into bonding using  $p$ -rich orbitals having low hybridisation energy. Therefore,  $H_2S$  is not considered to have  $sp^3$ -hybridisation.

The index of hybridisation is not necessarily a whole number :

$$\cos \theta = \frac{s}{s-1}$$

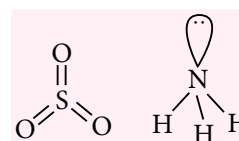
The bond angle between the hybrids is  $107.1^\circ$ , the hybridisation is  $sp^{3.4}$ . The gradual decrease in bond angles from  $180^\circ$ , lowers the  $p$ -character in the hybrid orbitals.

### Different combinations give rise to different hybridisations :

Types of hybridisation	Geometry	Orbitals hybridised	Example
$sp$	Linear	$s, p_z$	Monomeric $BeCl_2$
$sp^2$	Trigonal planar	$s, p_x, p_y$	$BF_3$
$sp^3$ or $sd^3$	Tetrahedral	$s, p_x, p_y, p_z$	$CH_4$
		$d_{xy}, d_{yz}, d_{zx}, s$	$MnO_4^-$
$sp^3d$	Trigonal bipyramidal (more appropriately $sp^2pd$ )	$d_{z^2}, s, p_x, p_y, p_z$	$PCl_5$
$sp^3d^2$	Octahedral	$d_{z^2}, d_{x^2-y^2}, s, p_x, p_y, p_z$	$SF_6$

### PREDICTING HYBRIDISATION IN SIMPLE MOLECULES OR IONS

In simple molecules or ions, the hybridisation of the central atom can be predicted by understanding of requirement of orbitals to form sigma bonds and carry lone pairs.



In  $SO_3$ , there are three sigma bonds; no lone pairs on the central atom. So it must be  $sp^2$ -hybridised. In ammonia, the central atom carries three bond pairs and one lone pair; so four hybrid orbitals are needed and it is  $sp^3$ -hybridised.

There is a short-cut too developed by A.B.P. Lever.

The value of  $V$  is calculated for the given molecule or ion.

$$V = \{\Sigma \text{ group number}\} - \text{charge}$$

For these calculations, group number of H is taken as 1 and all other group numbers are taken as per old convention IA, IIA etc.

The value of  $V$  is then divided by 8 and the result (say 'a') is recorded.

Remainder, if any, is divided by 2 and the result (say 'b') is recorded.

The sum of 'a' and 'b' is determined. If the result is 2, hybridisation is  $sp$ . Similarly, for 3, 4, 5 and 6 the hybridisations are  $sp^2$ ,  $sp^3$ ,  $sp^3d$  and  $sp^3d^2$  respectively. Remember these rules are applicable most effectively to non-cyclic molecules/ions of representative elements having only one central atom.

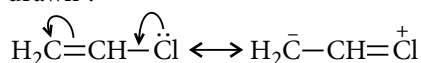
The state of hybridisation of carbon atom is always easy to recognize from the number of pi-bonds attached to it. If there is no pi-bond then it is  $sp^3$ . For 2 and 1 pi-bonds it is  $sp$  and  $sp^2$  respectively.

Consider the hybridisation of the central atom in  $I_3^-$  ion. For this ion,  $V = (7 \times 3) - (-1) = 22$ . Thus  $a + b = 5$  and the state of hybridisation of the central atom is  $sp^3d$ .

The state of hybridisation of various central atoms will be revisited after going through resonance and  $p\pi-d\pi$  bonds.

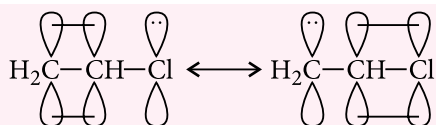
**A single valence bond structure may not explain all the observed properties – constraint is overpowered by resonance :**

Originally in vinyl chloride, carbon-chlorine has some double bond character in addition to double bond character in carbon-carbon bond. This cannot be explained by a single valence bond structure. The following two resonance structures for vinyl chloride are drawn :



These two structures donate characters to the original structure called hybrid proportionate to their stability.

In terms of orbital overlaps, they are :



These structures really want to say there is a delocalised overlap; means simultaneous overlaps of three  $p$ -orbitals altogether carrying four electrons in the resonance hybrid. There is no scope to show such bonding in VBT.

Out of the two resonating structures of vinyl chloride, the structure with no formal charge is more stable. When the things are seen closely it is realized that; VBT tries to explain the properties by giving various structures. But none of them really represents the behaviour perfectly. The most stable structure is the best attempt of VBT. The gap between the best attempt and the original structure in terms of energy is called resonance energy.

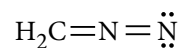
**Formal charge helps to know which resonating structure is close to the hybrid :**

There are examples of molecules where bonding situation does not respond to the normal valency of the bonded atoms. Such cases can be justified by the concept of formal charge. A formal charge on an atom is essentially the charge that would remain if all covalent bonds were broken and the electrons are distributed equally between the bonded atoms.

Mathematically,

Formal charge = (No. of valence electrons in neutral atom) - (No. of non-bonding electrons) -  $\frac{1}{2}$ (No. of electrons involved in bond formation)

The formal charges for the given structure of diazomethane is :

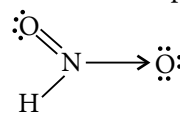


Formal charge on carbon =  $4 - 0 - \frac{1}{2}(8) = 0$

Formal charge on central nitrogen =  $5 - 0 - \frac{1}{2}(8) = +1$

Formal charge on the right nitrogen =  $5 - 4 - \frac{1}{2}(4) = -1$

For a co-ordinate covalent bond the rule concerning formal charge is amended, so that both electrons count for the donor neither for the recipient.



Formal charge on nitrogen =  $5 - 2 - \frac{1}{2}(6) = 0$

Formal charge on covalently bonded oxygen =  $6 - 4 - \frac{1}{2}(4) = 0$

Formal charge on co-ordinate bonded oxygen =  $6 - 6 - 0 = 0$

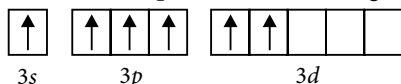
Formal charges are frequently drawn in organic chemistry, such as the positive charge on trivalent carbon of carbocation and negative charge on carbanion. They are extremely useful in judging the possibility of a proposed structure. Some general principles are :

- Structures, if possible without formal charges, are preferred.
- Structures with formal charges outside the range  $-1$  to  $+1$  are generally unfavourable.
- Negative formal charges should preferably be assigned to more electronegative atoms, positive charges to more electropositive atoms.

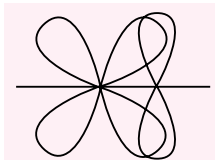
### Revisiting the concept of hybridisation and bringing in $p\pi-d\pi$ bonds :

In  $\text{SO}_3$ , the central sulphur atom is  $sp^2$ -hybridised. So naturally it is left with only one pure  $p$ -orbital in the valence shell. This can give rise to only one  $p\pi-p\pi$  bond. What about the other two  $\pi$ -bonds? The central atom must be using  $d$ -orbital to make these  $\pi$ -bonds.

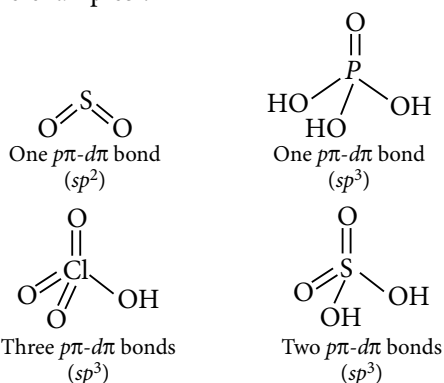
In the excited state sulphur has the configuration :



And  $p\pi-d\pi$  bonds are formed as shown below without taking into account which  $d$ -orbitals are involved :

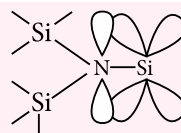


Such  $p\pi-d\pi$  bonds are best formed when one element is from 2<sup>nd</sup> and the other is from 3<sup>rd</sup> period. Consider few more examples :



Another fine example is trisilylamine,  $(\text{SiH}_3)_3\text{N}$ , which fails to form an adduct with  $\text{BF}_3$  implying the absence of lone pair on the nitrogen atom. This is explained by

saying the central nitrogen is  $sp^2$ -hybridised and the lone pair present in  $p$ -orbital of nitrogen overlaps with vacant  $d$ -orbital of one silicon atom in a resonating structure. The other two resonating structures will carry the only double bond in turn.

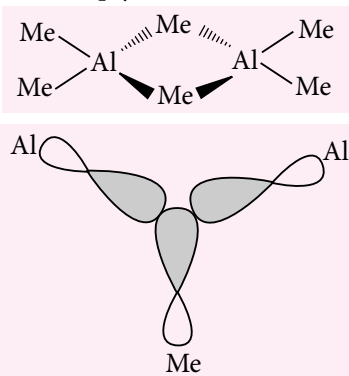


One resonating structure showing  $p\pi-d\pi$  bond

Similar case is found in  $\text{O}(\text{SiH}_3)_2$ , where the oxygen atom is  $sp^2$ -hybridised.

### Normal bonds are $2c-2e$ but there are bonds with $3c-2e$ :

In case of  $\text{Al}_2\text{Me}_6$  the two,  $3c(3 \text{ center}) - 2e(\text{electron})$  bonds are formed by overlapping of one  $sp^3$ -hybrid orbital from each aluminium atom and one  $sp^3$ -hybrid orbital of methyl group. Out of the two hybrid orbitals provided by the aluminium atoms, one is half-filled and the other is empty.



### Solution Senders of Chemistry Musing

#### Set 31

1. Rahul Dey, Jharkhand
2. Rajat Gupta, Mumbai
3. Rishabh Dutta Roy, Jharkhand
4. Hrishikesh Sarmah, Assam
5. Sayak Mandal, West Bengal
6. Ashwin Shenoy, Karnataka
7. Samrat Gupta, West Bengal
8. AVN Prasad, Visakhapatnam
9. Yakaiah Chennori, Warangal
10. Arunesh Varade, Nashik
11. Langa Bebartha, Odisha



# CONCEPT BOOSTER

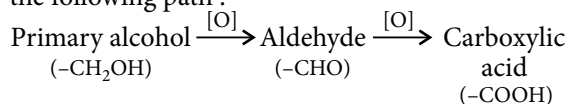
Dear students!! Last article was based on the reduction reactions and now this article is on oxidation reactions. Coupling both you can definitely make your concept strong to solve these type of questions asked in competitive examinations. All the very best for the board examinations. Thanks

\*Arunava Sarkar

## DEALING WITH OXIDATION

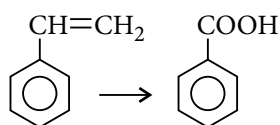
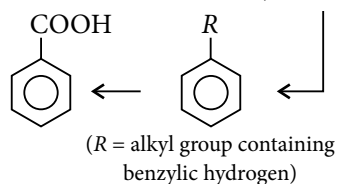
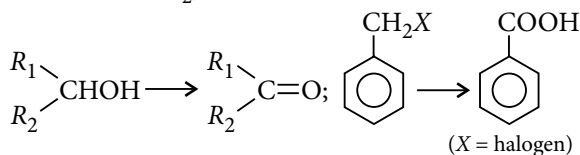
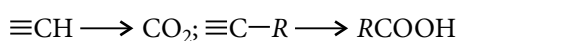
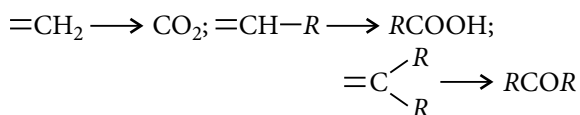
### Some Common Aspects

- In general, oxidation of primary alcohols follows the following path :



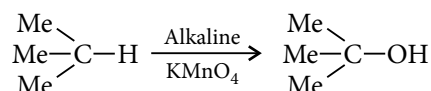
For this purpose either hot, alkaline or acidic  $\text{KMnO}_4$  or acidic  $\text{K}_2\text{Cr}_2\text{O}_7$  is used. They will not stop the oxidation at the aldehydic stage so, the final product is carboxylic acid.

- With hot alkaline  $\text{KMnO}_4$  or acidic  $\text{KMnO}_4$ , the following transformations take place :



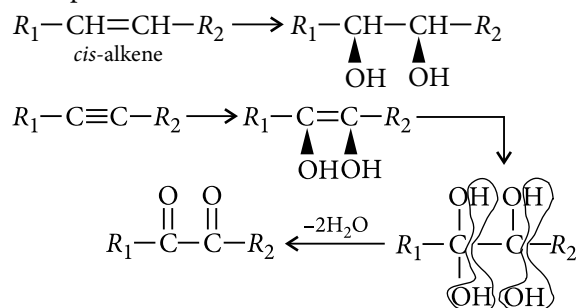
These reagents cannot oxidise a  $3^\circ$  alcohol or benzene ring as obvious in the above cases.

- $3^\circ$  H is oxidised to  $-\text{OH}$  :



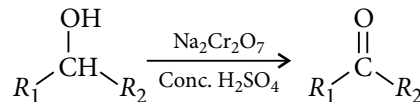
### Cold, dilute alkaline $\text{KMnO}_4$ or aqueous $\text{KMnO}_4$

Popularly, this reagent is known as Baeyer's reagent. Main function of this reagent is syn-hydroxylation of multiple bond as shown below :



### $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{Conc. H}_2\text{SO}_4$ , in acetone

Cr (VI) is oxidising in nature. During the oxidation, it gets converted to Cr(III). Cr(VI) form is available with  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  or  $\text{CrO}_3$ . Oxidation of this type is better known as Jones oxidation. One of the best uses of this oxidation is to convert  $2^\circ$  alcohols to ketones. *i.e.*

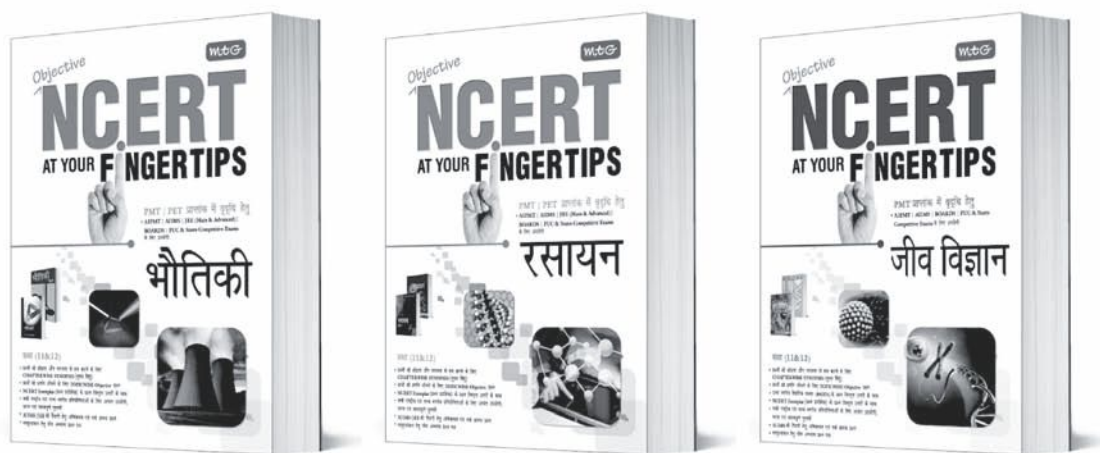


Reaction proceeds via the formation of chromate ester. In general, Jones Reagent is  $\text{H}_2\text{CrO}_4$  in anhydrous

\* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

# PMT/PET के Entrance Exam में हिंदी माध्यम छात्रों के लिए Triple धमाका

NCERT Textbook पर Based भौतिकी,  
रसायन और जीव विज्ञान की Objective पुस्तकें



NCERT पाठ्यक्रम पर आधारित और हमारे Subject Experts द्वारा निर्मित 10,000 से अधिक Objective Type प्रश्नों का अभ्यास कर इन तीनों विषयों पर अपनी महारत हासिल कर परीक्षाओं में अधिकतम सफलता प्राप्त करें और विजयी बनें।

## ये तीनों पुस्तकें ही क्यों पढ़नी जरूरी हैं?

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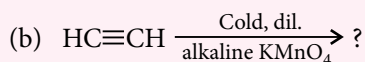
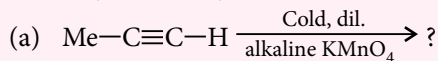


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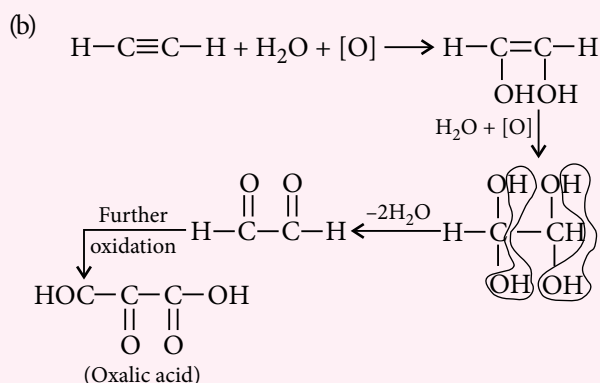
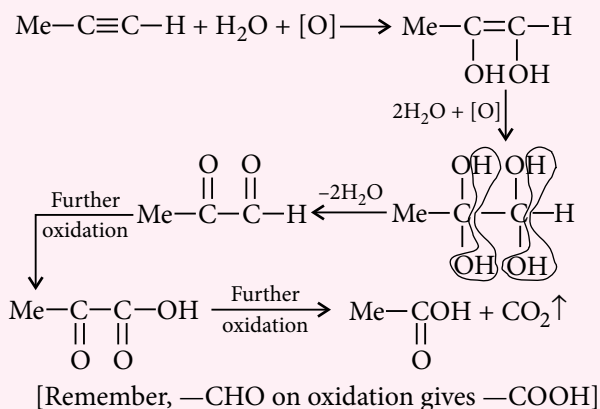
ये पुस्तकें देश के सभी शीर्ष पुस्तक विक्रेताओं के पास उपलब्ध हैं।  
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acetone or  $\text{CrO}_3 + \text{H}_2\text{SO}_4$  in acetone. It does not affect multiple bond or  $3^\circ$  alcohol. However, it converts  $1^\circ$  alcohol to carboxylic acid and  $2^\circ$  alcohol to ketone.

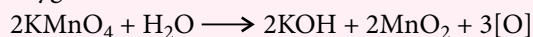
**Q.** Can you identify the product?



**Ans:** (a)

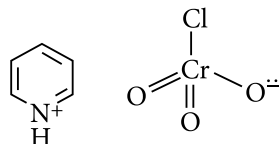


Usually, at the beginning, formation of nascent oxygen is shown as below :



### PCC

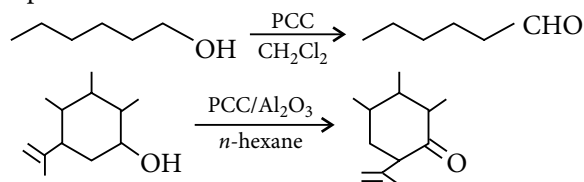
PCC is better known as pyridinium chlorochromate and its structure is represented as :



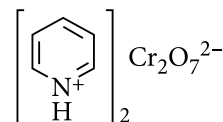
The best use of PCC is to stop the oxidation of alcohol at the aldehydic stage. PCC is used in dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) which is used as a solvent. Primary points regarding PCC are :

1. Converts  $1^\circ$  alcohol into aldehyde only. No further oxidation is possible.
2. Converts  $2^\circ$  alcohol into ketone.
3. Does not disturb multiple bond or  $3^\circ$  alcohol.
4. Oxidises allylic primary alcohol to aldehyde with no further oxidation.

Remember that the success of PCC to stop the oxidation of alcohol at aldehydic stage is due to the absence of water and presence of pyridine base. Follow these examples :



A similar reagent is PDC (Pyridinium dichromate) with the structure :



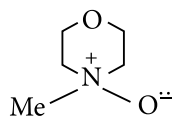
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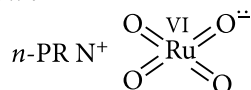
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### NMO with TPAP catalyst

NMO has the full form *N*-methyl morpholine-*N*-oxide with the structure :



TPAP (tee-pap) has the full form tetra-*n*-propyl ammonium perruthenate. Structure can be given as below :

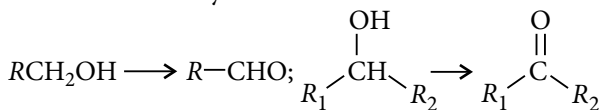


Now, function of both of these together is same as that of PCC, particularly, in converting 1° alcohol into aldehyde.

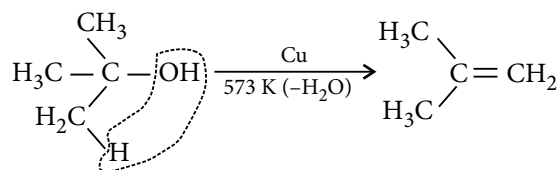
The use of this reagent has become popular because in chromium oxidation toxic heavy metal byproducts are obtained.

### Hot Cu/573 K

Conversion usually obtained are :



3° alcohols are usually not oxidisable and therefore are dehydrated under similar conditions.



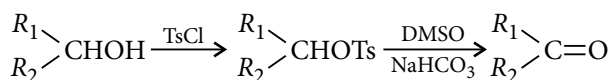
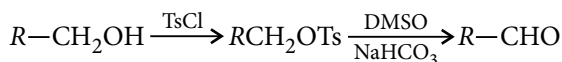
### CrO<sub>3</sub> in Glacial CH<sub>3</sub>COOH

CrO<sub>3</sub> is a strong oxidising agent. It carries out the following conversions :

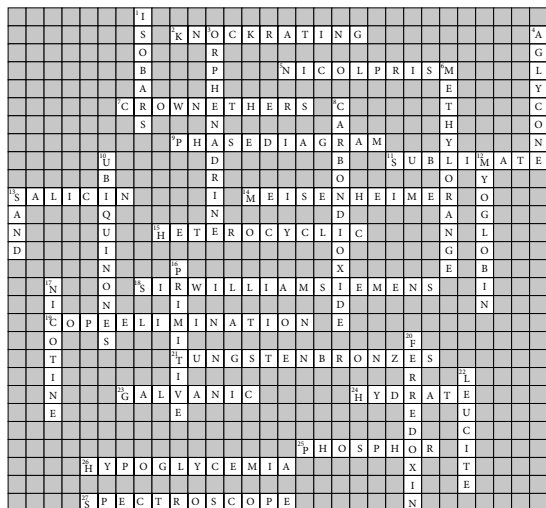
- $-CH_2OH \longrightarrow -CHO \longrightarrow -COOH$
- $>CHOH \longrightarrow >C=O$
- $>C=C< \longrightarrow -COOH$

It does not affect  $-C\equiv C-$  and 3° alcohol.

### TsCl (Tosyl chloride) + DMSO + NaHCO<sub>3</sub>



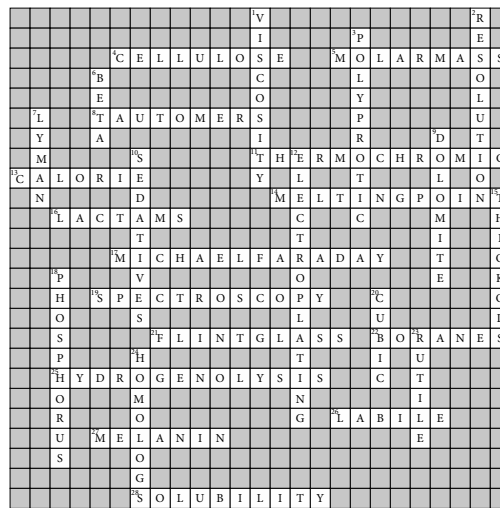
### SOLUTIONS OF JANUARY 2016 CROSSWORD



#### Winners of January 2016 Crossword

- Anshul Agnihotri (Chandigarh)
- Subhangi Gupta (Meerut)

### SOLUTIONS OF FEBRUARY 2016 CROSSWORD



#### Winners of February 2016 Crossword

- Tia Sharma (Surat)
- Ajay Bhardwaj (Punjab)

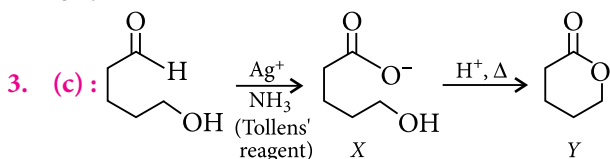


# CHEMISTRY MUSING

## SOLUTION SET 31

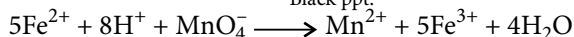
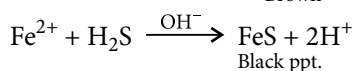
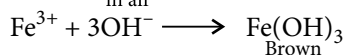
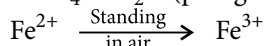
1. (b):  $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$  ionises to give 4 ions.  
 $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  ionises to give 3 ions.  
 $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$  ionises to give 2 ions.  
 Higher the number of ions a complex produces in solution, higher will be the conductivity of complex.

2. (b): Since  $t_{1/2} \propto \frac{1}{a^{n-1}} \Rightarrow t_{1/2} \propto \frac{1}{a^{1-1}} \Rightarrow t_{1/2} \propto \frac{1}{a^0}$   
*i.e.*,  $t_{1/2}$  is independent of  $a$ , hence order of reaction is 1.

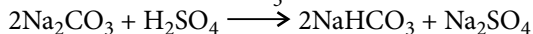


4. (b): Due to smaller size of oxygen there is higher charge density on oxygen as compared to sulphur. Thus, there is higher bond dissociation energy of H—O bond in  $\text{H}_2\text{O}$  which leads to difficulty in furnishing  $\text{H}^+$  ions than in the case of H—S bond in  $\text{H}_2\text{S}$ .

5. (d):  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (pale green salt)



6. (a): When phenolphthalein is used,  $\text{Na}_2\text{CO}_3$  gets converted into  $\text{NaHCO}_3$ .



$$N_{\text{H}_2\text{SO}_4} = 2M_{\text{H}_2\text{SO}_4} = 2 \times 0.1 = 0.2 \text{ N}$$

$$\text{meq of H}_2\text{SO}_4 = N_{\text{H}_2\text{SO}_4} \times V_{\text{H}_2\text{SO}_4} = 0.2 \text{ N} \times 2.5 = 0.5 \text{ meq of H}_2\text{SO}_4$$

0.5 meq of  $\text{H}_2\text{SO}_4$  is used to convert  $\text{Na}_2\text{CO}_3$  to  $\text{NaHCO}_3$  using phenolphthalein as indicator.

When methyl orange is used as an indicator, the end point appears when  $\text{NaHCO}_3$  is completely converted into  $\text{CO}_2$ .

$$N_{\text{H}_2\text{SO}_4} = 2 \times M_{\text{H}_2\text{SO}_4} = 2 \times 0.2 = 0.4 \text{ N}$$

No. of meq of 0.4 N  $\text{H}_2\text{SO}_4$  used to neutralise total  $\text{NaHCO}_3$  into  $\text{CO}_2 = 0.4 \times 2.5 = 1 \text{ meq}$

No. of meq of  $\text{H}_2\text{SO}_4$  used to neutralise  $\text{NaHCO}_3$  initially present in the sample solution =  $1.0 - 0.5 = 0.5 \text{ meq}$

Total meq of  $\text{H}_2\text{SO}_4$  used to neutralise  $\text{Na}_2\text{CO}_3$  completely =  $0.5 + 0.5 = 1.0 \text{ meq}$

10 mL of  $\text{Na}_2\text{CO}_3 \equiv 1 \text{ meq of Na}_2\text{CO}_3$

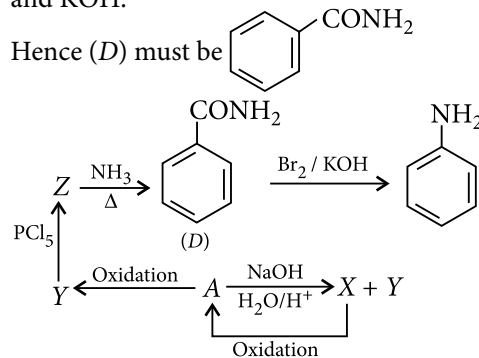
1000 mL of  $\text{Na}_2\text{CO}_3 \equiv 100 \text{ meq of Na}_2\text{CO}_3$

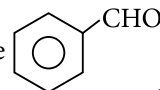
So, normality of  $\text{Na}_2\text{CO}_3$  in the sample

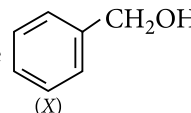
$$= \frac{100}{1000} = \frac{1}{10} = 0.1 \text{ N}$$

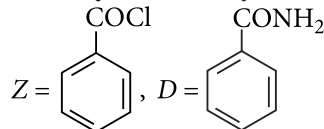
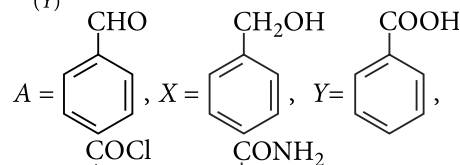
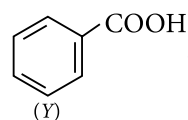
Strength in  $\text{g L}^{-1} = N \times \text{Eq. wt.} = 0.1 \times 53 = 5.3 \text{ g L}^{-1}$

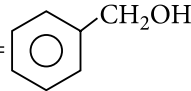
7. (b): Since (D) gives aniline on treatment with  $\text{Br}_2$  and  $\text{KOH}$ .



Hence (A) must be  which undergoes

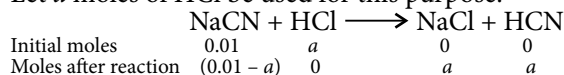
Cannizzaro reaction to give  and



8. (b): As compound X = , its molecular weight is  $108 \text{ g mol}^{-1}$ .

9. (3):  $\text{NaCN} + \text{HCl}$  is not a buffer but if  $\text{HCl}$  is present in less amount then, it produces  $\text{HCN}$ .

Let  $a$  moles of  $\text{HCl}$  be used for this purpose.



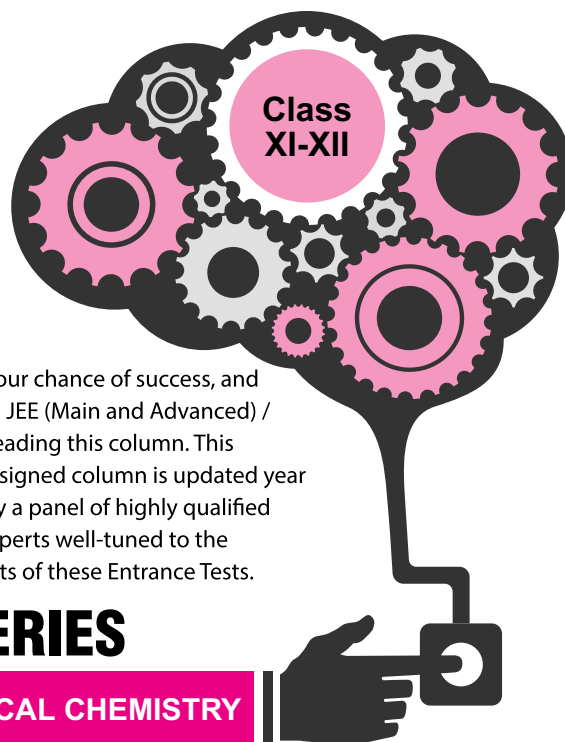
This is buffer of  $\text{HCN} + \text{NaCN}$ .

$$\therefore \text{pH} = -\log K_a + \log \frac{0.01 - a}{a}$$

$$8.5 = -\log 4.1 \times 10^{-10} + \log \frac{0.01 - a}{a}$$

$$\therefore a = 8.85 \times 10^{-3} \text{ mole of HCl}$$

10. (4): In alkaline condition  $\text{KMnO}_4$  reduces to  $\text{MnO}_2$   
 $2\text{KMnO}_4 + \text{H}_2\text{O} \longrightarrow 2\text{MnO}_2 + 2\text{KOH} + 3[\text{O}]$   
 Oxidation number of Mn in  $\text{MnO}_2$  is 4. □□



# JEE

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## ACCELERATED LEARNING SERIES

### Unit 9 PRINCIPLES RELATED TO PRACTICAL CHEMISTRY

#### PRACTICAL ORGANIC CHEMISTRY

- Detection of Extra Elements in Organic Compounds
- Detection of Functional Groups in Organic Compounds
- Preparation of Organic Compounds

#### TIPS TO REMEMBER

#### Detection of Extra Elements in Organic Compounds

- The principle elements present in organic compounds are carbon, hydrogen and oxygen while

nitrogen, sulphur and halogens are less commonly present thus are known as *extra elements*.

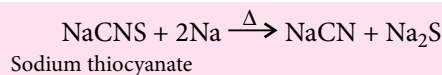
- The elements are usually tested in the form of ions. Since organic compounds are covalent in nature, they do not ionise. Therefore, to convert elements present in organic compounds into ions, the organic compound is fused with sodium metal which is then plunged in distilled water, boiled and filtered. The filtrate is called *Lassaigne's extract* or *sodium extract*.

Element	Lassaigne's extract (L.E.)	Confirmatory test	Reactions
Nitrogen	$\text{Na} + \text{C} + \text{N} \xrightarrow{\Delta} \text{NaCN}$ (L.E.)	L.E. + $\text{FeSO}_4 + \text{NaOH}$ , boil and cool + $\text{FeCl}_3 + \text{conc. HCl}$ Gives blue or green colour.	$\text{FeSO}_4 + 2\text{NaOH} \longrightarrow \text{Fe(OH)}_2 + \text{Na}_2\text{SO}_4$ $\text{Fe(OH)}_2 + 6\text{NaCN} \longrightarrow$ $\text{Na}_4[\text{Fe(CN)}_6] + 2\text{NaOH}$ $\text{Na}_4[\text{Fe(CN)}_6] + \text{FeCl}_3 \xrightarrow{\text{HCl}}$ $\text{NaFe[Fe(CN)}_6] + 3\text{NaCl}$ Prussian blue or $3\text{Na}_4[\text{Fe(CN)}_6] + 4\text{FeCl}_3 \longrightarrow$ $\text{Fe}_4[\text{Fe(CN)}_6]_3 + 12\text{NaCl}$ Prussian blue
Sulphur	$2\text{Na} + \text{S} \xrightarrow{\Delta} \text{Na}_2\text{S}$ (L.E.)	(i) L.E. + sodium nitroprusside A deep violet colour. (ii) L.E. + $\text{CH}_3\text{COOH}$ + $(\text{CH}_3\text{COO})_2\text{Pb}$ Gives a black ppt.	(i) $\text{Na}_2\text{S} + \text{Na}_2[\text{Fe(CN)}_5\text{NO}] \longrightarrow$ Sodium nitroprusside $\text{Na}_4[\text{Fe(CN)}_5\text{NOS}]$ Deep violet (ii) $\text{Na}_2\text{S} + (\text{CH}_3\text{COO})_2\text{Pb} \xrightarrow{\text{CH}_3\text{COOH}}$ $\text{PbS} \downarrow + 2\text{CH}_3\text{COONa}$ Black ppt.

Halogens	$\text{Na} + \text{X} \xrightarrow{\Delta} \text{NaX}$ (L.E.)	L.E. + $\text{HNO}_3$ + $\text{AgNO}_3$ (i) White ppt. soluble in aq. $\text{NH}_3$ (or $\text{NH}_4\text{OH}$ ) confirms Cl. (ii) Pale yellow ppt. partially soluble in aq. $\text{NH}_3$ (or $\text{NH}_4\text{OH}$ ) confirms Br. (iii) Yellow ppt. insoluble in aq. $\text{NH}_3$ (or $\text{NH}_4\text{OH}$ ) confirms I.	$\text{NaX} + \text{AgNO}_3 \xrightarrow{\text{HNO}_3} \text{AgX} \downarrow + \text{NaNO}_3$ ppt. $\text{AgCl} + 2\text{NH}_4\text{OH}_{(aq)} \longrightarrow$ White ppt. $[\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}_2\text{O}$ Soluble $\text{AgBr} + \text{NH}_4\text{OH}_{(aq)} \longrightarrow$ Sparingly soluble Pale yellow ppt. $\text{AgI} + \text{NH}_4\text{OH}_{(aq)} \longrightarrow$ Insoluble Yellow ppt.
Nitrogen and sulphur together	$\text{Na} + \text{C} + \text{N} + \text{S} \xrightarrow{\Delta} \text{NaSCN}$ (L.E.) Sodium thiocyanate	As in test for nitrogen, instead of green or blue colour, blood red colouration confirms presence of N and S both.	$3\text{NaSCN} + \text{FeCl}_3 \longrightarrow$ $[\text{Fe}(\text{SCN})_3] + 3\text{NaCl}$ Blood red colour

**KEY POINT**

- When sodium fusion is carried out with excess of sodium, thiocyanate decomposes to cyanide and sulphide ions which give their usual tests. Thus, we do not get blood red colour with ferric chloride even though N and S both are present.



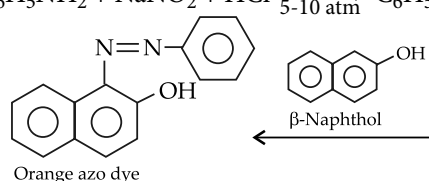
- Lassaigne's test fails in case of compounds which contain nitrogen but no carbon e.g., hydrazine ( $\text{NH}_2\text{NH}_2$ ) and hydroxylamine ( $\text{NH}_2\text{OH}$ ).

**Detection of Functional Groups in Organic Compounds**

Test	Reaction	Confirmation
<b>(A) Detection of unsaturation</b>		
(i) Baeyer's or $\text{KMnO}_4$ test	$2\text{KMnO}_4 + \text{H}_2\text{O} \longrightarrow 2\text{KOH} + 2\text{MnO}_2 + 3[\text{O}]$ $>\text{C}=\text{C}< + \text{H}_2\text{O} + [\text{O}] \longrightarrow$ $\begin{array}{c} >\text{C}-\text{C}< \\   \quad   \\ \text{OH} \quad \text{OH} \end{array}$	Disappearance of pink colour of $\text{KMnO}_4$ .
(ii) $\text{Br}_2 - \text{CCl}_4$ test	$>\text{C}=\text{C}< + \text{Br}_2 \xrightarrow{\text{CCl}_4} \begin{array}{c} \text{Br} \\   \\ >\text{C}-\text{C}< \\   \\ \text{Br} \end{array}$ Red brown	Disappearance of brown colour.
<b>(B) Detection of alcoholic group</b>		
(i) Ester test	$\text{RCOOH} + \text{R}'-\text{OH} \xrightarrow[\Delta]{\text{conc. H}_2\text{SO}_4} \text{RCOOR}' + \text{H}_2\text{O}$ Ester	Fruity smell of ester indicates -OH group.
(ii) Ceric ammonium nitrate test	$2\text{ROH} + (\text{NH}_4)_2[\text{Ce}(\text{NO}_3)_6] \longrightarrow$ $[(\text{ROH})_2\text{Ce}(\text{NO}_3)_4] + 2\text{NH}_4\text{NO}_3$ Pink or red	Appearance of pink or red colour.
(iii) Xanthate test	$\text{ROH} + \text{KOH}_{(s)} \xrightarrow{\Delta} \text{RO}^-\text{K}^+ + \text{H}_2\text{O}$ Pot. alkoxide $\text{RO}^-\text{K}^+ + \text{C} \begin{array}{l} \text{S} \\ // \\ \text{S} \end{array} \longrightarrow \text{R}-\text{O}-\text{C} \begin{array}{l} \text{S} \\ // \\ \text{S} \end{array} \text{K}^+$ Pot. alkyl xanthate (Yellow ppt.)	Formation of yellow ppt.

(C) Detection of phenolic group			
(i)	FeCl <sub>3</sub> test	$\text{FeCl}_3 + 6\text{C}_6\text{H}_5\text{OH} \longrightarrow [\text{Fe}(\text{OC}_6\text{H}_5)_6]^{3-} + 3\text{H}^+ + 3\text{HCl}$ <p style="text-align: center;">Violet</p>	Appearance of violet colouration.
(ii)	Azo dye test	$\text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + \text{HCl} \xrightarrow{0-5^\circ\text{C}} \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^-$ $\text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{C}_6\text{H}_5\text{OH} \xrightarrow{\text{pH } 9-10}$ $(p)\text{HO}-\text{C}_6\text{H}_4-\text{N}=\text{N}-\text{C}_6\text{H}_5$ <p style="text-align: center;"><i>p</i>-Hydroxyazobenzene</p>	Formation of orange or red dye.
(iii)	Phthalein test or fluorescein test	<p style="text-align: center;">Phthalic anhydride + Phenol (two molecules) <math>\xrightarrow[\Delta, -\text{H}_2\text{O}]{\text{Conc. H}_2\text{SO}_4}</math> Phenolphthalein (Colourless) <math>\xrightarrow{\text{NaOH}}</math> Pink</p>	Appearance of green, blue, pink, purple or red fluorescent solution.
(iv)	Br <sub>2</sub> -H <sub>2</sub> O test	<p style="text-align: center;">Phenol + 3Br<sub>2</sub> <math>\xrightarrow{\text{H}_2\text{O}}</math> 2,4,6-Tribromophenol (White ppt.) + 3HBr</p>	Appearance of white ppt.
(v)	Liebermann nitroso test	$\text{C}_6\text{H}_5\text{OH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{NaNO}_2} \text{HO}-\text{C}_6\text{H}_4-\text{N}=\text{O} \xrightleftharpoons{\text{Tautomerises}} \text{O}=\text{C}_6\text{H}_4=\text{N}-\text{OH}$ <p style="text-align: center;"><i>p</i>-Nitrosophenol <span style="margin-left: 100px;">Quinone monoxime (Green)</span></p> $\text{HO}-\text{C}_6\text{H}_4-\text{N}=\text{O} \xrightarrow{\text{NaOH}} \text{O}=\text{C}_6\text{H}_4=\text{N}-\text{C}_6\text{H}_4-\text{OH} \xrightarrow[\text{H}_2\text{SO}_4]{\text{Phenol}} \text{O}=\text{C}_6\text{H}_4=\text{N}-\text{C}_6\text{H}_4-\text{O}^- \text{Na}^+$ <p style="text-align: center;"><span style="margin-left: 100px;">Indophenol (Red)</span> Indophenol sod. salt (Blue)</p>	Appearance of deep blue or green colour which turns red on dilution and again blue on adding sodium hydroxide solution.

<b>(D) Detection of carbonyl group</b>			
<b>Aldehydic/Ketonic group</b>			
(i)	Brady's reagent (2, 4-DNP) test	$\text{>C=O} + \text{H}_2\text{NHN}-\text{C}_6\text{H}_3(\text{NO}_2)_2 \longrightarrow \text{>C=NHN}-\text{C}_6\text{H}_3(\text{NO}_2)_2$ <p style="text-align: center;">2,4-Dinitrophenylhydrazine Yellow, orange or red ppt.</p>	Appearance of yellow, orange or red ppt.
(ii)	Sod. bisulphite test	$\text{>C=O} + \text{NaHSO}_3 \longrightarrow \text{>C}\begin{matrix} \text{OH} \\ \text{SO}_3^-\text{Na}^+ \end{matrix}$ <p style="text-align: center;">White ppt.</p>	Appearance of white ppt.
<b>Aldehydic group</b>			
(i)	Tollens' test	$\text{RCHO} + 2[\text{Ag}(\text{NH}_3)_2]\text{OH} \longrightarrow \text{RCOONH}_4 + 3\text{NH}_3 + \text{H}_2\text{O} + 2\text{Ag}_{(s)}$ <p style="text-align: center;">Silver mirror</p>	Formation of silver mirror along the sides of the test tube.
(ii)	Fehling's test	$\text{RCHO} + 2\text{Cu}^{2+} + 5\text{OH}^- \longrightarrow \text{Cu}_2\text{O}\downarrow + \text{RCOO}^- + 3\text{H}_2\text{O}$ <p style="text-align: center;">Red ppt.</p>	A red ppt. is formed (only by aliphatic aldehydes).
(iii)	Schiff's test	$\text{RCHO} + p\text{-rosaniline hydrochloride in saturated solution of SO}_2 \text{ in water (colourless solution)}$	Appearance of pink colour.
<b>Ketonic group</b>			
(i)	Iodoform test	$\text{R}-\text{CO}-\text{CH}_3 + 3\text{I}_2 + 4\text{NaOH} \longrightarrow 3\text{NaI} + \text{CHI}_3\downarrow + \text{RCOONa} + 3\text{H}_2\text{O}$ <p style="text-align: center;">Yellow ppt.</p>	Formation of yellow ppt. of $\text{CHI}_3$ (for methyl ketones only).
(ii)	Sodium nitroprusside test	$\text{RCOR} + \text{sodium nitroprusside solution} + \text{NaOH}$	Appearance of wine-red colour (for methyl ketones only).
<b>(E) Detection of carboxylic group</b>			
(i)	Litmus test	Blue litmus paper turns red.	$-\text{COOH}$ group may be present.
(ii)	$\text{NaHCO}_3$ test	$\text{RCOOH} + \text{NaHCO}_3 \longrightarrow \text{RCOONa} + \text{H}_2\text{O} + \text{CO}_2\uparrow$	Brisk effervescence of $\text{CO}_2$ indicates $-\text{COOH}$ group.
(iii)	Ester test	$\text{RCOOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow[\Delta]{\text{Conc. H}_2\text{SO}_4} \text{RCOOC}_2\text{H}_5 + \text{H}_2\text{O}$	Fruity smell of esters formed.
(iv)	$\text{FeCl}_3$ test	$3\text{RCOOH} + 3\text{NH}_4\text{OH} + \text{FeCl}_3 \longrightarrow (\text{RCOO})_3\text{Fe} + 3\text{NH}_4\text{Cl} + 3\text{H}_2\text{O}$ <p style="text-align: center;">Coloured ppt.</p> $\downarrow \text{H}_2\text{O}$ $\text{Fe}(\text{OH})(\text{OOCR})_2 + \text{RCOOH}$ <p style="text-align: center;">Basic iron salt</p>	Red : acetic acid, formic acid No colour change or light yellow colour : oxalic acid Violet : salicylic acid Buff : benzoic acid

(F) Detection of amino group			
Primary amines			
(i)	Nitrous acid test	$R-NH_2 + HNO_2 \longrightarrow R-OH + N_2\uparrow + H_2O$	$N_2$ effervescence indicates 1° amino group.
(ii)	Carbylamine test	$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{\Delta} R-N \equiv C + 3KCl + 3H_2O$ Isocyanide	Offensive smell of isocyanide indicates 1° aliphatic or aromatic amino group.
(iii)	Azo dye test	$C_6H_5NH_2 + NaNO_2 + HCl \xrightarrow[5-10 \text{ atm}]{0-5^\circ C} C_6H_5N_2^+Cl^-$ 	A red or orange coloured dye confirms 1° aromatic amino group.
Secondary amines			
(i)	Liebermann nitroso test	$C_6H_5-N(CH_3)-H + HNO_2 \longrightarrow C_6H_5-N(CH_3)-N=O + H_2O$ Nitrosoamine	Formation of a yellow oily nitrosoamine indicates 2° aliphatic or aromatic amino group.
(G) Detection of nitro group			
(i)	Mulliken Barker test	$RNO_2 + 4[H] \xrightarrow{Zn + NH_4Cl} RNHOH + H_2O$ $RNHOH + 2[Ag(NH_3)_2]OH \longrightarrow RNO + 2H_2O + 4NH_3 + 2Ag\downarrow$ Grey black ppt.	Appearance of grey black ppt.
(ii)	Ferrous hydroxide test	$RNO_2 + 6Fe(OH)_2 + 4H_2O \longrightarrow RNH_2 + 6Fe(OH)_3\downarrow$ Light green Brown ppt.	Appearance of brown ppt.

□ Distinction tests

Test	Phenol	Alcohol
Blue litmus test	Turns red	×
FeCl <sub>3</sub> test	Gives blue, violet, green or red colouration	×
Azo dye test	Forms orange-red colour dye	×
Br <sub>2</sub> -water test	Gives white ppt.	×

Test	Phenol	Carboxylic acid
NaHCO <sub>3</sub> test	×	Gives brisk effervescence

Test	Aldehyde	Ketone
Tollens' test	Gives shiny silver mirror	×
Fehling's solution test	Gives red ppt.	×
Schiff's reagent test	Gives pink colour	×
Reduction with LiAlH <sub>4</sub>	Reduced to 1° alcohol	Reduced to 2° alcohol

Peroxy acid (Caro's acid, peroxy benzoic acid)	Acid is formed.	Ester is formed.
--	-----------------	------------------

**KEY POINT**

- *Ceric ammonium nitrate test* : Many easily oxidisable aromatic amines also give this test. Some phenols also give green or brown ppt.
- *Ferric chloride test* : Also given by enols  $\left[ \begin{array}{c} OH \\ | \\ -C=C- \end{array} \right]$
- *Sodium bisulphite test* : Aliphatic aldehydes and methyl ketones which are not sterically hindered such as acetaldehyde, acetone, ethyl methyl ketone give this test. Among aromatic aldehydes and ketones, only benzaldehyde gives this test but acetophenone, benzophenone do not give this test.
- *NaHCO<sub>3</sub> test* : Some phenols such as 2,4-dinitrophenol and 2,4,6-trinitrophenol (picric acid) also respond to this test.

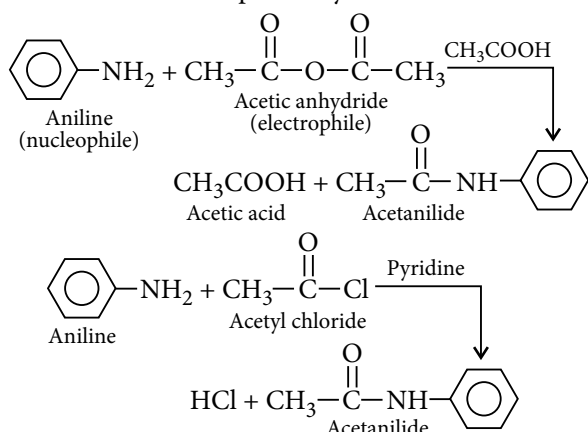
- **Carbylamine test** : Isocyanide formed has very offensive smell and may also be poisonous hence must be carefully decomposed by adding conc. HCl before throwing it in the sink.

### SELF CHECK

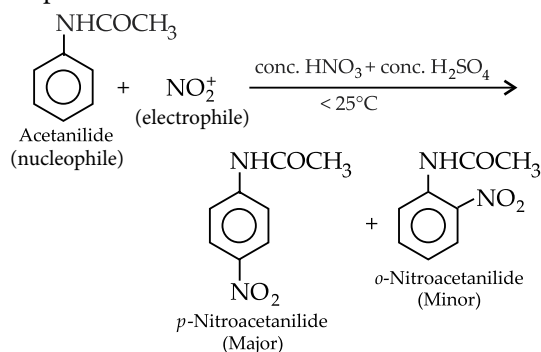
- For the identification of  $\beta$ -naphthol using dye test, it is necessary to use
  - dichloromethane solution of  $\beta$ -naphthol
  - acidic solution of  $\beta$ -naphthol
  - neutral solution of  $\beta$ -naphthol
  - alkaline solution of  $\beta$ -naphthol.
 (JEE Advanced 2014)
- Which of the following reagents may be used to distinguish between phenol and benzoic acid?
  - Aqueous NaOH
  - Tollens' reagent
  - Molisch reagent
  - Neutral  $\text{FeCl}_3$
 (AIEEE 2011)

### Preparation of Organic Compounds

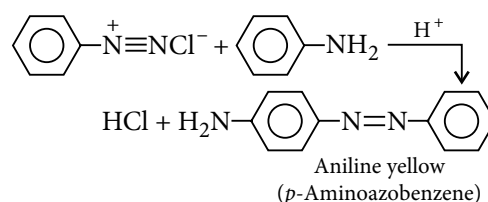
- **Acetanilide** : It is prepared by acetylation of aniline which is a nucleophilic acyl substitution reaction.



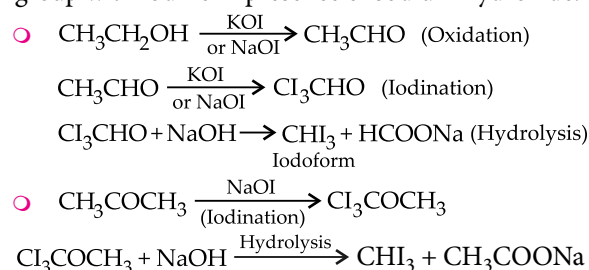
- ***p*-Nitroacetanilide** : It is prepared by nitration of acetanilide with nitrating mixture which is an electrophilic substitution reaction.



- **Aniline yellow** : It is prepared by coupling benzenediazonium chloride with aniline in acidic medium.



- **Iodoform** : It is prepared by treating organic compound containing  $\text{CH}_3-\text{CH}(\text{OH})-$  or  $\text{CH}_3-\text{C}(=\text{O})-$  group with iodine in presence of sodium hydroxide.



### KEY POINT

- Nitrating mixture is the equimolar mixture of conc.  $\text{HNO}_3$  and conc.  $\text{H}_2\text{SO}_4$ . The role of conc.  $\text{H}_2\text{SO}_4$  is that it reacts with  $\text{HNO}_3$  to form nitronium ion.

### PRACTICAL INORGANIC CHEMISTRY

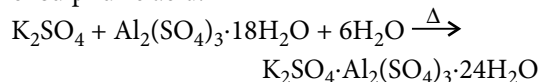
- Preparation of Inorganic Compounds
- Qualitative Salt Analysis
- Titrimetric Analysis

### TIPS TO REMEMBER

#### Preparation of Inorganic Compounds

- **Mohr's salt (Ferrous ammonium sulphate)**
  - It is a double salt containing ferrous sulphate and ammonium sulphate in equimolar amounts.
  - It is prepared by dissolving an equimolar mixture of hydrated ferrous sulphate and ammonium sulphate in water containing a little of sulphuric acid.
 
$$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4 \longrightarrow \text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O} + \text{H}_2\text{O}$$
- **Potash alum (*Phitkari*)**
  - It is a double salt containing potassium sulphate and aluminium sulphate in equimolar amounts.

- It is prepared by dissolving an equimolar mixture of hydrated aluminium sulphate and potassium sulphate in water containing a little of sulphuric acid.



### Qualitative Salt Analysis

#### □ Preliminary tests

- Physical examination**
  - Colour** :  $\text{NH}_4^+$ ,  $\text{Pb}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mg}^{2+}$  (white),  $\text{Cu}^{2+}$  (blue),  $\text{Ni}^{2+}$ ,  $\text{Cr}^{3+}$  (green),  $\text{Fe}^{2+}$  (light green),  $\text{Fe}^{3+}$  (brown),  $\text{Co}^{2+}$  (pink),  $\text{Mn}^{2+}$  (light pink or flesh colour)
  - Odour** :  $\text{NH}_4^+$  (ammoniacal smell),  $\text{CH}_3\text{COO}^-$  (smell of vinegar),  $\text{S}^{2-}$  (smell of rotten eggs)
- Dry heating test**

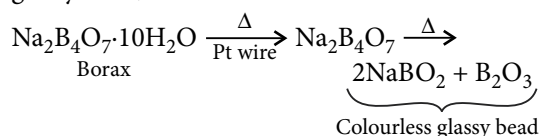
Observation	Radicals
<b>Gas evolved</b>	
Colourless	$\text{CO}_3^{2-}$ , $\text{SO}_3^{2-}$ , $\text{S}^{2-}$ , $\text{Cl}^-$
Brown	$\text{Br}^-$ , $\text{NO}_3^-$
Violet	$\text{I}^-$
<b>Residue</b>	
Yellow when hot, white when cold	$\text{Zn}^{2+}$
Brown when hot, yellow when cold	$\text{Pb}^{2+}$
Reddish brown	$\text{Fe}^{2+}$
Black	$\text{Ni}^{2+}$ , $\text{Co}^{2+}$ , $\text{Mn}^{2+}$ , $\text{Cu}^{2+}$
<b>Change in colour of salt</b>	
Blue to white	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Pink to blue	$\text{CoCl}_2$
Green to yellow	$\text{Ni}^{2+}$ salt
Blue/green to brown/black	$\text{Cu}^{2+}$ salt
<b>Sound produced</b>	
Crackling sound	$\text{NaCl}$ , $\text{KI}$ , $\text{Pb}(\text{NO}_3)_2$ , $\text{Ba}(\text{NO}_3)_2$

- Flame test** : A paste of salt with 1 or 2 drops of conc. HCl is introduced in the non-luminous (oxidising part) flame of the Bunsen burner

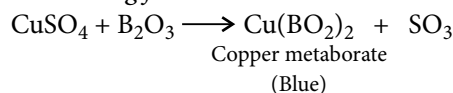
using platinum wire. Some basic radicals impart characteristic colour to the flame.

Colour of flame	Radicals
Golden yellow	$\text{Na}^+$
Lilac or violet	$\text{K}^+$
Brick red	$\text{Ca}^{2+}$
Apple green	$\text{Ba}^{2+}$ , $\text{Mo}^{2+}$
Crimson red	$\text{Sr}^{2+}$
Greenish blue	$\text{Cu}^{2+}$ , $\text{BO}_3^{3-}$

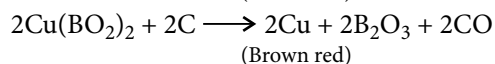
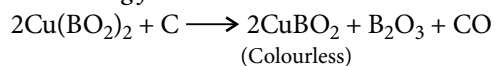
- Borax bead test** : Coloured salts are heated on the glassy bead, coloured metaborates are formed.



- In oxidising flame** :



- In reducing flame** :



Hence, different colours appear in different flames.

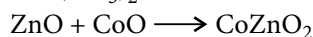
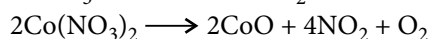
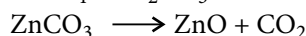
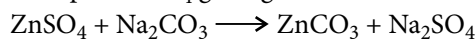
Metal	Colour in			
	Oxidising flame		Reducing flame	
	Hot	Cold	Hot	Cold
Cu	Green	Blue	Colourless	Brownish red
Fe	Brownish yellow	Pale yellow	Bottle green	Bottle green
Cr	Green	Green	Green	Green
Co	Blue	Blue	Blue	Blue
Mn	Violet	Amethyst red	Grey	Grey
Ni	Violet	Brown	Grey	Grey

- Charcoal cavity test (Reduction test)** : Salt is heated with fusion mixture ( $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ ) in a charcoal cavity in reducing flame to form metallic oxides which are left as coloured residues. The colour of the residue being characteristic of the basic radical present.



Residue (hot)	Residue (cold)	Radical
Yellow	White	Zn <sup>2+</sup>
Reddish brown	Yellow	Pb <sup>2+</sup>

- **Cobalt nitrate test** : If the residue in charcoal cavity test is white, it is moistened with a drop of cobalt nitrate and on heating in an oxidising flame, colour of the residue changes. For example, ZnSO<sub>4</sub> gives green residue.



Rinnmann's green

Observation	Inference
Blue mass	Aluminium
Green residue	Zinc
Pink residue	Magnesium
Bluish green	Tin

### KEY POINT

- Flame test should not be performed in the presence of As, Sb, Bi, Sn and Pb as these radicals form alloy with platinum and hence, the wire is spoiled.
- The yellow colouration due to sodium masks the colour due to potassium. In such cases, view the flame through cobalt glass, the yellow sodium colour is absorbed and the potassium flame appears crimson.
- Cobalt nitrate test should be performed with 2-3 drops of cobalt nitrate solution otherwise black cobalt oxide is formed which will mask the colour of the residue.

### Identification and confirmatory tests of acidic radicals

- **Group I acidic radicals** : Effervescence or evolution of gases on addition of dilute HCl or dilute H<sub>2</sub>SO<sub>4</sub> to the salt indicates the presence of group I acidic radicals.

Gas	Radical	Confirmatory Tests
CO <sub>2</sub> (Colourless, odourless gas)	Carbonate (CO <sub>3</sub> <sup>2-</sup> )	$\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ <p style="text-align: center;">Salt</p> $\text{Ca}(\text{OH})_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$ <p style="text-align: center;">Limewater                      White ppt. (milky)</p> $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{Ca}(\text{HCO}_3)_2$ <p style="text-align: center;">Soluble</p>
H <sub>2</sub> S (Colourless gas with smell of rotten eggs)	Sulphide (S <sup>2-</sup> )	<ul style="list-style-type: none"> <li>• <math>\text{Na}_2\text{S} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S} \uparrow</math> Salt</li> <li>• <math>(\text{CH}_3\text{COO})_2\text{Pb} + \text{H}_2\text{S} \longrightarrow \text{PbS} \downarrow + 2\text{CH}_3\text{COOH}</math> Black ppt.</li> <li>• <math>\text{Na}_2\text{S} + \text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \longrightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}]</math> Sodium nitroprusside                      Violet</li> </ul>
SO <sub>2</sub> (Colourless gas with suffocating odour having smell of burning sulphur)	Sulphite (SO <sub>3</sub> <sup>2-</sup> )	<ul style="list-style-type: none"> <li>• <math>\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2 \uparrow</math> Salt</li> <li>• <math>\text{K}_2\text{Cr}_2\text{O}_7 + 3\text{SO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}</math> Green</li> <li>• <math>\text{Na}_2\text{SO}_3 + \text{BaCl}_2 \longrightarrow \text{BaSO}_3 \downarrow + 2\text{NaCl}</math> White ppt.</li> <li>• <math>\text{BaSO}_3 + 2\text{HCl} \longrightarrow \text{BaCl}_2 + \text{H}_2\text{O} + \text{SO}_2 \uparrow</math> Soluble</li> </ul>
NO <sub>2</sub> (Brown gas)	Nitrite (NO <sub>2</sub> <sup>-</sup> )	$2\text{NaNO}_2 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HNO}_2$ <p style="text-align: center;">Salt                                      Nitrous acid</p> $3\text{HNO}_2 \longrightarrow \text{H}_2\text{O} + 2\text{NO} + \text{HNO}_3$ $2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2 \uparrow$ <p style="text-align: center;">Brown</p> $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{NO} \longrightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4 + 2\text{H}_2\text{O}$ <p style="text-align: center;">Brown</p>

<p><math>\text{CH}_3\text{COOH}</math> (Colourless gas with smell of vinegar)</p>	<p>Acetate (<math>\text{CH}_3\text{COO}^-</math>)</p>	<ul style="list-style-type: none"> <li><math>2\text{CH}_3\text{COONa} + \text{H}_2\text{SO}_4 \longrightarrow 2\text{CH}_3\text{COOH} + \text{Na}_2\text{SO}_4</math> Salt</li> <li><math>3\text{CH}_3\text{COONa} + \text{FeCl}_3 \longrightarrow (\text{CH}_3\text{COO})_3\text{Fe} + 3\text{NaCl}</math> Blood red</li> <li><math>2\text{CH}_3\text{COONa} + \begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array} \longrightarrow \begin{array}{c} \text{COONa} \\   \\ \text{COONa} \end{array} + 2\text{CH}_3\text{COOH}</math> Smell of vinegar</li> </ul>
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**KEY POINT**

- $\text{SO}_2$  gas evolved from  $\text{SO}_3^{2-}$  ion, also turns limewater milky. Thus, for test of  $\text{CO}_3^{2-}$  ion, odour of gas should be carefully observed as  $\text{SO}_2$  is a pungent gas while  $\text{CO}_2$  is odourless gas.
- $\text{PbS}$ ,  $\text{CdS}$ ,  $\text{NiS}$ ,  $\text{CoS}$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{SnS}$  are not decomposed by dil.  $\text{H}_2\text{SO}_4$ , therefore a pinch of zinc dust is added along with it. Conc.  $\text{HCl}$  should also be used.

- Before testing  $\text{CH}_3\text{COO}^-$  ion with neutral  $\text{FeCl}_3$  solution, make sure that the solution is free from  $\text{CO}_3^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{I}^-$  ions as they combine with  $\text{Fe}^{3+}$  ions.
- Carbonates of Bi and Ba are not easily decomposed by dil.  $\text{H}_2\text{SO}_4$  thus, dil.  $\text{HCl}$  should be used.

- Group II acidic radicals** : Effervescence or evolution of gases on addition of conc.  $\text{H}_2\text{SO}_4$  or conc.  $\text{HCl}$  to the salt (heat if necessary) indicates the presence of group II acidic radicals.

Gas	Radical	Observations and Reactions	Confirmatory Tests
<p><math>\text{HCl}</math> (Colourless gas with pungent smell)</p> <p><math>\text{Cl}_2</math> (Yellowish green, suffocating odour)</p>	<p>Chloride (<math>\text{Cl}^-</math>)</p>	<ul style="list-style-type: none"> <li><math>\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}\uparrow</math> Salt</li> <li><math>\text{NH}_4\text{OH} + \text{HCl} \longrightarrow \text{NH}_4\text{Cl}\uparrow + \text{H}_2\text{O}</math> White dense fumes</li> <li><math>\text{NaCl} + \text{AgNO}_3 \longrightarrow \text{AgCl}\downarrow + \text{NaNO}_3</math> White ppt.</li> <li><math>\text{AgCl} + 2\text{NH}_4\text{OH} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl} + 2\text{H}_2\text{O}</math> Soluble</li> <li><math>2\text{NaCl} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{NaHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Cl}_2\uparrow</math></li> </ul>	<p><b>Chromyl chloride test :</b></p> <p><math>\text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HCl}</math> Salt (Conc.)</p> <p><math>\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{KHSO}_4 + 2\text{CrO}_3 + \text{H}_2\text{O}</math></p> <p><math>\text{CrO}_3 + 2\text{HCl} \longrightarrow \text{CrO}_2\text{Cl}_2\uparrow + \text{H}_2\text{O}</math> Chromyl chloride (Deep red vapours)</p> <p><math>\text{CrO}_2\text{Cl}_2 + 4\text{NaOH} \longrightarrow \text{Na}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{O}</math> Yellow colour</p> <p><math>\text{Na}_2\text{CrO}_4 + (\text{CH}_3\text{COO})_2\text{Pb} \longrightarrow \text{PbCrO}_4\downarrow + 2\text{CH}_3\text{COONa}</math> Yellow ppt.</p>
<p><math>\text{Br}_2</math> (Brown gas)</p>	<p>Bromide (<math>\text{Br}^-</math>)</p>	<ul style="list-style-type: none"> <li><math>\text{NaBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{NaHSO}_4 + \text{HBr}</math> Salt</li> <li><math>2\text{HBr} + \text{H}_2\text{SO}_4 \longrightarrow \text{Br}_2\uparrow + 2\text{H}_2\text{O} + \text{SO}_2</math> Brown</li> <li><math>\text{AgNO}_3 + \text{NaBr} \longrightarrow \text{AgBr}\downarrow + \text{NaNO}_3</math> Pale yellow ppt.</li> <li><math>\text{AgBr} + 2\text{NH}_4\text{OH} \longrightarrow [\text{Ag}(\text{NH}_3)_2]\text{Br} + 2\text{H}_2\text{O}</math> Sparingly soluble</li> <li><math>2\text{NaBr} + \text{MnO}_2 + 3\text{H}_2\text{SO}_4 \longrightarrow 2\text{NaHSO}_4 + \text{MnSO}_4 + 2\text{H}_2\text{O} + \text{Br}_2\uparrow</math></li> </ul>	<p><b>Layer test :</b></p> <p><math>2\text{NaBr} + \text{Cl}_2 \text{ water} \xrightarrow[\text{CHCl}_3 \text{ or } \text{CCl}_4]{\text{dil. } \text{H}_2\text{SO}_4} 2\text{NaCl} + \text{Br}_2</math> Brown coloured layer</p>

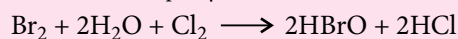
I <sub>2</sub> (Deep violet gas)	Iodide (I <sup>-</sup> )	<ul style="list-style-type: none"> <li>2KI + 2H<sub>2</sub>SO<sub>4</sub> → 2KHSO<sub>4</sub> + 2HI Salt</li> <li>2HI + H<sub>2</sub>SO<sub>4</sub> → I<sub>2</sub>↑ + SO<sub>2</sub> + 2H<sub>2</sub>O Violet</li> <li>AgNO<sub>3</sub> + NaI → AgI↓ + NaNO<sub>3</sub> Yellow ppt.</li> <li>AgI + NH<sub>4</sub>OH → Not soluble</li> <li>2KI + MnO<sub>2</sub> + 3H<sub>2</sub>SO<sub>4</sub> → 2KHSO<sub>4</sub> + MnSO<sub>4</sub> + 2H<sub>2</sub>O + I<sub>2</sub>↑</li> </ul>	<p><i>Layer test :</i></p> <p>2NaI + Cl<sub>2</sub> → 2NaCl + I<sub>2</sub> Salt</p> <p>I<sub>2</sub> + Chloroform → Violet coloured layer</p> <p><i>Starch paper test :</i></p> <p>I<sub>2</sub> + Starch → I<sub>2</sub>-starch complex Violet vapours                      Blue colour</p>
NO <sub>2</sub> (Light brown gas having pungent smell)	Nitrate (NO <sub>3</sub> <sup>-</sup> )	<p>NaNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → NaHSO<sub>4</sub> + HNO<sub>3</sub> Salt</p> <p>4HNO<sub>3</sub> → 2H<sub>2</sub>O + 4NO<sub>2</sub>↑ + O<sub>2</sub> Light brown fumes</p> <p>Cu + 4HNO<sub>3</sub> → Cu(NO<sub>3</sub>)<sub>2</sub> + 2NO<sub>2</sub>↑ + 2H<sub>2</sub>O</p>	<p><i>Brown ring test :</i></p> <p>NaNO<sub>3</sub> + H<sub>2</sub>SO<sub>4</sub> → NaHSO<sub>4</sub> + HNO<sub>3</sub> Salt</p> <p>6FeSO<sub>4</sub> + 2HNO<sub>3</sub> + 3H<sub>2</sub>SO<sub>4</sub>(conc.) → 3Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> + 4H<sub>2</sub>O + 2NO</p> <p>[Fe(H<sub>2</sub>O)<sub>6</sub>]SO<sub>4</sub>·H<sub>2</sub>O + NO → Ferrous sulphate      [Fe(H<sub>2</sub>O)<sub>5</sub>NO]SO<sub>4</sub> + Brown ring 2H<sub>2</sub>O</p>
CO + CO <sub>2</sub> (Colourless, odourless gas)	Oxalate (C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> )	<p>Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub> → Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> Salt</p> <p>H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + [H<sub>2</sub>SO<sub>4</sub>] → CO + CO<sub>2</sub> Burns with blue flame      Turns lime water milky + H<sub>2</sub>O + [H<sub>2</sub>SO<sub>4</sub>]</p>	<p>Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + CaCl<sub>2</sub> → Sodium carbonate extract      CaC<sub>2</sub>O<sub>4</sub>↓ + 2NaCl White ppt.</p> <p>CaC<sub>2</sub>O<sub>4</sub> + H<sub>2</sub>SO<sub>4</sub>(dil.) → H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + CaSO<sub>4</sub></p> <p>2KMnO<sub>4</sub>(few drops) + 3H<sub>2</sub>SO<sub>4</sub> → Purple K<sub>2</sub>SO<sub>4</sub> + 2MnSO<sub>4</sub> + 3H<sub>2</sub>O + 5[O] Colourless</p> <p> <math>\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array} + [\text{O}] \longrightarrow 2\text{CO}_2 + \text{H}_2\text{O}</math> </p>

### KEY POINT

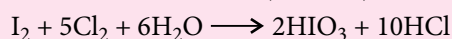
- Chromyl chloride test :** Dry test tube should be used to prevent the hydrolysis of chromyl chloride vapours.  
CrO<sub>2</sub>Cl<sub>2</sub> + 2H<sub>2</sub>O → H<sub>2</sub>CrO<sub>4</sub> + 2HCl  
In case of chlorides of Hg, Sn, Ag, Pb and Sb, this test is performed by taking residue obtained after evaporation of sodium carbonate extract.
- Brown ring test is not reliable in the presence of NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> ions.
- While performing layer test for Br<sup>-</sup> and I<sup>-</sup> ions, excess of Cl<sub>2</sub> water should be avoided.



Bromine monochloride  
(pale yellow colour)



Hypobromous acid  
(colourless)



Iodic acid  
(colourless)

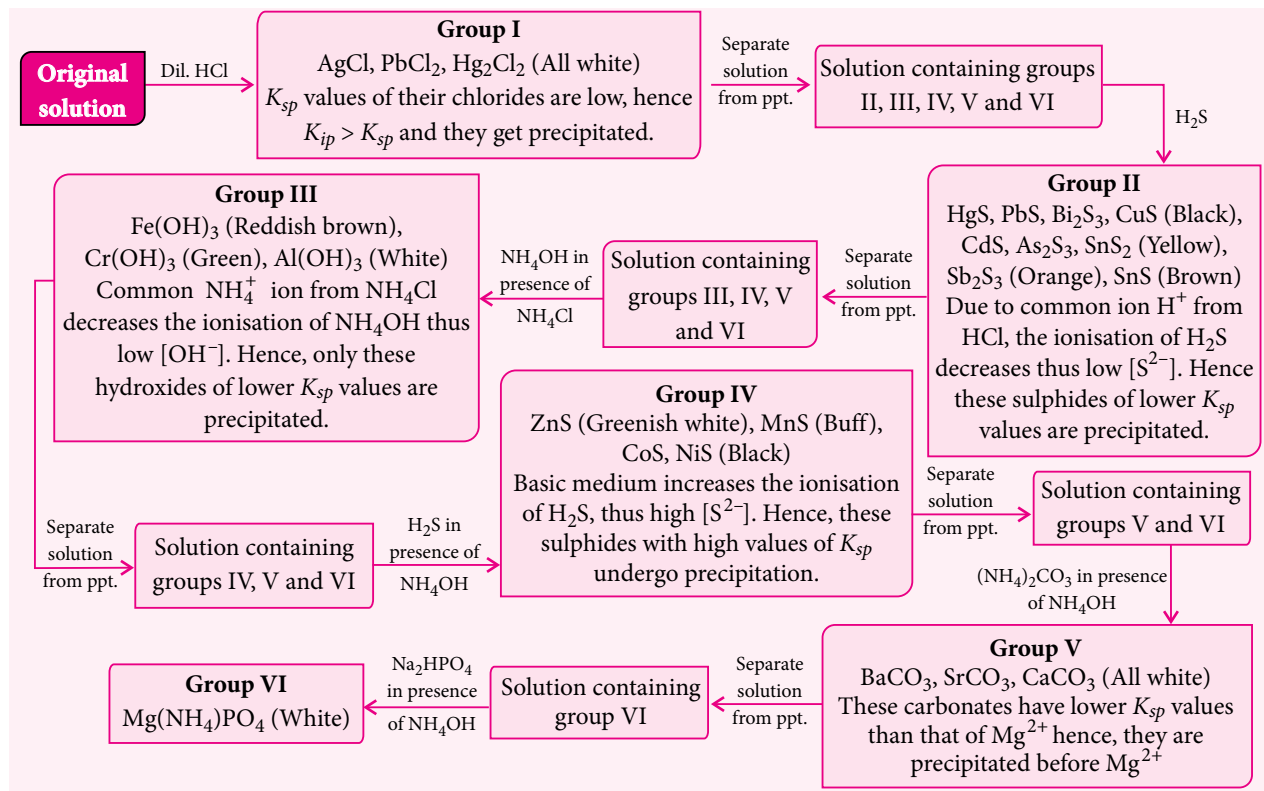
- Group III acidic radicals :** These radicals cannot be detected by either dil. H<sub>2</sub>SO<sub>4</sub> or conc. H<sub>2</sub>SO<sub>4</sub>. For detection of these acidic radicals some specific tests are required.

Radical	Observations and Reactions
Sulphate ( $\text{SO}_4^{2-}$ )	$\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \longrightarrow \text{BaSO}_4\downarrow + 2\text{NaCl}$ Salt White ppt. (insoluble in conc. $\text{HNO}_3$ )
Phosphate ( $\text{PO}_4^{3-}$ )	$\text{Ca}_3(\text{PO}_4)_2 + 6\text{HNO}_3 \longrightarrow 3\text{Ca}(\text{NO}_3)_2 + 2\text{H}_3\text{PO}_4$ Salt $\text{H}_3\text{PO}_4 + 12(\text{NH}_4)_2\text{MoO}_4 + 21\text{HNO}_3 \longrightarrow (\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3\downarrow + 21\text{NH}_4\text{NO}_3 + 12\text{H}_2\text{O}$ Ammonium molybdate Conc. Canary yellow ppt.
Borate ( $\text{BO}_3^{3-}$ )	$2\text{Na}_3\text{BO}_3 + 3\text{H}_2\text{SO}_4 \longrightarrow 3\text{Na}_2\text{SO}_4 + 2\text{H}_3\text{BO}_3$ Salt $\text{H}_3\text{BO}_3 + 3\text{C}_2\text{H}_5\text{OH} \longrightarrow (\text{C}_2\text{H}_5)_3\text{BO}_3\uparrow + 3\text{H}_2\text{O}$ Ethyl borate (burns with green edged flame)
Fluoride ( $\text{F}^-$ )	$2\text{NaF} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{F}_2$ Salt Hydrofluoric acid $\text{SiO}_2 + 2\text{H}_2\text{F}_2 \longrightarrow \text{SiF}_4 + 2\text{H}_2\text{O}$ Silica Silicon tetrafluoride $3\text{SiF}_4 + 4\text{H}_2\text{O} \longrightarrow \text{H}_4\text{SiO}_4 + 2\text{H}_2\text{SiF}_6$ Silicic acid (Gelatinous white)

**KEY POINT**

- Test for  $\text{F}^-$  ion should be performed in perfectly dry test tube, otherwise waxy white deposit will not be formed on the rod.

- During the test of  $\text{F}^-$  ion, if  $\text{HgCl}_2$  and  $\text{NH}_4\text{Cl}$  are present then they also produce a deposit under these conditions, but this deposit is crystalline in nature.

**Identification of basic radicals**


□ Confirmatory tests of basic radicals

Precipitates of	Confirmatory Tests
<b>Group I</b>	
AgCl	Dissolves in $\text{NH}_4\text{OH}$ , white ppt. of AgCl is again obtained on adding dil. $\text{HNO}_3$ . Yellow ppt. of AgI is formed on adding KI.
PbCl <sub>2</sub>	Dissolves in hot water, gives yellow ppt. of $\text{PbCrO}_4$ with $\text{K}_2\text{CrO}_4$ and yellow ppt. of $\text{PbI}_2$ with KI.
Hg <sub>2</sub> Cl <sub>2</sub>	Turns black with $\text{NH}_4\text{OH}$ . Black residue {Hg + $\text{Hg}(\text{NH}_2)\text{Cl}$ } dissolves in aqua-regia. Add stannous chloride solution to it then white ppt. is formed which turns grey.
<b>Group II A</b>	
Precipitates do not dissolve in yellow ammonium sulphide.	
HgS	Dissolves in aqua-regia, grey ppt. of Hg is obtained with $\text{SnCl}_2$ or Cu turnings.
PbS	Dissolves in dil. $\text{HNO}_3$ , white ppt. of $\text{PbSO}_4$ is obtained on adding dil. $\text{H}_2\text{SO}_4$ .
Bi <sub>2</sub> S <sub>3</sub>	Dissolves in dil. HCl, white ppt. of $\text{BiOCl}$ is obtained on adding excess of water. Black ppt. of Bi is obtained on adding $\text{Na}_2\text{SnO}_2$ solution.
CuS	Blue coloured solution is obtained on adding dil. $\text{HNO}_3$ and excess of $\text{NH}_4\text{OH}$ which gives chocolate brown ppt. of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ with $\text{K}_4[\text{Fe}(\text{CN})_6]$ .
CdS	Colourless solution is obtained on adding dil. $\text{HNO}_3$ and excess of $\text{NH}_4\text{OH}$ which gives yellow ppt. of CdS again on adding $\text{H}_2\text{S}$ .
<b>Group II B</b>	
Precipitates dissolve in yellow ammonium sulphide.	
As <sub>2</sub> S <sub>3</sub>	Insoluble sulphide, As <sub>2</sub> S <sub>5</sub> is obtained by treating with conc. HCl which gives yellow ppt. of ammonium arsenomolybdate on adding conc. $\text{HNO}_3$ and heating with ammonium molybdate.
SnS <sub>2</sub> or SnS	Filtrate of sulphide in conc. HCl is reduced to $\text{SnCl}_2$ by treating with Fe or Zn which on adding $\text{HgCl}_2$ solution initially gives white ppt. of $\text{Hg}_2\text{Cl}_2$ and finally turns to grey Hg.
Sb <sub>2</sub> S <sub>3</sub>	Filtrate of sulphide in conc. HCl gives white ppt. of $\text{SbOCl}$ on adding excess of water and orange ppt. of $\text{Sb}_2\text{S}_3$ on passing $\text{H}_2\text{S}$ gas.
<b>Group III</b>	
Fe(OH) <sub>3</sub>	Dissolves in dil. HCl, gives prussian blue solution or ppt. of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ on adding $\text{K}_4[\text{Fe}(\text{CN})_6]$ and blood red coloured $\text{Fe}(\text{CNS})_3$ on adding KCNS.
Cr(OH) <sub>3</sub>	The solution obtained on heating precipitate with NaOH and $\text{Br}_2$ water contains $\text{Na}_2\text{CrO}_4$ which gives yellow ppt. of $\text{PbCrO}_4$ on treating with acidified lead acetate solution.
Al(OH) <sub>3</sub>	Dissolves in NaOH and is again precipitated out on boiling with $\text{NH}_4\text{Cl}$ .
<b>Group IV</b>	
Soluble in conc. HCl	
ZnS	Solution ( $\text{ZnCl}_2$ ) is treated with NaOH, a white ppt. of $\text{Zn}(\text{OH})_2$ appears which dissolves in excess of NaOH and on passing $\text{H}_2\text{S}$ , white ppt. of ZnS is obtained.
MnS	Precipitate of $\text{MnO}_2$ is obtained on heating the solution with NaOH and $\text{Br}_2$ water. Pink colour of $\text{HMnO}_4$ is formed on supernatant liquid on treating the ppt. with excess of $\text{HNO}_3$ and red lead ( $\text{Pb}_3\text{O}_4$ ).
<b>Group IV</b>	
Insoluble in conc. HCl	
CoS	Dissolves in aqua-regia. Yellow ppt. of potassium cobaltnitrite $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ is obtained on adding $\text{CH}_3\text{COOH}$ in excess and $\text{KNO}_2$ .
NiS	Dissolves in aqua-regia. Red ppt. of Ni-dmg complex is obtained on adding $\text{NH}_4\text{OH}$ in excess and dimethyl glyoxime.

<b>Group V</b>	Soluble in acetic acid
BaCO <sub>3</sub>	Yellow ppt. of BaCrO <sub>4</sub> is obtained on adding K <sub>2</sub> CrO <sub>4</sub> to solution.
SrCO <sub>3</sub>	White ppt. of SrSO <sub>4</sub> is obtained on adding (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> to solution.
CaCO <sub>3</sub>	White ppt. of CaC <sub>2</sub> O <sub>4</sub> is obtained on adding (NH <sub>4</sub> ) <sub>2</sub> C <sub>2</sub> O <sub>4</sub> .
<b>Group VI</b>	
Mg <sup>2+</sup>	White ppt. of Mg(NH <sub>4</sub> )PO <sub>4</sub> is formed on adding Na <sub>2</sub> HPO <sub>4</sub> and NH <sub>4</sub> OH to solution.
<b>Zero</b>	
NH <sub>4</sub> <sup>+</sup>	Salt evolves NH <sub>3</sub> gas on heating with NaOH which gives dense white fumes of NH <sub>4</sub> Cl with HCl and a brown ppt. of H <sub>2</sub> N·HgO·HgI on adding Nessler's reagent, K <sub>2</sub> HgI <sub>4</sub> .

### KEY POINT

- NH<sub>4</sub>Cl is added in group-V to convert NH<sub>4</sub>HCO<sub>3</sub> (always contain in (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) into (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> so that Ba<sup>2+</sup>, Sr<sup>2+</sup> and Ca<sup>2+</sup> are completely precipitated.

### SELF CHECK

- An aqueous solution of a salt X turns blood red on treatment with SCN<sup>-</sup> and blue on treatment with K<sub>4</sub>[Fe(CN)<sub>6</sub>]. X also gives a positive chromyl chloride test. The salt X is
  - CuCl<sub>2</sub>
  - FeCl<sub>3</sub>
  - Cu(NO<sub>3</sub>)<sub>2</sub>
  - Fe(NO<sub>3</sub>)<sub>3</sub>
 (JEE Main 2015)
- The cation that will not be precipitated by H<sub>2</sub>S in the presence of dil. HCl is
  - Cu<sup>2+</sup>
  - Pb<sup>2+</sup>
  - As<sup>3+</sup>
  - Co<sup>2+</sup>
 (JEE Main 2015)
- Upon treatment with ammoniacal H<sub>2</sub>S, the metal ion that precipitates as a sulphide is
  - Fe(III)
  - Al(III)
  - Mg(II)
  - Zn(II)
 (JEE Advanced 2013)
- Passing H<sub>2</sub>S gas into a mixture of Mn<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Hg<sup>2+</sup> ions in an acidified aqueous solution precipitates
  - CuS and HgS
  - MnS and CuS
  - MnS and NiS
  - NiS and HgS
 (IIT-JEE 2011)

### Titrimetric Analysis

- Titrimetric or volumetric analysis is a method of finding the volume of one solution which reacts with a definite amount of another solution.

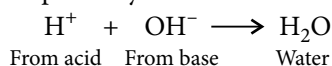
- In this process, known volume of solution of known concentration (standard solution) is allowed to react with the other solution of unknown concentration till the reaction is complete.
- Standard solution** : It is a solution of known strength.
  - Primary standard solutions* : They can be prepared directly by dissolving a known weight of the substance and making a known volume of the solution. e.g., oxalic acid, sodium carbonate, Mohr's salt.
  - Secondary standard solutions* : They cannot be prepared directly by weighing. e.g., KMnO<sub>4</sub> or hygroscopic substances like NaOH, KOH, or whose concentrations are known only approximately like HCl, H<sub>2</sub>SO<sub>4</sub>, etc.
- Titrate** : It is the substance whose concentration is to be determined by titration.
- Titrant** : It is the solution of known strength (usually taken in the burette).
- Indicator** : It is the substance which indicates the end point of titration (by change of colour).
- Equivalence point** : It is the point at which the chemical reaction involved in the titration is just complete.
- Strength of a solution** : It is the amount of solute in grams present per litre of the solution.
  - Strength (g/L) = Normality × Eq. wt.
  - Strength (g/L) = Molarity × Mol. mass
- Normality equation** :  $N_1 V_1 = N_2 V_2$   
(Solution 1) (Solution 2)
- Molarity equation** :  $M_1 V_1 n_1 = M_2 V_2 n_2$   
(Solution 1) (Solution 2)  
[∵  $N = M \times n$ , where  $n$  = valency factor]

- Percentage purity of a given salt

$$= \frac{\text{Strength of given sample}}{\text{Strength of pure sample}} \times 100$$

### Types of Titrations

- Acid-base titrations** : In acid-base titration, the strength of an acid or a base is determined by titrating it against a standard solution of base or acid respectively. It involves neutralisation reaction.



- Choice of indicators** : The choice of an indicator should be made in such a way that indicator used shows change in colour in the same pH range as developed around the equivalence point.

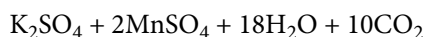
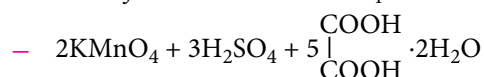
- pH range of indicators** :

Indicators	pH range	Colour of indicator	
		Acid medium	Basic medium
Methyl orange	3.1 – 4.4	Red	Orange
Bromophenol blue	3 – 4.6	Yellow	Blue
Methyl red	4.2 – 6.3	Red	Yellow
Litmus	5 – 8	Red	Blue
Bromothymol blue	6 – 7.6	Yellow	Blue
Phenol red	6.8 – 8.4	Yellow	Red
Thymolphthalein	9.3 – 10.5	Colourless	Blue
Phenolphthalein	8.3-10	Colourless	Pink

Acid	Alkali	Indicator	End point
Strong acid (HCl, H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> )	Strong alkali (NaOH, KOH)	Phenolphthalein or methyl orange	Pink to colourless or yellow/orange to red, vice versa
Weak acid (oxalic acid, acetic acid)	Strong alkali (NaOH, KOH)	Phenolphthalein	Pink to colourless, vice versa
Strong acid (HCl, H <sub>2</sub> SO <sub>4</sub> , HNO <sub>3</sub> )	Weak alkali (Na <sub>2</sub> CO <sub>3</sub> , NaHCO <sub>3</sub> , KHCO <sub>3</sub> , NH <sub>4</sub> OH)	Methyl orange	Yellow/orange to red, vice versa

- Redox titrations** : These titrations proceed with transfer of electrons among the reacting ions in aqueous solutions.

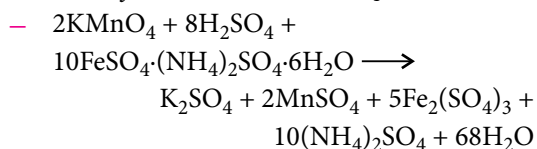
- Titration of oxalic acid vs KMnO<sub>4</sub>**



- Calculations**

$$\frac{M_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{M_{\text{oxalic acid}} \times V_{\text{oxalic acid}}} = \frac{2}{5}$$

- Titration of Mohr's salt vs KMnO<sub>4</sub>**



- Calculations**

$$\frac{M_{\text{KMnO}_4} \times V_{\text{KMnO}_4}}{M_{\text{Mohr's salt}} \times V_{\text{Mohr's salt}}} = \frac{1}{5}$$

### KEY POINT

- When the reaction is just complete the stage of titration is called equivalence point but when one extra drop is added which is utilised by indicator to show a visual change then this stage is called end point.

### PRACTICAL PHYSICAL CHEMISTRY

- Enthalpy of Solution of CuSO<sub>4</sub>
- Enthalpy of Neutralisation of Strong Acid and Strong Base
- Preparation of Lyophilic and Lyophobic Sols
- Kinetic Study of Reaction of Iodide Ion with Hydrogen Peroxide at Room Temperature

### TIPS TO REMEMBER

#### Enthalpy of Solution of CuSO<sub>4</sub>

- Enthalpy of solution is the heat change involved during the dissolution of one mole of a solute in such a large excess of solvent so that no further heat change occur on dilution.  

$$\text{CuSO}_{4(s)} + \text{H}_2\text{O} \longrightarrow \text{CuSO}_{4(aq)}; \Delta_{\text{sol}}H^\circ$$
- Dissolution of CuSO<sub>4</sub> in water is exothermic. The enthalpy of solution of CuSO<sub>4(s)</sub> is calculated from the highest temperature attained during its dissolution.

- **Calculations** : If dissolution of  $w$  g of  $\text{CuSO}_4$  in 200 g solvent (water) causes  $\Delta t^\circ\text{C}$  change in temperature, then

$$\text{Heat evolved } (q) = \text{Mass} \times \text{Specific heat} \times$$

Change in temperature

$$q = (200 + W) \times 4.2 \times \Delta t \text{ J, where } W \text{ is water equivalent of calorimeter (given).}$$

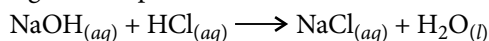
Enthalpy of solution per mole of  $\text{CuSO}_4$  in water

$$= -\frac{q \times 159.5 \times 10^{-3}}{w} \text{ kJ mol}^{-1}$$

$$[\because \text{Molar mass of } \text{CuSO}_4 = 159.5 \text{ g mol}^{-1}]$$

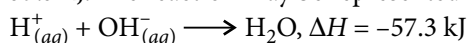
### Enthalpy of Neutralisation of Strong Acid and Strong Base

- Enthalpy of neutralisation is the enthalpy change accompanying neutralisation of one gram equivalent of a base by an acid in dilute solutions at a given temperature.



It is an exothermic reaction.

- The heat of neutralisation of a strong acid by a strong base in their dilute solutions is generally 57.3 kJ. The reaction may be represented as



- **Calculations** : Heat evolved during neutralisation of 100 mL of 0.5 N HCl,

$$q = (200 + W) \times \Delta t \times 4.2 \text{ J, where } W \text{ is water equivalent of calorimeter (given).}$$

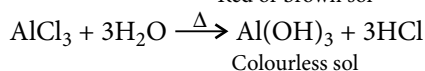
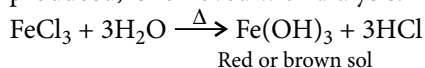
Thus, enthalpy of neutralisation of 1000 mL of

$$1 \text{ N HCl and NaOH} = -\frac{q}{0.5 \times 100} \text{ kJ}$$

### Preparation of Lyophilic and Lyophobic Sols

- **Preparation of lyophilic sols** : These sols are prepared by shaking the lyophilic material with the dispersion medium. *e.g.*, colloidal sols of gelatin, gum, starch, egg albumin, etc.

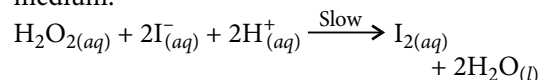
- **Preparation of lyophobic sols** : These sols do not form simply by mixing the lyophobic material with dispersion medium instead they are prepared indirectly. *e.g.*, colloidal sols of ferric hydroxide and aluminium hydroxide can be prepared by hydrolysis of  $\text{FeCl}_3$  and  $\text{AlCl}_3$  with boiled distilled water. HCl produced, is removed with dialysis.



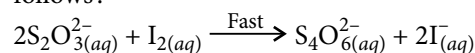
### Kinetic Study of Reaction of Iodide Ion with Hydrogen Peroxide at Room Temperature

- It is based on the principle of set of following three reactions, collectively called *clock reaction*.

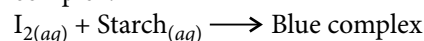
- **Main reaction** : Hydrogen peroxide oxidises iodide ion (from KI) to iodine in acidic medium.



- **Monitor reaction** : When this reaction is carried out in presence of a small amount of sodium thiosulphate and starch, the iodine produced first reacts with sodium thiosulphate as follows:



- **Indicator reaction** : When thiosulphate ions get completely consumed, the liberated iodine reacts with starch solution to give blue coloured complex.

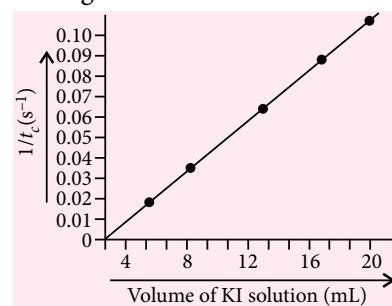


As the concentration of thiosulphate ion is kept constant, the different time taken ( $t_c$ ) for the appearance of blue colour with change in concentration of either reactant indicates the relative rate of reaction.

$$\text{Initial rate} \propto \frac{1}{t_c}$$

The rate of reaction decreases with decrease in concentration of KI.

The graph of  $1/t_c$  versus volume of KI solution is a straight line.



Rate of reaction  $\propto$  Concentration of KI

Similarly, by keeping  $\text{I}^-$  ion concentration constant and taking different concentrations of  $\text{H}_2\text{O}_2$ , the rate with respect to  $\text{H}_2\text{O}_2$  can be found out.

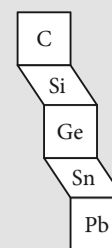
### ANSWER KEYS (SELF CHECK)

1. (d) 2. (d) 3. (b) 4. (d) 5. (d)  
6. (a)





# THE *p*-BLOCK ELEMENTS (Group 14)

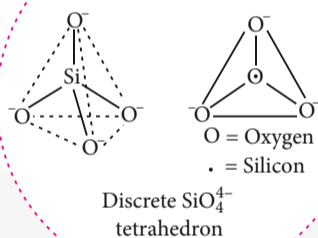


Group 14 elements show a pronounced discontinuity in their general properties between the first and second row elements followed by a gradual transition towards more metallic character.

## GROUP 14: THE CARBON FAMILY

### Atomic and Physical Properties

- **Elements:** C, Si, Ge, Sn, Pb
- **Electronic configuration:** [Noble gas]  $ns^2np^2$
- **Oxidation states:** +2 and +4
- **Atomic radii, metallic character and stability of +2 O.S.:** Generally increase down the group.
- **Ionisation enthalpy, melting point, boiling point, reducing character and stability of +4 O.S.:** Generally decrease down the group.
  - *IE* of Pb is slightly higher than Sn due to lanthanide contraction.
  - *IE*<sub>1</sub> and *IE*<sub>2</sub> are higher and lower than the corresponding group 13 elements respectively.
- **Catenation:** Tendency of catenation decreases down the group.
- **Allotropy:** Except Pb, all others show allotropy.
- **Complex formation:** Except C, all other form complexes due to presence of vacant *d*-orbitals.

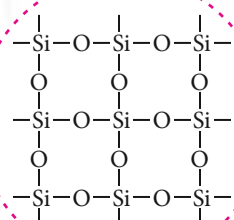


### Silicates

- Basic unit is  $\text{SiO}_4^{4-}$ .
- They exist either as discrete unit or joined together by sharing 1, 2, 3 or 4 oxygen atoms per silicate unit to form different structures like chain, ring, sheet or 3-D network.
- Zeolites are 3-D silicates in which some of the Si atoms are replaced by  $\text{Al}^{3+}$  ions and to balance the negative charge some cations like  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Ca}^{2+}$  are incorporated. They are used in water softening.

### Silicon Dioxide ( $\text{SiO}_2$ )

- Covalent, three dimensional network solid.
- Almost non-reactive due to high Si - O bond enthalpy.



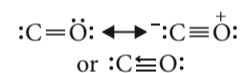
### Chemical Properties

- **Reactivity towards air:**
  - They form oxides of the formula  $\text{EO}$  and  $\text{EO}_2$  on heating with air.
  - Acidic strength of their oxides decreases down the group.
 

$\text{CO}_2, \text{SiO}_2$	$\text{GeO}_2$	$\text{SnO}_2, \text{PbO}_2$
Acidic	Less acidic	Amphoteric
- **Reactivity towards water:**
  - Only Sn can decompose water.  
 $\text{Sn} + 2\text{H}_2\text{O} \xrightarrow{\Delta} \text{SnO}_2 + 2\text{H}_2$
  - Pb is unaffected by water due to formation of protective oxide film.
- **Reactivity towards halogens:**
  - They form halides of the formula  $\text{EX}_4$  and  $\text{EX}_2$ .
  - Except C, all react directly with halogens.
  - Except C and Si, all form dihalides.

### Anomalous Behaviour of C

- The anomalous behaviour of C is due to small size, high ionisation energy and absence of *d*-orbitals.
- C is hardest having highest m.pt. and b.pt. amongst the elements of group 14.
- C shows maximum covalency of 4 while rest show maximum covalency of 6.
- C has maximum tendency for catenation and multiple bonding ( $p\pi-p\pi$ ) and shows allotropy.



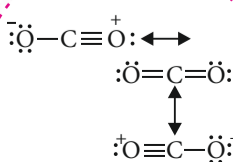
### Important Compounds of C and Si

### Carbon Monoxide (CO)

- **Preparation:**
  - $\text{C} + \text{H}_2\text{O} \longrightarrow \text{CO} + \text{H}_2$   
Water gas
  - $2\text{C} + \text{O}_2 + 4\text{N}_2 \xrightarrow{1273\text{ K}} 2\text{CO} + 4\text{N}_2$   
Producer gas
- Highly poisonous due to the formation of a complex with haemoglobin (Hb) which is 300 times more stable than  $\text{O}_2\text{-Hb}$  complex thus, prevents Hb in the RBCs from carrying  $\text{O}_2$  round the body.

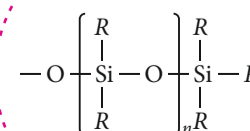
### Carbon Dioxide ( $\text{CO}_2$ )

- **Preparation:**
  - $\text{CaCO}_3 + 2\text{HCl} \longrightarrow \text{CaCl}_2 + \text{CO}_2 + \text{H}_2\text{O}$
  - It is consumed during photosynthesis.  
 $6\text{CO}_2 + 12\text{H}_2\text{O} \xrightarrow{h\nu} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 + 6\text{H}_2\text{O}$



### Silicones

- Synthetic organosilicon polymers containing repeated  $\text{R}_2\text{SiO}$  units held by Si - O - Si linkage.
- They are water repelling due to non-polar alkyl groups.



# Exam Café

## QUESTIONS FOR PRACTICE

- Which of the following compounds is responsible for yellow colour in the xanthate test for alcoholic group?
 

(a)  $\text{RO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}^-\text{K}^+$  (b)  $\text{RO}-\overset{\text{S}}{\parallel}{\text{C}}-\text{S}^-\text{K}^+$

(c)  $\text{RO}-\overset{\text{S}}{\parallel}{\text{C}}-\text{SR}$  (d)  $\text{RO}-\overset{\text{S}}{\parallel}{\text{C}}-\text{OR}$
- Radical that gives rosy red ppt. with DMG is
 

(a)  $\text{Cd}^{2+}$  (b)  $\text{Ni}^{2+}$

(c)  $\text{Mn}^{2+}$  (d)  $\text{Ba}^{2+}$
- In the green edged flame test for borate, the flame is green only on the edges because
 

(a) edges represent hottest part of flame where combustion of ethyl borate is complete

(b) it is characteristic property of ethyl borate

(c) ethyl borate vapourises only on the edges

(d) ethyl borate decomposes only on the edges.
- The number of moles of  $\text{KMnO}_4$  needed to react completely with one mole of ferrous oxalate in acidic solution is
 

(a)  $\frac{3}{5}$  (b)  $\frac{2}{5}$

(c)  $\frac{4}{5}$  (d) 1
- Identify the correct order of solubility of  $\text{Na}_2\text{S}$ ,  $\text{CuS}$  and  $\text{ZnS}$  in aqueous medium.
 

(a)  $\text{CuS} > \text{ZnS} > \text{Na}_2\text{S}$  (b)  $\text{ZnS} > \text{Na}_2\text{S} > \text{CuS}$

(c)  $\text{Na}_2\text{S} > \text{CuS} > \text{ZnS}$  (d)  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$
- Before testing for halogens, the Lassaigne's extract is boiled with
 

(a) conc.  $\text{HCl}$  (b)  $\text{NaOH}$

(c) conc.  $\text{HNO}_3$  (d) all of these.
- A student is given a solution which may contain carbonate ions. She decides to add aqueous barium nitrate to the solution first, followed by dilute nitric acid. Choose the correct statements about her experiment.
 

(a) Dilute nitric acid reacts with both soluble and insoluble carbonates.

(b) The above procedure is strictly to test the presence of sulphate ions only.

(c) The unknown compound will only react with dilute nitric acid and not with barium nitrate.

(d) The acid must be added directly to the solution to test the presence of carbonates.
- In Lassaigne's test, organic compound is fused with a piece of sodium metal so as to
 

(a) convert the covalent compound into a mixture of ionic compounds

(b) decrease the melting point of the compound

(c) increase the reactivity of the compound

(d) increase the ionisation of the compound.
- Which salt would give  $\text{SO}_2$  with hot and dilute  $\text{H}_2\text{SO}_4$  and also decolourise  $\text{Br}_2$  water?
 

(a)  $\text{Na}_2\text{SO}_3$  (b)  $\text{NaHSO}_4$

(c)  $\text{Na}_2\text{SO}_4$  (d)  $\text{Na}_2\text{S}$
- An excess of sodium hydroxide is added to an aqueous solution of salt X and boiled. Ammonia gas is only given off after aluminium foil is added to the hot solution. What could be X?
 

(a) Sodium nitrate (b) Ammonium nitrate

(c) Calcium sulphate (d) Barium nitrate
- $\text{H}_2\text{S}$  in the presence of  $\text{HCl}$  precipitates group II but not group IV because
 

(a)  $\text{HCl}$  activates  $\text{H}_2\text{S}$

(b)  $\text{HCl}$  increases concentration of  $\text{Cl}^-$

(c)  $\text{HCl}$  decreases concentration of  $\text{S}^{2-}$

(d)  $\text{HCl}$  lowers the solubility of  $\text{H}_2\text{S}$  in solution.
- Sodium carbonate cannot be used in place of  $(\text{NH}_4)_2\text{CO}_3$  for the identification of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$  and  $\text{Sr}^{2+}$  ions (in group V) during mixture analysis because
 

(a)  $\text{Mg}^{2+}$  ions will be precipitated

(b) concentration of  $\text{CO}_3^{2-}$  ions is very low

(c) sodium ions will react with acid radicals

(d)  $\text{Na}^+$  ions will interfere with the detection of  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  ions.
- To perform azo dye test, the organic compounds needed are
 

(a)  $1^\circ$  aliphatic amine and  $\text{CHCl}_3$

(b)  $1^\circ$  aromatic amine and 2-naphthol

(c) phenol and aniline

(d) both (b) and (c).



27. A test tube containing nitrate and another containing bromide and  $\text{MnO}_2$  are treated with conc.  $\text{H}_2\text{SO}_4$ . The brown fumes evolved are passed in water. The water will be coloured by  
 (a) the nitrate (b) the bromide  
 (c) both of these (d) none of these.
28. Salt which does not respond to dilute and concentrated sulphuric acid is  
 (a)  $\text{Na}_2\text{SO}_4$  (b)  $\text{Na}_3\text{PO}_4$   
 (c)  $\text{CaF}_2$  (d) all of these.
29. How do we differentiate between  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  in qualitative analysis of group III?  
 (a) By taking excess of  $\text{NH}_4\text{OH}$ .  
 (b) By increasing  $\text{NH}_4^+$  ion concentration.  
 (c) By decreasing  $\text{OH}^-$  ion concentration.  
 (d) Both (b) and (c)
30. In a charcoal cavity test in an oxidising flame (using cobalt nitrate), salts of aluminium, zinc and magnesium produce residues of specific colour. Which of the following gives the correct match of the composition and colour of the residue?  
 (a)  $\text{CoAl}_2\text{O}_4 \rightarrow$  Thenard's blue  
 (b)  $\text{CoZnO}_2 \rightarrow$  Rinnmann's green  
 (c)  $\text{CoMgO}_2 \rightarrow$  Pale pink  
 (d) All of these

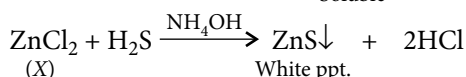
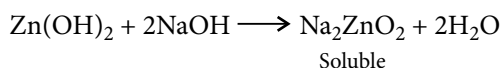
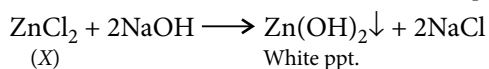
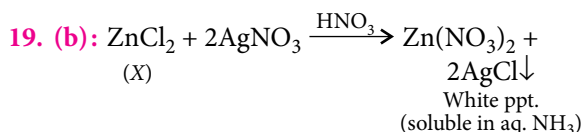
### SOLUTIONS

1. (b):  $\text{ROH} + \text{KOH} \rightarrow \text{RO}^- \text{K}^+ + \text{H}_2\text{O}$
- $$\text{RO}^- \text{K}^+ + \text{CS}_2 \xrightarrow{\Delta} \text{R}-\text{O}-\overset{\text{S}^- \text{K}^+}{\underset{\text{S}}{\text{C}}}$$
- Xanthate  
(yellow ppt.)
2. (b):  $\text{Ni}^{2+}$  in presence of ammonia gives rosy red ppt. of bis(dimethylglyoximate)nickel(II) complex.
- $$\text{NiCl}_2 + 2\text{NH}_4\text{OH} + 2 \begin{array}{c} \text{CH}_3-\text{C}=\text{NOH} \\ | \\ \text{CH}_3-\text{C}=\text{NOH} \\ \text{Dimethylglyoxime} \end{array}$$
- $$\downarrow$$
- $$\begin{array}{c} \text{OH} \\ | \\ \text{CH}_3-\text{C}=\text{N} \rightarrow \text{Ni} \leftarrow \text{N}=\text{C}-\text{CH}_3 \\ | \quad \quad \quad | \\ \text{CH}_3-\text{C}=\text{N} \rightarrow \quad \quad \quad \leftarrow \text{N}=\text{C}-\text{CH}_3 \\ | \quad \quad \quad | \\ \text{O} \quad \quad \quad \text{OH} \end{array}$$
- Bright red complex (ppt.)
- $$+ 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$$

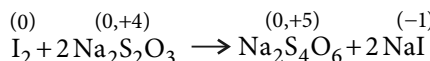
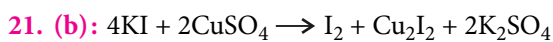
3. (a)

4. (a):  $\text{FeC}_2\text{O}_4 \xrightarrow{+2} \text{Fe}^{3+} + 2\text{CO}_2 + 3e^-$   
 In acidic medium,  $\text{MnO}_4^-$  changes to  $\text{Mn}^{2+}$  and consumes  $5e^-$ .  
 $\therefore 3e^-$  will be consumed by 3/5 moles of  $\text{KMnO}_4$ .
5. (d):  $\text{Na}_2\text{S}$  is strongly electrovalent. Copper belongs to group II and precipitates first as  $\text{CuS}$  (black) whereas zinc belongs to group IV and precipitates later as  $\text{ZnS}$  (greenish white), hence solubility order is  $\text{Na}_2\text{S} > \text{ZnS} > \text{CuS}$ .
6. (c): Lassaigne's extract is boiled with conc.  $\text{HNO}_3$  to decompose  $\text{Na}_2\text{S}$  and  $\text{NaCN}$  which would otherwise interfere with the tests of halogens.  $\text{HCl}$  cannot be used because we cannot add  $\text{Cl}^-$  ion when we have to test for  $\text{Cl}$  in the organic compound.  $\text{NaOH}$  also cannot be used because it would precipitate  $\text{AgNO}_3$  as  $\text{AgOH}$ .
7. (a): When barium nitrate is added, a white precipitate of barium carbonate is formed. This precipitate reacts with dilute nitric acid added, to produce effervescence with the liberation of  $\text{CO}_2$  gas.  
 $\text{Ba}^{2+}_{(aq)} + \text{CO}_3^{2-}_{(aq)} \rightarrow \text{BaCO}_{3(s)}$   
 $\text{BaCO}_{3(s)} + 2\text{H}^+_{(aq)} \rightarrow \text{Ba}^{2+}_{(aq)} + \text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)}$
8. (a): This is done to get a mixture of ionic compounds such as  $\text{NaCN}$ ,  $\text{Na}_2\text{S}$ ,  $\text{NaX}$ , etc.
9. (a):  $\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2$   
 $\text{Na}_2\text{SO}_3 + \text{Br}_2 + \text{H}_2\text{O} \rightarrow 2\text{HBr} + \text{Na}_2\text{SO}_4$
10. (a): This is a specific test for nitrate ions ( $\text{NO}_3^-$ ). If ammonia is evolved before the aluminium foil, then salt  $X$  contains ammonium ions. Since ammonia is only liberated when heated with aluminium foil, the presence of nitrate ions is confirmed.
11. (c): Due to common ion effect,  $\text{HCl}$  decreases concentration of  $\text{S}^{2-}$  ions and only group II basic radicals are precipitated.
12. (a): In group V,  $(\text{NH}_4)_2\text{CO}_3$  is used in the presence of  $\text{NH}_4\text{Cl}$ . In presence of  $\text{NH}_4\text{Cl}$  dissociation of  $(\text{NH}_4)_2\text{CO}_3$  decreases and due to low concentration of  $\text{CO}_3^{2-}$  ions only group V radicals are precipitated out. If  $\text{Na}_2\text{CO}_3$  is used, concentration of  $\text{CO}_3^{2-}$  ions will increase and group VI radical,  $\text{Mg}^{2+}$  ions will also be precipitated.
13. (d)
14. (b):  $\text{ZnCO}_3 \xrightarrow{\Delta} \text{ZnO} + \text{CO}_2 \uparrow$   
 It is an example of decomposition reaction. Colour of zinc oxide product is yellow when hot and white when cold.

15. (b)
16. (c): Radicals such as  $\text{NO}_3^-$  oxidise  $\text{H}_2\text{S}$  to S which appears as yellow turbidity.
17. (a): Both  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions form coloured precipitates of metal hydroxides *i.e.*, dirty green  $\text{Fe}(\text{OH})_2$  and reddish brown  $\text{Fe}(\text{OH})_3$ . Ion with the lower oxidation number,  $\text{Fe}^{2+}$  changes the colour on standing.
18. (a):  $\text{H}_2\text{SO}_4$  and  $\text{NaOH}$  are strong acid and strong base.  $\text{HCl}$  and  $\text{NaOH}$  are also strong acid and strong base. Hence, their enthalpies of neutralisation are same.



20. (a): A brown ppt. of hydrated  $\text{MnO}_2$  will be formed, if insufficient quantity of dil.  $\text{H}_2\text{SO}_4$  is added or  $\text{H}_2\text{SO}_4$  is not added at all in the titration process. This is due to incomplete reduction of  $\text{KMnO}_4$ .



22. (b):  $N_{\text{NaOH}} = 1 \text{ N}$  ( $\because 40 \text{ g/L} \equiv 1 \text{ N NaOH}$ )

$$N_1 V_1(\text{acid}) = N_2 V_2(\text{NaOH})$$

$$N_1 \times 100 = 1 \times 95$$

$$N_1 = 0.95 \text{ N}$$

$$N = \frac{w_B \times 1000}{E_B \times V}$$

$$0.95 = \frac{39 \times 1000}{E_B \times 1000}$$

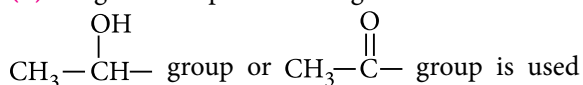
$$E_B = 41$$

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{\text{Basicity}}$$

$$41 = \frac{82}{\text{Basicity}}$$

or, Basicity = 2

23. (d): Organic compound having either

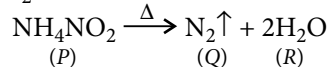
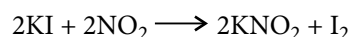


for the preparation of iodoform. Propan-1-ol,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  does not contain such groups.

24. (d):  $\text{Fe}(\text{OH})_3$  sol is prepared by shaking  $\text{FeCl}_3$  with boiling water.

25. (c)

26. (b): When ammonium nitrite (P) treated with dil.  $\text{H}_2\text{SO}_4$  gives light brown fumes of  $\text{NO}_2$ . The light brown gas ( $\text{NO}_2$ ) decomposes iodides to free iodine which when treated with starch solution gives blue colour.



27. (b):  $\text{NO}_3^-$  gives  $\text{NO}_2$  with conc.  $\text{H}_2\text{SO}_4$  which when passed through water gives  $\text{HNO}_3$  which is colourless. On the other hand,  $\text{Br}^- + \text{MnO}_2$  on heating with conc.  $\text{H}_2\text{SO}_4$  gives  $\text{Br}_2$  which gives its colour (orange) to water when added to it.

28. (d): Salts of sulphate, phosphate, fluoride and borate do not respond to dilute and concentrated sulphuric acid.

29. (d):  $K_{sp}$  of  $\text{Fe}(\text{OH})_3 < K_{sp}$  of  $\text{Cr}(\text{OH})_3$ . Thus,  $\text{Fe}^{3+}$  is precipitated at lower  $\text{OH}^-$  concentration.

30. (d)



#### Form IV

- |   |   |
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I, Mahabir Singh, here by declare that particulars given above are true to the best of my knowledge and belief.

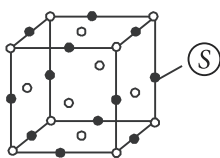
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# PRACTICE PAPER 2016

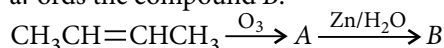
# JEE MAIN

Exam Dates  
OFFLINE : 3<sup>rd</sup> April  
ONLINE : 9<sup>th</sup> & 10<sup>th</sup> April

- Indicate the organic structure for product expected when 2-methylpropene is heated with acetyl chloride in the presence of anhydrous  $\text{ZnCl}_2$ .
  - $$\begin{array}{c} \text{CH}_3-\text{C}-\text{C}=\text{CH}_2 \\ \parallel \quad | \\ \text{O} \quad \text{CH}_3 \end{array}$$
  - $$\begin{array}{c} \text{CH}_3-\text{C}-\text{C}-\text{CH}_3 \\ \parallel \quad | \\ \text{O} \quad \text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$$
  - $$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2\text{COCH}_3 \\ | \\ \text{Cl} \\ | \\ \text{H} \end{array}$$
  - $$\begin{array}{c} \text{CH}_3-\text{C}-\text{CH}_2\text{COCH}_3 \\ | \\ \text{CH}_3 \end{array}$$
- Phospholipids are esters of glycerol with
  - three carboxylic acid residues
  - two carboxylic acid residues and one phosphate group
  - one carboxylic acid residue and two phosphate groups
  - three phosphate groups.
- Which of the following alkali metal ions has the highest conductivity in aqueous solution?
  - $\text{Li}^+$
  - $\text{Cs}^+$
  - $\text{Na}^+$
  - $\text{K}^+$
- In order to convert aniline into chlorobenzene, the reagent used is
  - $\text{NaNO}_2/\text{HCl}$ ,  $\text{CuCl}$
  - $\text{Cl}_2/\text{CCl}_4$
  - $\text{Cl}_2/\text{AlCl}_3$
  - $\text{CuCl}_2$
- For the given structure, the site marked as S is a
  - tetrahedral void
  - cubic void
  - octahedral void
  - none of these.
- Which one of the following cyano complexes would exhibit the lowest value of paramagnetic behaviour?
  - $[\text{Cr}(\text{CN})_6]^{3-}$
  - $[\text{Mn}(\text{CN})_6]^{3-}$
  - $[\text{Fe}(\text{CN})_6]^{3-}$
  - $[\text{Co}(\text{CN})_6]^{3-}$
- If the nitrogen atom has electronic configuration  $1s^7$ , it would have energy lower than that of the normal ground state configuration  $1s^2 2s^2 2p^3$ , because the electrons would be closer to the nucleus. Yet,  $1s^7$  is not observed because it violates
  - Heisenberg uncertainty principle
  - Hund's rule
  - Pauli's exclusion principle
  - Bohr's postulates of stationary orbits.
- Amoxicillin is semi-synthetic modification of
  - penicillin
  - streptomycin
  - tetracycline
  - chloramphenicol.
- The decreasing order of the ionisation potential of the following elements is
  - $\text{Ne} > \text{Cl} > \text{P} > \text{S} > \text{Al} > \text{Mg}$
  - $\text{Ne} > \text{Cl} > \text{P} > \text{S} > \text{Mg} > \text{Al}$
  - $\text{Ne} > \text{Cl} > \text{S} > \text{P} > \text{Mg} > \text{Al}$
  - $\text{Ne} > \text{Cl} > \text{S} > \text{P} > \text{Al} > \text{Mg}$
- Which of the following factors is of no significance for roasting sulphide ores to the oxides and not subjecting the sulphide ores to carbon reduction directly?
  - $\text{CO}_2$  is more volatile than  $\text{CS}_2$ .
  - Metal sulphides are thermodynamically more stable than  $\text{CS}_2$ .
  - $\text{CO}_2$  is thermodynamically more stable than  $\text{CS}_2$ .
  - Metal sulphides are less stable than the corresponding oxides.

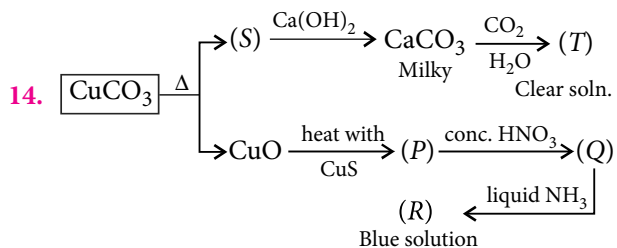


11. In the following sequence of reactions, the alkene affords the compound B.



The compound B is

- (a)  $\text{CH}_3\text{CHO}$  (b)  $\text{CH}_3\text{CH}_2\text{CHO}$   
 (c)  $\text{CH}_3\text{COCH}_3$  (d)  $\text{CH}_3\text{CH}_2\text{COCH}_3$
12. The volume of a colloidal particle,  $V_c$  as compared to the volume of a solute particle in a true solution  $V_s$  could be
- (a)  $\sim 1$  (b)  $\sim 10^{23}$   
 (c)  $\sim 10^{-3}$  (d)  $\sim 10^3$
13. The isomeric *cis*-but-2-ene and *trans*-but-2-ene can be distinguished on the basis of
- (a) their physical states  
 (b) their reduction products  
 (c) the products they give on ozonolysis  
 (d) the products they give on addition of bromine.



Identify P, R, S and T

- | P                         | R                                 | S                           | T                                 |
|---------------------------|-----------------------------------|-----------------------------|-----------------------------------|
| (a) Cu                    | $\text{CO}_2$                     | $\text{Ca}(\text{HCO}_3)_2$ | $[\text{Cu}(\text{NO}_3)_4]^{2+}$ |
| (b) $\text{Cu}_2\text{S}$ | Cu                                | $\text{Cu}_2\text{O}$       | $\text{Ca}(\text{HCO}_3)_2$       |
| (c) Cu                    | $[\text{Cu}(\text{NH}_3)_4]^{2+}$ | $\text{CO}_2$               | $\text{Ca}(\text{HCO}_3)_2$       |
| (d) $\text{CO}_2$         | $[\text{Cu}(\text{NO}_3)_4]^{2+}$ | $\text{Cu}_2\text{O}$       | $\text{Ca}(\text{HCO}_3)_2$       |

15. Which of the following has  $p\pi-d\pi$  bonding?
- (a)  $\text{NO}_3^-$  (b)  $\text{SO}_3^{2-}$   
 (c)  $\text{BO}_3^{3-}$  (d)  $\text{CO}_3^{2-}$
16. The degree of hardness of water is usually expressed in terms of
- (a) parts per million by weight of  $\text{MgSO}_4$   
 (b) grams per litre of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  actually present  
 (c) parts per million by weight of  $\text{CaCO}_3$  regardless of whether it is actually present  
 (d) parts per million of  $\text{CaCO}_3$  actually present in water.
17. The emf of a Daniell cell at 298 K is  $E_1$   
 $\text{Zn} | \text{ZnSO}_4(0.01 \text{ M}) || \text{CuSO}_4(1.0 \text{ M}) | \text{Cu}$   
 When the concentration of  $\text{ZnSO}_4$  is 1.0 M and that of  $\text{CuSO}_4$  is 0.01 M, the emf is changed to  $E_2$ .

What is the relationship between  $E_1$  and  $E_2$ ?

- (a)  $E_2 = 0 \approx E_1$  (b)  $E_1 > E_2$   
 (c)  $E_1 < E_2$  (d)  $E_1 = E_2$

18. Which of the following does not have optical isomer?
- (a)  $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$  (b)  $[\text{Co}(\text{en})_3]\text{Cl}_3$   
 (c)  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  (d)  $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]\text{Cl}$

19. 29.5 mg of an organic compound containing nitrogen was digested according to Kjeldahl's method and the evolved ammonia was absorbed in 20 mL of 0.1 M HCl solution. The excess of the acid required 15 mL of 0.1 M NaOH solution for complete neutralisation. The percentage of nitrogen in the compound is

- (a) 29.5 (b) 59.0  
 (c) 47.4 (d) 23.7

20. The basic character of the transition metal monoxides follows the order

- (a)  $\text{VO} > \text{CrO} > \text{TiO} > \text{FeO}$   
 (b)  $\text{CrO} > \text{VO} > \text{FeO} > \text{TiO}$   
 (c)  $\text{TiO} > \text{FeO} > \text{VO} > \text{CrO}$   
 (d)  $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$

21. Match list I (compounds) with list II (uses) and select the correct answer using the code given below the lists :

**List I**

- i. Acetyl salicylic acid  
 ii. DDT  
 iii. Naphthalene  
 iv. Carbon tetrachloride

**List II**

- (A) Insecticide  
 (B) Drug  
 (C) Moth repelling  
 (D) Fire extinguisher  
 (E) Refrigerant

- (a) i-(B), ii-(A), iii-(C), iv-(D)  
 (b) i-(E), ii-(C), iii-(D), iv-(A)  
 (c) i-(B), ii-(C), iii-(D), iv-(A)  
 (d) i-(E), ii-(A), iii-(C), iv-(D)

22. A welding fuel gas contains carbon and hydrogen only. Burning a small sample of it in oxygen gives 3.38 g carbon dioxide, 0.690 g of water and no other products. A volume of 10.0 L (measured at STP) of this welding gas is found to weigh 11.6 g. The molecular formula of gas is

- (a)  $\text{C}_2\text{H}_2$  (b)  $\text{CH}_4$   
 (c)  $\text{C}_2\text{H}_4$  (d)  $\text{C}_2\text{H}_6$



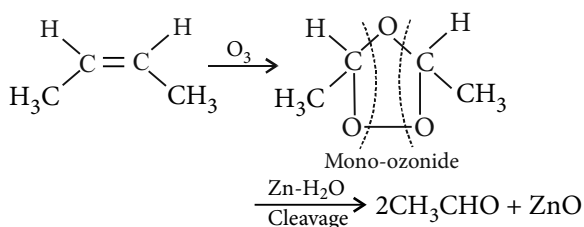


There is no unpaired electron, so the lowest value of paramagnetic behaviour is observed.

7. (c): According to Pauli's exclusion principle an orbital can accommodate a maximum of two electrons.
8. (a): Amoxicillin (an antibiotic) is semi-synthetic modification of penicillin.
9. (b): Ionisation energy increases from left to right in a period but ionisation energy of group-2 is greater than ionisation energy of group-13 and ionisation energy of group-15 is greater than ionisation energy of group-16.

This is because of stable electronic configuration of group 2 ( $ns^2$ ) and group 15 ( $ns^2np^3$ ). Thus, order of ionisation potential is  $Ne > Cl > P > S > Mg > Al$ .

10. (d): The reduction process of metal sulphides by carbon is non-spontaneous while the reduction process of metal oxides by carbon is spontaneous. Thus, it can be concluded that  $CO_2$  is thermodynamically more stable than  $CS_2$  and the metal sulphides are more stable than the corresponding oxides.
11. (a): The complete reaction sequence is as follows :



12. (d): For true solution the diameter range is 1 to  $10 \text{ \AA}$  and for colloidal solution diameter range is 10 to  $1000 \text{ \AA}$ .

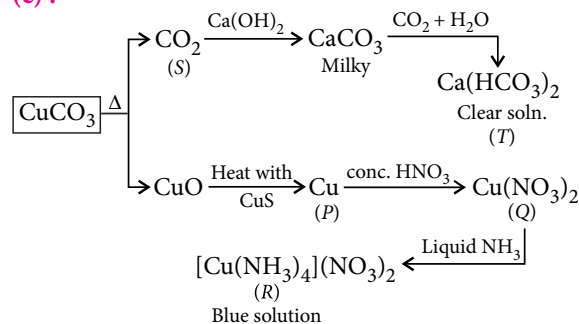
$$\frac{V_c}{V_s} = \frac{(4/3)\pi r_c^3}{(4/3)\pi r_s^3} = \left(\frac{r_c}{r_s}\right)^3$$

$$\text{Ratio of diameters} = \left(\frac{10}{1}\right)^3 = 10^3$$

$$\frac{V_c}{V_s} \approx 10^3$$

13. (d): *cis*-but-2-ene yields racemic mixture whereas *trans*-but-2-ene gives the meso compound on addition of bromine.

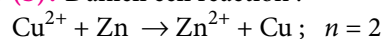
14. (c):



15. (b): In  $SO_3^{2-}$ , *d*-orbital of sulphur overlaps with *p*-orbital of oxygen to form  $p\pi-d\pi$  bond. N, B and C do not have *d*-orbitals.

16. (c): Degree of hardness of water is expressed in terms of parts per million by weight of  $CaCO_3$  equivalent to various calcium and magnesium salts present.

17. (b): Daniell cell reaction :



$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$E_1 = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{0.01}{1.0},$$

$$E_2 = E_{\text{cell}}^\circ - \frac{0.0591}{2} \log \frac{1.0}{0.01}$$

On increasing  $[\text{Zn}^{2+}]$  and decreasing  $[\text{Cu}^{2+}]$ ,  $E_2$  becomes less than  $E_1$  i.e.,  $E_1 > E_2$ .

18. (a): Octahedral complexes of type  $[MA_3B_3]$  does not show optical isomerism.

19. (d): The % of N according to Kjeldahl's method

$$= \frac{1.4 \times N_1 \times V}{w}$$

$N_1$  = Normality of the standard acid = 0.1 N

$w$  = Mass of the organic compound taken

$$= 29.5 \text{ mg} = 29.5 \times 10^{-3} \text{ g}$$

$V$  = Volume of  $N_1$  acid neutralised by ammonia

$$= (20 - 15) = 5 \text{ mL}$$

$$\Rightarrow \%N = \frac{1.4 \times 0.1 \times 5}{29.5 \times 10^{-3}} = 23.7$$

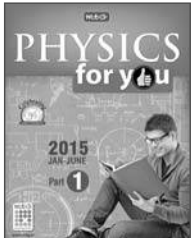
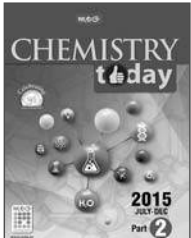
20. (d): Metal oxide with more ionic character will be more basic. Ionic radii of metal ion decreases from  $Ti^{2+}$  to  $Fe^{2+}$ , the basic character of their metal oxides decrease from  $TiO$  to  $FeO$ . Thus, order of basic character is  $TiO > VO > CrO > FeO$ .

21. (a): Acetyl salicylic acid - Drug  
DDT - Insecticide  
Naphthalene - Moth repelling  
Carbon tetrachloride - Fire extinguisher
22. (a): Number of moles of  $\text{CO}_2 = \frac{3.38}{44} = 0.0768$   
No. of moles of C = 0.0768  
No. of moles of  $\text{H}_2\text{O} = \frac{0.690}{18} = 0.0383$   
 $\therefore$  No. of moles of H =  $2 \times 0.0383 = 0.0766$   
(i) The ratio of moles of C to H is 0.0768 : 0.0766  
or 1 : 1  
Therefore, empirical formula = CH  
(ii) 10.0 L of fuel gas at STP weighs  
 $= \frac{11.6 \times 22.4}{10} = 25.98 \text{ g}$   
 $\therefore$  Molar mass of gas =  $25.98 \text{ g} \approx 26 \text{ g mol}^{-1}$   
(iii)  $n = \frac{\text{molar mass}}{\text{empirical formula mass}} = \frac{26}{13} = 2$   
 $\therefore$  Molecular formula = (empirical formula)<sub>n</sub>  
 $= (\text{CH})_2 = \text{C}_2\text{H}_2$
23. (d):  $\frac{p^\circ - p_s}{p_s} = \frac{n}{N}$   
 $\frac{760 - p_s}{p_s} = \frac{18/180}{178.2/18} = \frac{1}{9.9}$   
 $\Rightarrow 760 - p_s = \frac{1}{99} p_s \Rightarrow 760 \times 99 - 99 p_s = p_s$   
 $\Rightarrow 100 p_s = 760 \times 99$   
 $\Rightarrow p_s = \frac{760 \times 99}{100} = 752.4 \text{ torr}$

24. (b): Interhalogen compounds are covalent compounds. Since chlorine has higher electronegativity than iodine, iodine monochloride can be represented as  $\text{I}^{\delta+}\text{Cl}^{\delta-}$ .
25. (a):  $2\text{BrCl}_{(g)} \rightleftharpoons \text{Br}_{2(g)} + \text{Cl}_{2(g)}$   
Initial  $3.30 \times 10^{-3} \text{ mol L}^{-1}$       0      0  
At eq.  $(3.30 \times 10^{-3} - x)$        $\frac{x}{2}$        $\frac{x}{2}$   
 $K_c = \frac{(x/2)(x/2)}{(3.30 \times 10^{-3} - x)^2} = 32$  (Given)  
or  $\frac{x}{2(3.30 \times 10^{-3} - x)} = \sqrt{32} = 5.66$   
or  $x = 11.32(3.30 \times 10^{-3} - x)$   
or  $12.32x = 11.32 \times 3.30 \times 10^{-3}$   
or  $x = 3.0 \times 10^{-3}$   
 $\therefore$  At eq.,  $[\text{BrCl}] = (3.30 \times 10^{-3} - 3.0 \times 10^{-3})$   
 $= 0.30 \times 10^{-3}$   
 $= 3.0 \times 10^{-4} \text{ mol L}^{-1}$
26. (a): Colourless fumes of HCl become greenish yellow because  $\text{MnO}_2$  oxidises HCl to chlorine gas.
27. (b): Solid  $\text{XeF}_6$  exists as  $\text{XeF}_5^+$  and  $\text{F}^-$ .
28. (d)
29. (b): As volume is constant,  $\Delta V = 0$   
 $W = -P\Delta V = 0$   
 $\Delta U = q + W$   
 $\Delta U = 500 \text{ J} + 0$   
 $\therefore \Delta U = q = +500 \text{ J}$
30. (d): A dilute solution of  $\text{H}_2\text{O}_2$  can be concentrated by heating (distillation) under reduced pressure.

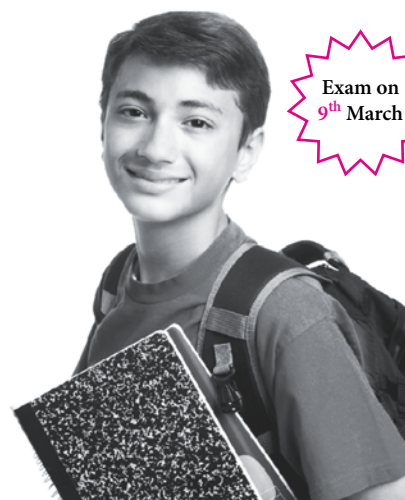


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# ACE

YOUR WAY **CBSE XII**



Exam on  
9<sup>th</sup> March

## PRACTICE PAPER 2016

Time Allowed : 3 hours

Maximum Marks : 70

### GENERAL INSTRUCTIONS

- (i) All questions are compulsory.
- (ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
- (iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
- (iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
- (v) Q. no. 23 is a value based question and carries 4 marks.
- (vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.

1. Why are powdered substances more effective adsorbents than their crystalline forms?
2. Arrange the following alkyl halides in the order of increasing dipole moment.  
 $\text{CH}_3\text{-F}$ ,  $\text{CH}_3\text{-Cl}$ ,  $\text{CH}_3\text{-Br}$ ,  $\text{CH}_3\text{-I}$
3. Trimethylamine and *n*-propylamine have the same molecular weight but the former boils at lower temperature than the latter. Give reason.
4. Why is Frenkel defect not found in pure alkali metal halides?
5. Why outer octahedral complexes are called high spin complexes?
6. 4% NaOH solution (mass/volume) and 6% urea solution (mass/volume) are equimolar but not isotonic. Why?
7. The  $E^\circ$  values corresponding to the following two reduction electrode processes are :  
 $\text{Cu}^+/\text{Cu} = + 0.52 \text{ V}$   
 $\text{Cu}^{2+}/\text{Cu}^+ = + 0.16 \text{ V}$   
Formulate the galvanic cell for their combination. What will be the standard cell potential for it? Calculate  $\Delta_r G^\circ$  for the cell reaction.
8. (i) In the transition series, starting from lanthanum ( $_{57}\text{La}$ ), the next element hafnium ( $_{72}\text{Hf}$ ) has an atomic number of 72. Why do we observe this jump in atomic number?  
(ii) Ce(IV) is a good analytical reagent. Why?
9. Give reason for the following :  
(i) Ferric iodide is very unstable but ferric chloride is stable.  
(ii)  $\text{ClF}_3$  molecule has a T-shaped structure and not a trigonal planar one.
10. How can propan-2-one be converted into *tert*-butyl alcohol?

OR

What happens when

- (i) ethyl alcohol reacts with red P and  $\text{Br}_2$ ?
- (ii) ethanol is heated with conc.  $\text{H}_2\text{SO}_4$  at 443 K?

11. (i) Explain why does conductivity of germanium crystals increase on doping with gallium.  
 (ii) Why does table salt, NaCl, sometimes appear yellow in colour?
12. (i) Heptane and octane form ideal solution. At 373 K, the vapour pressure of the two liquid components are 105.2 kPa and 46.8 kPa respectively. What will be the vapour pressure of a mixture of 26.0 g of heptane and 35.0 g of octane?  
 (ii) Give an example of a material used for making semipermeable membrane for carrying out reverse osmosis.
13. Write the overall reaction that occurs during the use of nickel-cadmium cell. Is it a primary or a secondary cell? Mention its one merit over the lead storage cell.
14. (i) What is meant by van't Hoff factor?  
 (ii) The osmotic pressure of a 0.0103 molar solution of an electrolyte is found to be 0.70 atm at 27°C. Calculate the van't Hoff factor. ( $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$ )  
 What conclusion do you draw about the molecular state of the solute in the solution?
15. Explain the following :  
 (i)  $\text{CO}_2$  is a better reducing agent below 710 K whereas CO is a better reducing agent above 710 K.  
 (ii) Silica is added to the sulphide ore of copper in the reverberatory furnace.  
 (iii) Vapour phase refining method is used for the purification of Ti.
- OR**
- (i) Indicate the principle behind the method used for the refining of zinc.  
 (ii) How is cast iron different from pig iron?  
 (iii) Which form of the iron is the purest form of commercial iron?
16. (i) What type of battery is mercury cell? Why is it more advantageous than dry cell?  
 (ii) Electrolysis of aqueous  $\text{CuCl}_2$  solution liberates  $\text{Cl}_2$  at anode not  $\text{O}_2$ . Why?
17. Using crystal field theory, draw energy level diagram, write electronic configuration of the central metal atom/ion and determine the magnetic moment value for the following :  
 $[\text{FeF}_6]^{3-}$ ,  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$
18. Compound (A) with molecular formula  $\text{C}_4\text{H}_9\text{Br}$  is treated with aqueous KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.  
 (i) Write down the structural formula of both compounds 'A' and 'B'.  
 (ii) Out of these two compounds, which one will be converted to the product with inverted configuration.
19. Accomplish the following conversions :  
 (i) Aniline to 2,4,6-tribromofluorobenzene  
 (ii) Benzamide to toluene
20. (i) Mention the type of linkage responsible for the formation of the following :  
 (a) Primary structure of protein  
 (b) Cross linkage of polypeptide chains  
 (c)  $\alpha$ -helix formation  
 (d)  $\beta$ -sheet structure  
 (ii) What is meant by reducing sugars?
21. Explain each of the following terms with one suitable example.  
 (i) A sweetening agent for diabetic patients  
 (ii) Enzymes  
 (iii) Analgesics
22. (i) Write the name of the reagents and equations in the conversion of  
 (a) phenol to salicylaldehyde  
 (b) anisole to *p*-methoxyacetophenone.  
 (ii) Ethers are soluble in water. Why?
23. Seema went to market to buy vegetables. The vendor put the vegetables in the polythene bag but Seema refused to take polythene bag and told the vendor to put the things in the cloth bag which she was carrying with her.  
 (i) What values are shown by Seema?  
 (ii) Why did Seema carry cloth bag with her instead of taking polythene bag from vendor?  
 (iii) What are the bad effects of non-biodegradable polymers?

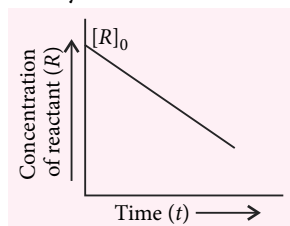
24. Compound 'A' ( $C_6H_{12}O_2$ ) on reduction with  $LiAlH_4$  yields two compounds 'B' and 'C'. The compound 'B' on oxidation gives 'D' which on treatment with aqueous alkali and subsequent heating furnishes 'E'. The later on catalytic hydrogenation gives 'C'. The compound 'D' on further oxidation gives  $CH_3COOH$ . Deduce the structures of A, B, C, D and E.

OR

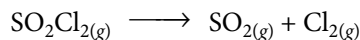
- (i) Give chemical tests to distinguish between the following pairs of compounds :
- Propanoyl chloride and propanoic acid
  - Benzaldehyde and acetophenone
- (ii) How would you account for the following?
- Aldehydes are more reactive than ketones towards nucleophiles.
  - The boiling points of aldehydes and ketones are lower than the corresponding acids.
  - The aldehydes and ketones undergo a number of addition reactions.

25. (i) The graph for the reaction,  
 $R \rightarrow P$

is represented by



- Predict the order of the reaction in this case.
  - What does the slope of the graph represent?
- (ii) The following data were obtained during the first order thermal decomposition of  $SO_2Cl_2$  at a constant volume :



Experiment	Time/s	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

[Given :  $\log 4 = 0.6021$ ,  $\log 2 = 0.3010$ ]

OR

- (i) The thermal decomposition of  $HCO_2H$  is a first order reaction with a rate constant of  $2.4 \times 10^{-3} s^{-1}$  at a certain temperature. Calculate

how long will it take for three-fourth of initial quantity of  $HCO_2H$  to decompose?(Given :  $\log 4 = 0.6021$ )

- (ii) The decomposition of a compound is found to follow a first order rate law. If it takes 15 minutes for 20 percent of original material to react, calculate
- the specific rate constant
  - the time at which 10 percent of the original material remains unreacted
  - the time it takes for the next 20 percent of the reactant left after the first 15 minutes.
26. (i) Why do noble gases form compounds with fluorine and oxygen only?
- (ii) Why HF is stored in wax coated glass bottles?
- (iii)  $SF_6$  is not easily hydrolysed though thermodynamically it should be. Why?
- (iv) Structures of xenon fluorides cannot be explained by valence bond approach. Explain?
- (v) Draw the structure of  $H_2SO_5$ .

OR

- (i) Explain the Ostwald's process for the manufacture of nitric acid.
- (ii) Write the balanced reactions when nitric acid reacts with
- $I_2$
  - C
  - $S_8$
  - $P_4$
- (iii) Give any two uses of  $HNO_3$ .

### SOLUTIONS

- Powdered substances have large surface area which increases the extent of adsorption than their crystalline forms.
- Increasing order of dipole moment :  
 $CH_3-I < CH_3-Br < CH_3-F < CH_3-Cl$
- n*-Propylamine has two H-atoms on N-atom and hence, undergoes intermolecular H-bonding whereas trimethylamine being a  $3^\circ$  amine does not undergo H-bonding.
- Frenkel defect is not found in pure alkali metal halides because alkali metal ions cannot fit into the interstitial sites.
- Pairing does not occur in outer octahedral complexes, hence, they have unpaired electrons and show large values of magnetic moments.

6. Both the solutions, 4% NaOH (W/V) and 6% urea (W/V) have same concentration (1 M) but these are not isotonic because NaOH undergoes dissociation in solution. Therefore, number of particles in NaOH solution is more than that in urea solution.

7. At cathode :  $\text{Cu}^+ + e^- \longrightarrow \text{Cu}$   $E^\circ = +0.52 \text{ V}$   
 At anode :  $\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + e^-$   $E^\circ = +0.16 \text{ V}$

Cell reaction :  $2\text{Cu}^+ \longrightarrow \text{Cu} + \text{Cu}^{2+}$

Cell representation is

$\text{Cu}^+ | \text{Cu}^{2+} || \text{Cu}^+ | \text{Cu}$

$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.52 - 0.16 = 0.36 \text{ V}$

$\Delta_r G^\circ = -nE^\circ F = -1 \times 0.36 \times 96500$   
 $= -34740 \text{ J mol}^{-1}$

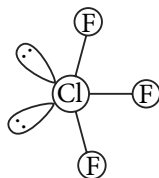
8. (i) This is because after  $_{57}\text{La}$ , filling of  $4f$ -orbital starts which is completed at atomic number 71. These 14 elements therefore, belong to  $f$ -block and are placed separately at the bottom of the periodic table.

(ii) The  $E^\circ$  value for  $\text{Ce}^{4+}/\text{Ce}^{3+}$  is 1.74 V which suggests that it can oxidise water however, the reaction rate is very slow and hence, Ce (IV) is a good analytical reagent.

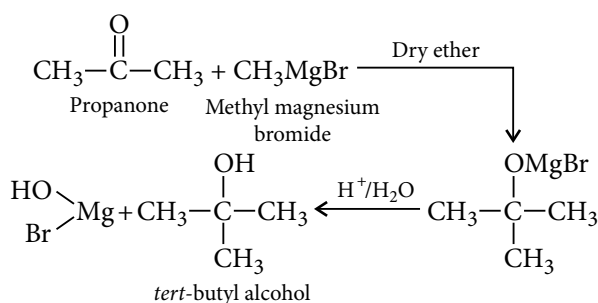
9. (i) Iodide ion ( $\text{I}^-$ ) is a strong reducing agent and reduces  $\text{Fe}^{3+}$  ion to  $\text{Fe}^{2+}$  ion. Therefore, ferric iodide does not exist.

Chloride ion ( $\text{Cl}^-$ ) being a weak reducing agent cannot reduce  $\text{Fe}^{3+}$  ion hence, ferric chloride is quite stable.

(ii) In  $\text{ClF}_3$ , central atom Cl has three bond pairs and two lone pairs. According to VSEPR theory, the two lone pairs will occupy the equatorial positions to minimise  $lp-lp$  and  $lp-bp$  repulsions. In addition, the axial fluorine atoms will be bent towards the equatorial fluorine in order to minimise the  $lp-lp$  repulsions. That is why  $\text{ClF}_3$  has a bent T-shaped structure.



10.  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$  can be converted into *tert*-butyl alcohol by its reaction with Grignard's reagent ( $\text{CH}_3\text{MgBr}$ ) as shown :



OR

(i)  $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{Red P} + \text{Br}_2} \text{CH}_3\text{CH}_2\text{Br} + \text{H}_3\text{PO}_3$   
 Ethyl alcohol  $\quad \quad \quad$  Ethyl bromide

(ii)  $\text{C}_2\text{H}_5\text{OH} \xrightarrow[443 \text{ K}]{\text{Conc. H}_2\text{SO}_4} \text{CH}_2=\text{CH}_2$   
 Ethanol  $\quad \quad \quad$  Ethene

11. (i) When germanium is doped with gallium, some of the positions of lattice of germanium are occupied by gallium. Valence electrons in germanium are four while gallium has only three valence electrons. The vacancy of fourth valence electron of germanium creates an electron hole or electron vacancy. Under the influence of electric field the electron starts moving towards positively charged plates through the holes and conduct electricity.

(ii) Yellow colour in sodium chloride is due to metal excess defect due to which unpaired electrons occupy anionic sites. These sites are called F-centres. These electrons absorb energy from the visible region for the excitation which makes crystal appear yellow.

12. (i) Molar mass of heptane ( $\text{C}_7\text{H}_{16}$ ) =  $100 \text{ g mol}^{-1}$   
 Molar mass of octane ( $\text{C}_8\text{H}_{18}$ ) =  $114 \text{ g mol}^{-1}$

Number of moles of heptane =  $\frac{26.0 \text{ g}}{100 \text{ g mol}^{-1}}$   
 $= 0.26 \text{ mol}$

No. of moles of octane =  $\frac{35.0 \text{ g}}{114 \text{ g mol}^{-1}} = 0.31 \text{ mol}$

$x_{(\text{heptane})} = \frac{0.26}{0.26 + 0.31} = 0.456$

$x_{(\text{octane})} = 1 - 0.456 = 0.544$

$p_{(\text{heptane})} = 0.456 \times 105.2 \text{ kPa} = 47.97 \text{ kPa}$

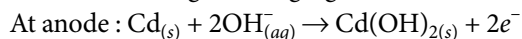
$p_{(\text{octane})} = 0.544 \times 46.8 \text{ kPa} = 25.46 \text{ kPa}$

$p_{\text{Total}} = 47.97 + 25.46 = 73.43 \text{ kPa}$

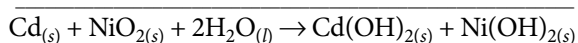
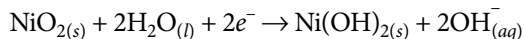
(ii) Cellulose acetate is used for making semipermeable membrane for carrying out reverse osmosis.

13. Nickel-cadmium batteries are rechargeable storage batteries. It has anode cadmium metal and a metal grid containing nickel (IV) oxide as cathode immersed in KOH solution.

Reactions during discharging,



At cathode :



When charging takes place, reactions are reversed.

It is a secondary cell. It has longer life than the lead storage cell but is more expensive to manufacture.

Since reactant and product are metals or solids, emf remains constant throughout in its operation.

14. (i) van't Hoff factor is the ratio of the normal molecular mass to the observed molecular mass or the ratio of the observed colligative property to the normal colligative property.

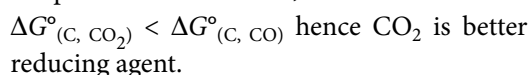
(ii)  $\pi = iCRT$

or,  $0.70 = i \times 0.0103 \times 0.082 \times (27 + 273)$

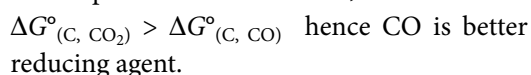
or,  $i = \frac{0.70}{0.0103 \times 0.082 \times 300} = 2.76$

Since  $i > 1$ , solute molecules are dissociated in the solution.

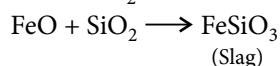
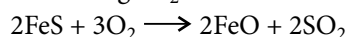
15. (i) According to Ellingham diagram, at temperature below 710 K,



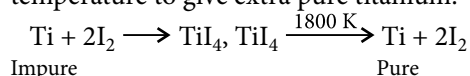
At temperature above 710 K,



- (ii) Copper pyrites contain iron sulphide in addition to copper sulphide. In the reverberatory furnace, copper ore is roasted to give oxides. FeO is removed by adding silica from the matte containing  $Cu_2S$  and some unchanged FeS.



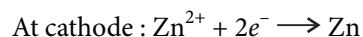
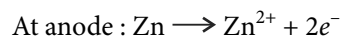
- (iii) Ti reacts with iodine to form  $TiI_4$  which is volatile and decomposes to give Ti at high temperature to give extra pure titanium.



OR

- (i) Zinc is refined by electrolytic refining.

In this method, the impure metal is made to act as anode. A strip of the same metal in pure form is used as cathode. They are put in a suitable electrolytic bath containing soluble salt of the same metal. When electric current is passed,  $Zn^{2+}$  ions from the electrolyte are deposited at the cathode and an equivalent amount of metal goes into the electrolyte as  $Zn^{2+}$  ions.



- (ii) The iron obtained from Blast furnace contains about 4% carbon and many impurities in smaller amount (e.g., S, P, Si, Mn). This is known as pig iron and cast into variety of shapes.

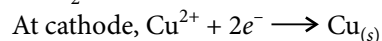
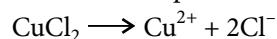
Cast iron is different from pig iron and is made by melting pig iron with scrap iron and coke using hot air blast. It has slightly lower carbon content (about 3%) and is extremely hard and brittle.

- (iii) Wrought iron is the purest form of commercial iron. It contains 0.2–0.5% carbon besides traces of P and Si in the form of slag.

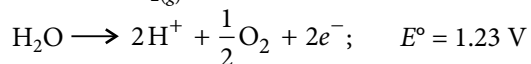
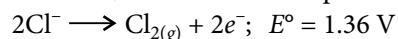
16. (i) Mercury cell is a primary battery hence, it can be used only once and cannot be recharged after discharging.

Advantage : The cell potential remains constant during its life time. Hence, it is useful for devices requiring constant current e.g., hearing aids and watches.

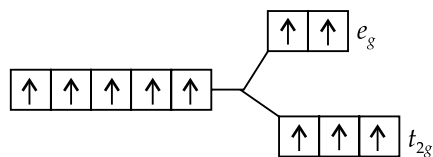
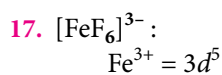
- (ii) During electrolysis of aqueous  $CuCl_2$  following reactions take place :



At anode, two reactions are possible

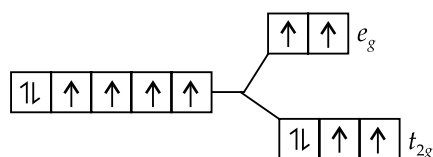
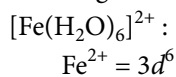


At anode the reaction with lower value of  $E^\circ$  should take place and thus, water should get oxidised to give  $O_2$ . But on account of overpotential of oxygen, chlorine is produced at anode.



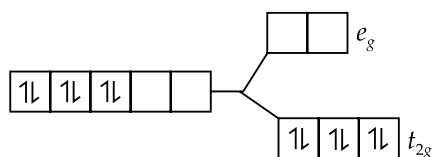
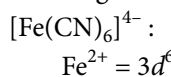
Number of unpaired electrons = 5

Magnetic moment =  $\sqrt{5(5+2)} = 5.92$  B.M.

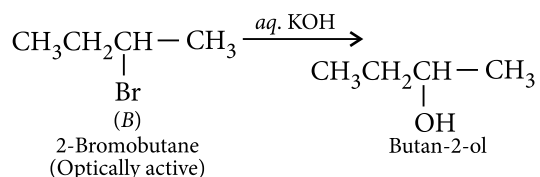
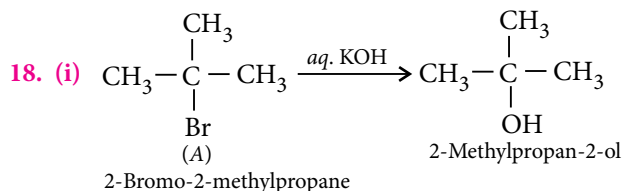


Number of unpaired electrons = 4

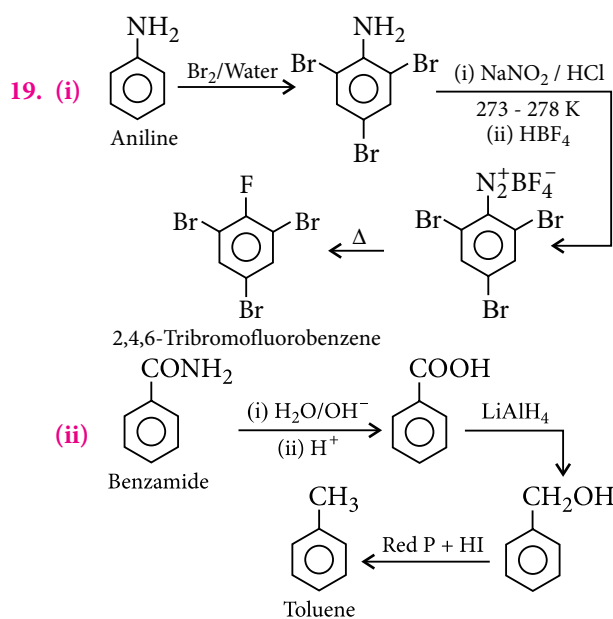
Magnetic moment =  $\sqrt{4(4+2)} = 4.9$  B.M.



Diamagnetic and its magnetic moment is zero.



(ii) Compound (B) will be converted to product with inverted configuration as it undergoes  $\text{S}_{\text{N}}2$  nucleophilic substitution in which the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. Compound (A) being a tertiary halide, undergoes  $\text{S}_{\text{N}}1$  substitution which is accompanied by racemisation.



20. (i)

	Biomolecule	Type of linkage
(a)	Primary structure of protein	Peptide bond (linkage)
(b)	Cross linkage of polypeptide chain	Hydrogen bond, disulphide linkage, electrostatic force of attraction
(c)	$\alpha$ -helix formation	Hydrogen bond
(d)	$\beta$ -sheet structure	Intermolecular hydrogen bond.

(ii) Carbohydrates which reduce Tollens' reagent are reducing sugars. All monosaccharides, aldoses or ketoses are reducing sugars.

21. (i) Artificial sweetening agents are chemical substances which are sweet in taste but do not add calories to our body. For example, aspartame, it is 150 times sweeter than sucrose.

(ii) Enzymes are bio-catalysts which accelerate various cellular reactions without themselves undergoing any apparent change during the course of action. Enzymes are highly specific in their action on substrate. Almost all the enzymes are globular proteins. For example, urease catalyses decomposition of urea to  $\text{CO}_2$  and  $\text{NH}_3$ .

(iii) Analgesics are chemical compounds which are used for relieving pain. Analgesics relieve

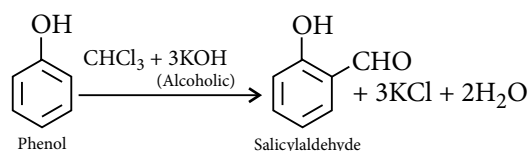


pain by acting on central nervous system or on peripheral pain mechanism, without significantly affecting consciousness. There are two types of analgesics :

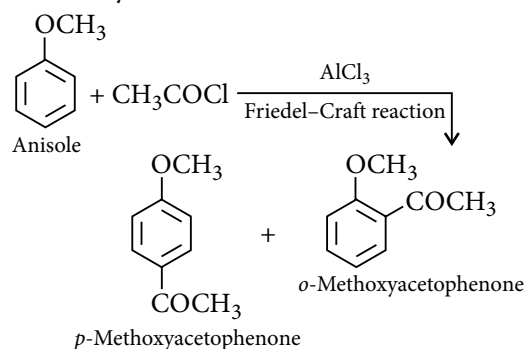
Narcotics – Morphine, codeine, heroine

Non-narcotics – Aspirin, ibuprofen, etc

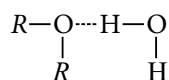
22. (i) (a) Reagents : Chloroform and alcoholic alkali.



- (b) Reagents : Acetyl chloride and Lewis acid catalyst.



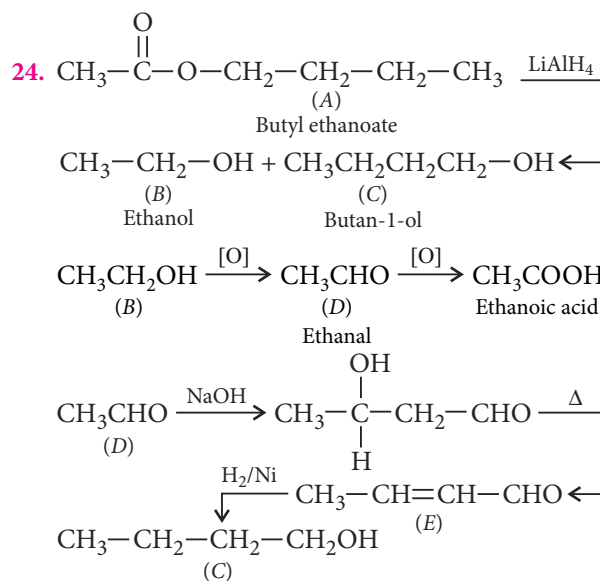
- (ii) The oxygen present in ether forms H-bond with water due to which they are soluble in water.



23. (i) Concern, aware and alert for environmental pollution are the values displayed by Seema.  
(ii) Polythene is non-biodegradable which causes

environmental pollution while cloth bags are biodegradable and can be reuse again.

- (iii) Non-biodegradable polymers are quite resistant to the environmental degradation processes and cause accumulation of solid polymeric waste materials. These waste materials remain undegraded for quite a long time and cause acute environmental problems.




Hence (A)  $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

- (B)  $\text{CH}_3\text{CH}_2\text{OH}$   
 (C)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$   
 (D)  $\text{CH}_3\text{CHO}$   
 (E)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CHO}$

OR

- (i) (a) Propanoic acid reacts with aq.  $\text{NaHCO}_3$  with the evolution of  $\text{CO}_2$  gas while propanoyl chloride does not react with  $\text{NaHCO}_3$ .  
 $\text{CH}_3\text{CH}_2\text{COOH} + \text{NaHCO}_3 \rightarrow \text{CH}_3\text{CH}_2\text{COONa} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$
- (b) Iodoform test : Warm each compound with iodine and sodium hydroxide solution on a water bath.  
 Acetophenone ( $\text{C}_6\text{H}_5\text{COCH}_3$ ) gives yellow precipitate of iodoform, benzaldehyde does not give this test.



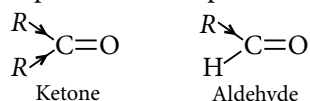
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- (ii) (a) Ketones are less reactive than aldehydes towards nucleophilic addition reactions because the two electron releasing alkyl groups decrease the magnitude of positive charge on carbonyl carbon and make it less susceptible to nucleophilic attack.



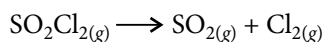
Also, the two bulkier alkyl groups hinder the approach of the nucleophile to the carbonyl carbon. This is called steric factor.

- (b) The boiling points of aldehydes and ketones are lower than the corresponding acids and alcohols due to absence of intermolecular hydrogen bonding.
- (c) Aldehydes and ketones undergo a number of addition reactions as both possess the carbonyl functional group which reacts with a number of nucleophiles such as HCN, NaHSO<sub>3</sub>, alcohols, ammonia derivatives and Grignard reagents.

25. (i) (a) The reaction is of zero order.  
 (b) Slope of the straight line graph gives rate constant.

$$-k = \frac{d[R]}{dt}$$

- (ii) The given reaction is



$$\text{At } t = 0, \quad 0.4 \text{ atm} \quad \quad 0 \quad \quad 0$$

$$\text{At time } t, \quad (0.4 - x) \text{ atm} \quad \quad x \text{ atm} \quad \quad x \text{ atm}$$

Total pressure at time  $t$  will be

$$P_{\text{Total}} = (0.4 - x) + x + x = 0.4 + x$$

$$x = (P_{\text{Total}} - 0.4)$$

Pressure of SO<sub>2</sub>Cl<sub>2</sub> at time  $t$  will be

$$p_{\text{SO}_2\text{Cl}_2} = 0.4 - x = 0.4 - (P_{\text{Total}} - 0.4) \\ = 0.8 - P_{\text{Total}}$$

$$\text{At time } (t = 100 \text{ s}), P_{\text{Total}} = 0.7 \text{ atm}$$

$$\therefore p_{\text{SO}_2\text{Cl}_2} = 0.8 - 0.7 = 0.1 \text{ atm}$$

According to first order kinetic equation,

$$k = \frac{2.303}{t} \log \left( \frac{P_{\text{SO}_2\text{Cl}_2(\text{initial})}}{P_{\text{SO}_2\text{Cl}_2(\text{after reaction})}} \right) \\ = \frac{2.303}{100} \log \left( \frac{0.4}{0.1} \right) = 1.38 \times 10^{-2} \text{ s}^{-1}$$

OR

- (i) For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]_t}$$

$$\text{Given } k = 2.4 \times 10^{-3} \text{ s}^{-1}$$

$$[R]_t = \frac{[R]_0}{4}, t = ?$$

Substituting these values in the equation, we get

$$t = \frac{2.303}{2.4 \times 10^{-3} \text{ s}^{-1}} \log \frac{[R]_0}{[R]_t}$$

$$t = \frac{2.303}{2.4 \times 10^{-3} \text{ s}^{-1}} \log 4 = \frac{2.303}{2.4 \times 10^{-3}} \times 0.6021 \text{ s}$$

$$t = 577.7 \text{ s} \approx 578 \text{ s}$$

- (ii) (a) For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]_t}$$

$$\text{Given } t = 15 \text{ min}, [R]_t = 0.8[R]_0$$

$$\text{or, } k = \frac{2.303}{15} \log \frac{[R]_0}{0.8[R]_0}$$

$$\text{or, } k = \frac{2.303}{15} \log \frac{10}{8} \quad \dots(i)$$

$$\text{or, } k = 0.015 \text{ min}^{-1}$$

- (b) When  $[R]_t = 0.1 [R]_0$ ,  $t = ?$

$$k = \frac{2.303}{t_1} \log \frac{[R]_0}{0.1 [R]_0} = \frac{2.303}{t_1} \log 10$$

$$\text{or, } 0.015 \text{ min}^{-1} = \frac{2.303}{t_1}$$

$$\text{or, } t_1 = \frac{2.303}{0.015 \text{ min}^{-1}}$$

$$t_1 = 153.53 \text{ min}$$

$\therefore$  After 153.53 min, 10% of the original material remains unreacted.

- (c) Also,

$$k = \frac{2.303}{t_2} \log \frac{0.8 [R]_0}{0.64 [R]_0} = \frac{2.303}{t_2} \log \frac{10}{8} \quad \dots(ii)$$

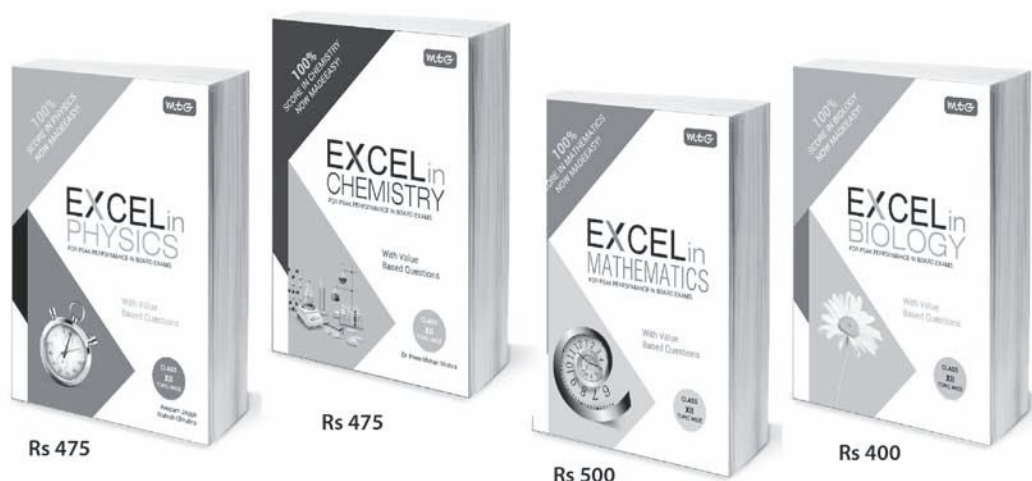
From (i) and (ii), we get

$$\frac{2.303}{15} \log \frac{10}{8} = \frac{2.303}{t_2} \log \frac{10}{8}$$

$$\therefore t_2 = 15 \text{ min}$$

26. (i) Fluorine and oxygen are the most electronegative elements hence, they are very

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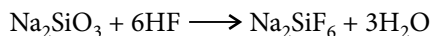


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reactive and form compounds with noble gases, particularly with xenon.

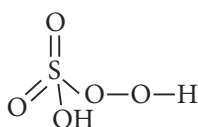
- (ii) HF does not attack wax but attacks sodium silicate which is the main constituent of glass. As a result, the glass bottles are slowly corroded or eaten up.



- (iii) In  $\text{SF}_6$  molecule, sulphur is surrounded by six fluorine atoms which protect sulphur atom from attack by reagents to such an extent that even thermodynamically most favourable reactions like hydrolysis do not occur. So,  $\text{H}_2\text{O}$  cannot attack  $\text{SF}_6$  easily.

- (iv) According to the valence bond approach, orbitals containing unpaired electrons only take part in covalent bond formation. Xenon has no unpaired electrons. Hence, structure of its fluorides cannot be explained by valence bond approach.

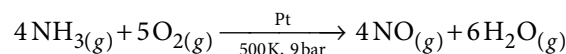
(v)



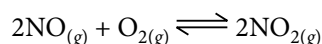
Peroxomonosulphuric acid or Caro's acid

OR

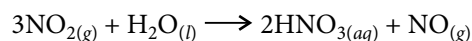
- (i) This method is based on catalytic oxidation of  $\text{NH}_3$  by atmospheric oxygen.



Nitric oxide thus formed combines with oxygen to give  $\text{NO}_2$ .



Nitrogen dioxide so formed dissolves in water to give nitric acid  $\text{HNO}_3$ .



- (ii) (a)  $\text{I}_2 + 10\text{HNO}_3 \longrightarrow 2\text{HIO}_3 + 10\text{NO}_2 + 4\text{H}_2\text{O}$   
 (b)  $\text{C} + 4\text{HNO}_3 \longrightarrow \text{CO}_2 + 2\text{H}_2\text{O} + 4\text{NO}_2$   
 (c)  $\text{S}_8 + 48\text{HNO}_3(\text{conc.}) \longrightarrow 8\text{H}_2\text{SO}_4 + 48\text{NO}_2 + 16\text{H}_2\text{O}$   
 (d)  $\text{P}_4 + 20\text{HNO}_3(\text{conc.}) \longrightarrow 4\text{H}_3\text{PO}_4 + 20\text{NO}_2 + 4\text{H}_2\text{O}$

- (iii) (a) Nitric acid is used to manufacture ammonium nitrate for fertilisers.

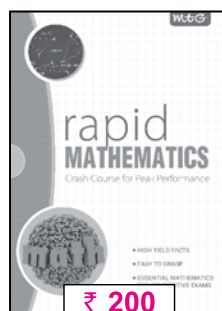
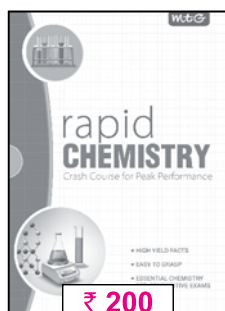
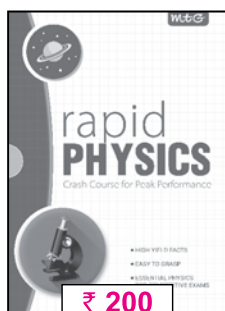
- (b) It is used for the preparation of trinitrotoluene and other organic nitro compounds.



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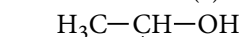
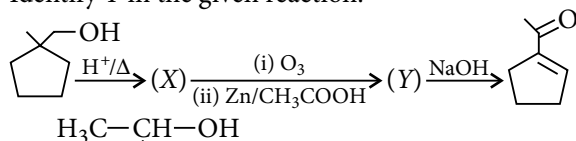
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# OLYMPIAD PROBLEMS



- The line spectra of two elements are not identical because
  - the elements do not have the same number of neutrons
  - they have different mass numbers
  - their outermost electrons are at different energy levels
  - they have different valencies.

- Identify Y in the given reaction.



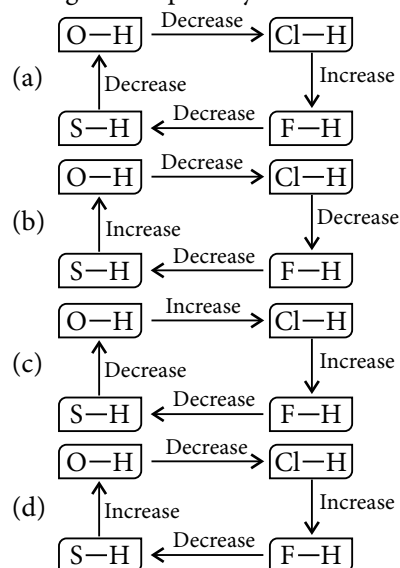
- - CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CHO
  - CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>·CHO
  -
- One litre of oxygen at NTP weighs 1.46 g. How many litres of oxygen are needed for the combustion of 21.0 g of Mg whose equivalent weight is  $\frac{1}{2}$  mole?
    - 2.5 L
    - 9.59 L
    - 8.42 L
    - 32 L
  - How does H<sub>2</sub>O<sub>2</sub> differ from O<sub>3</sub> in its chemical action?
    - In oxidising PbS to PbSO<sub>4</sub>
    - In liberating I<sub>2</sub> from KI
    - In decolorising acidified KMnO<sub>4</sub>
    - In oxidising K<sub>4</sub>[Fe(CN)<sub>6</sub>] to K<sub>3</sub>[Fe(CN)<sub>6</sub>]
  - An organic compound (A) C<sub>5</sub>H<sub>8</sub>O adds Br<sub>2</sub> to give C<sub>5</sub>H<sub>8</sub>Br<sub>2</sub>O. It does not react with Tollen's reagent

but enters into reaction with phenyl hydrazine. Ozonolysis of (A) gives acetaldehyde and C<sub>3</sub>H<sub>4</sub>O<sub>2</sub> which readily loses CO to form acetaldehyde. A is

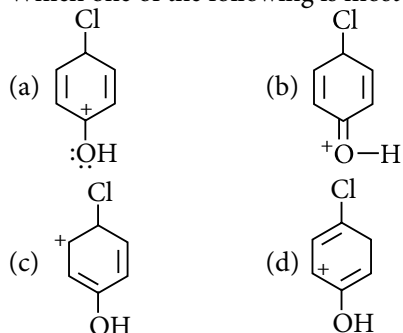
- CH<sub>3</sub>CH=CHCOCH<sub>3</sub>
- CH<sub>3</sub>CH=CHCH<sub>2</sub>CHO
- CH<sub>2</sub>=CHCH<sub>2</sub>COCH<sub>3</sub>
- CH<sub>3</sub>CH<sub>2</sub>-C(=O)-CHO  
||  
CH<sub>2</sub>

- The enthalpy change involved in the oxidation of glucose is -2880 kJ mol<sup>-1</sup>. 25% of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one km. What is the maximum distance that a person will be able to walk after eating 120 g of glucose?
  - 4.80 km
  - 5.2 km
  - 100 km
  - 30 km

- Which of the following diagrams shows correct change in the polarity of bond?



8. Which one of the following is most stable?



9. A sample of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  is strongly heated in air. The residue is  $\text{Mn}_3\text{O}_4$ .

- The residue is dissolved in 100 mL of 0.1 N  $\text{FeSO}_4$  containing dilute  $\text{H}_2\text{SO}_4$ .
- The solution reacts completely with 50 mL of  $\text{KMnO}_4$  solution.
- 25 mL of  $\text{KMnO}_4$  solution used in step (II) requires 30 mL of 0.1 N  $\text{FeSO}_4$  solution for the complete reaction.

Find the amount of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  in the sample.

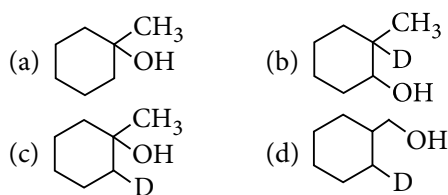
(Mn = 55, Fe = 56, S = 32)

- (a) 1.4210 g                      (b) 1.50 g  
(c) 1.338 g                        (d) 2.2 g

10. A colourless solid (X) on heating evolved  $\text{CO}_2$  and also gave a white residue, soluble in water. Residue also gave  $\text{CO}_2$  when treated with dilute acid. (X) is

- (a)  $\text{Na}_2\text{CO}_3$                       (b)  $\text{CaCO}_3$   
(c)  $\text{Ca}(\text{HCO}_3)_2$                 (d)  $\text{NaHCO}_3$

11. Product A, A is



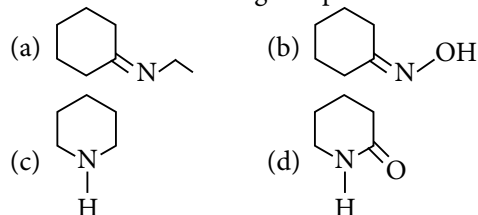
12. Barium titanate has a pyrolusite structure (a cubic lattice), with barium ions occupying the corners of the unit cell, oxide ions the face centres and titanium ions the centres. Assuming that  $\text{Ti}^{4+}$  ions occupy the holes of the  $\text{BaO}$  lattice, what type of hole and what fraction of such holes do these ions occupy?

- (a) 25% of the octahedral holes  
(b) 75% of the tetrahedral holes  
(c) 50% of the tetrahedral holes  
(d) 100% of the octahedral holes

13. Which of the following statements is not correct?

- (a)  $(s + p_y)$  produces  $sp$  hybrid orbitals which are lying in the  $yz$  plane.  
(b)  $(s + p_y)$  produces  $sp$  hybrid orbitals which are lying in the  $xz$  plane.  
(c)  $(s + p_x + p_z)$  produces  $sp^2$  hybrid orbitals which are lying in the  $xz$  plane.  
(d) None of these

14. Which of the following compounds is an amine?



15. The rate constant for two parallel reactions were found to be  $1.0 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $3.0 \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . If the corresponding energies of activation of the parallel reactions are  $60.0 \text{ kJ mol}^{-1}$  and  $70.0 \text{ kJ mol}^{-1}$  respectively, what is the apparent overall energy of activation?

- (a)  $130.0 \text{ kJ mol}^{-1}$               (b)  $67.5 \text{ kJ mol}^{-1}$   
(c)  $100.0 \text{ kJ mol}^{-1}$               (d)  $65.0 \text{ kJ mol}^{-1}$

16. Consider the following statements :

- (i) IUPAC name of  $\text{K}_2[\text{OsCl}_5\text{N}]$  is Potassium pentachloronitridoosmate (VI).  
(ii)  $[\text{Cr}(\text{H}_2\text{O})_6][\text{Fe}(\text{CN})_6]$  contain four unpaired electrons.  
(iii)  $[\text{Fe}(\text{acac})_3]$  is high spin organometallic complex.  
(iv)  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  has 6 electrons in  $t_{2g}$  and 2 electrons in  $e_g$  orbital.

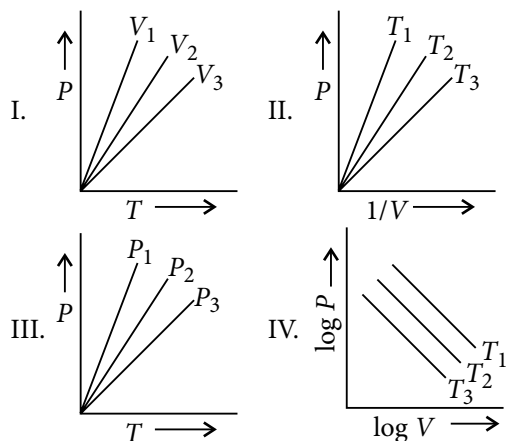
Give initial 'T' for true statement and 'F' for false statement.

- (a) TTTT (b) FTFT (c) TTFF (d) FFTT

17. An organic compound  $\text{C}_x\text{H}_{2y}\text{O}_y$ , was burnt with twice the oxygen needed for complete combustion to produce  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The hot gases when cooled at  $0^\circ\text{C}$  and 1 atm pressure measured 2.24 litre. The water collected during cooling was 0.9 g. The vapour pressure of pure water at  $20^\circ\text{C}$  is 17.5 mm of Hg and it reduces by 0.104 mm when 50 g of organic compound is dissolved in 1000 g of water. The molecular formula of the organic compound is

- (a)  $\text{C}_6\text{H}_{12}\text{O}_6$                       (b)  $\text{C}_5\text{H}_{10}\text{O}_5$   
(c)  $\text{C}_2\text{H}_4\text{O}_2$                         (d)  $\text{C}_8\text{H}_{16}\text{O}_8$

18. For 1 mol of an ideal gas,  $V_1 > V_2 > V_3$  in Fig. (I),  $T_1 > T_2 > T_3$  in Fig. (II),  $P_1 > P_2 > P_3$  in Fig. (III), and  $T_1 > T_2 > T_3$  in Fig. (IV), then which curves are correct.



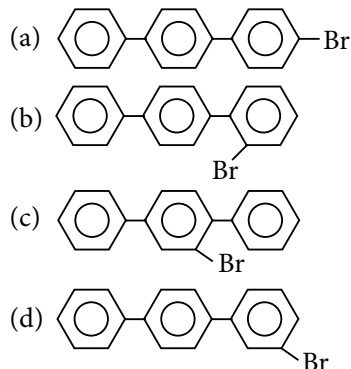
- (a) I, II  
(b) I, II, III  
(c) II, IV  
(d) I, III, IV

19. A jeweller is selling 22-carat gold articles with 95% purity, it is approximately  
(a) exact  
(b) 3.5% higher  
(c) 3.5% lower  
(d) 5% lower.

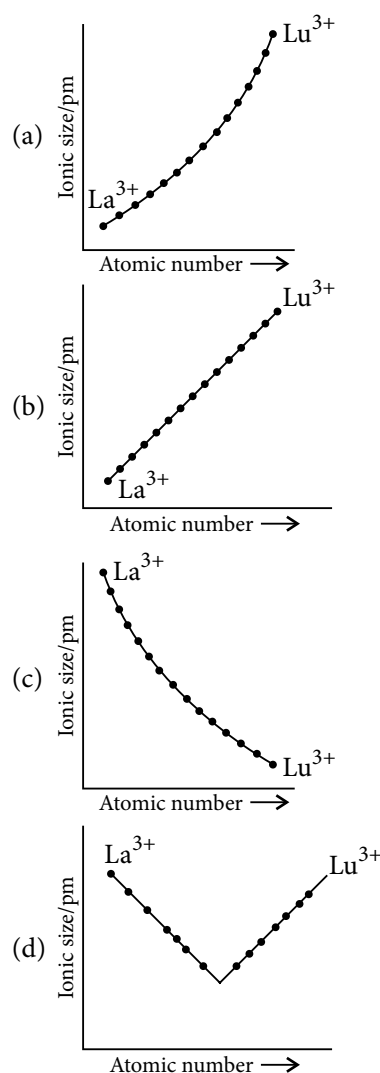
20. Consider the following reaction :



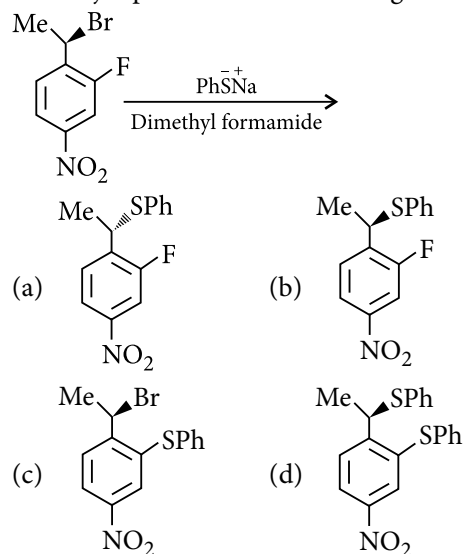
The product is



21. A piece of charcoal from the ruins of a settlement in Japan was found to have  $^{14}\text{C}/^{12}\text{C}$  ratio that was 0.617 times that found in living organisms. How old is this piece of charcoal? ( $t_{1/2}$  for  $^{14}\text{C}$  is 5770 years)  
(a) 4400 years  
(b) 2123 years  
(c) 1529 years  
(d) 4023 years
22. Which of the following graphs shows correct trend in the size of +3 ions of lanthanides?



23. The major product of the following reaction is

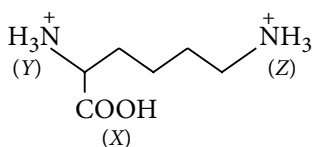


24. A 100 watt, 110 volt incandescent lamp is connected in series with an electrolytic cell containing cadmium sulphate solution. What weight of cadmium will be deposited by the current flowing for 10 hours? [Atomic weight of Cd = 112.4]
- (a) 20.02 g                      (b) 35.52 g  
(c) 19.06 g                      (d) 11.11 g

25. In the following statements which combination of true (T) and false (F) options is correct?

- I. Ionic mobility is the highest for  $I^-$  in water as compared to other halides.  
 II. Stability order is  $Cl^- > Br^- > I^-$   
 III. Reactivity order is  $F < Cl > Br > I$   
 IV. Oxidizing power order is  $F_2 < Cl_2 < Br_2 < I_2$ .
- (a) TFFT                      (b) TTFF  
(c) TFFT                      (d) FTFT

26. In the compound given below :

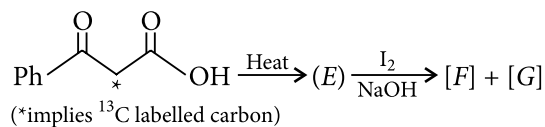


The correct order of acidic nature is

- (a)  $Z > X > Y$                       (b)  $X > Y > Z$   
(c)  $X > Z > Y$                       (d)  $Y > X > Z$
27. When KI (excess) is added to  
 I :  $CuSO_4$     II :  $HgCl_2$     III :  $Pb(NO_3)_2$
- (a) a white ppt. of  $CuI$  in I, an orange ppt. of  $HgI_2$  in II and a yellow ppt. of  $PbI_2$  in III  
 (b) a white ppt. of  $CuI$  in I, an orange ppt. dissolving  $HgI_4^{2-}$  in II and a yellow ppt. of  $PbI_2$  in III  
 (c) a white ppt. of  $CuI$ ,  $HgI_2$  and  $PbI_2$  in each case  
 (d) none of these.

28. A solution containing  $NH_4Cl$  and  $NH_4OH$  has  $[OH^-] = 10^{-6} \text{ mol L}^{-1}$ , which of the following hydroxides would be precipitated when this solution is added in equal volume to a solution containing 0.1 M of metal ions?
- (a)  $Mg(OH)_2$ , ( $K_{sp} = 3 \times 10^{-11}$ )  
 (b)  $Fe(OH)_2$ , ( $K_{sp} = 8 \times 10^{-16}$ )  
 (c)  $Cd(OH)_2$ , ( $K_{sp} = 8 \times 10^{-6}$ )  
 (d)  $AgOH$  ( $K_{sp} = 5 \times 10^{-3}$ )

29. In the following reaction sequence, the correct structures of E, F and G are :



- (a)  $E = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$      $F = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{ONa}$      $G = \text{CHI}_3$   
 (b)  $E = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$      $F = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{ONa}$      $G = \text{CHI}_3$   
 (c)  $E = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$      $F = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{ONa}$      $G = \overset{\text{O}}{\parallel}{\text{C}}-\text{CHI}_3$   
 (d)  $E = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$      $F = \text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{O}}{\parallel}{\text{C}}-\text{ONa}$      $G = \overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3\text{I}$

30. A mixture of formic acid and oxalic acid is heated with concentrated  $H_2SO_4$ . The gas produced is collected and on its treatment with  $KOH$  solution the volume of the gas decreased by one-sixth. Calculate the molar ratio of the two acids in the original mixture.

- (a) 2 : 1                      (b) 4 : 1  
(c) 3 : 4                      (d) 3 : 2

## ANSWER KEYS

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



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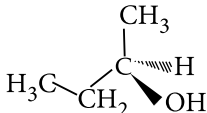

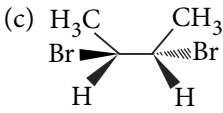
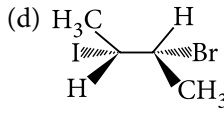
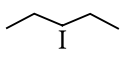


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Exam on 1<sup>st</sup> May

# AIPMT 2016

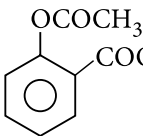
## MODEL TEST PAPER

- From the stability constants (hypothetical values) given below, predict which is the strongest ligand?
  - $\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4]^{2+}$ ; ( $K = 4.5 \times 10^{11}$ )
  - $\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons [\text{Cu}(\text{CN})_4]^{2-}$ ; ( $K = 2.0 \times 10^{27}$ )
  - $\text{Cu}^{2+} + 2\text{en} \rightleftharpoons [\text{Cu}(\text{en})_2]^{2+}$ ; ( $K = 3.0 \times 10^{15}$ )
  - $\text{Cu}^{2+} + 4\text{H}_2\text{O} \rightleftharpoons [\text{Cu}(\text{H}_2\text{O})_4]^{2+}$ ; ( $K = 9.5 \times 10^8$ )
- Which of the following molecules has the maximum number of stereoisomers?
  - 
  - 
  - 
  - 
- Which one of the following oxides is expected to exhibit paramagnetic behaviour?
  - $\text{CO}_2$
  - $\text{SiO}_2$
  - $\text{SO}_2$
  - $\text{ClO}_2$
- Which of the following reagents can be used to convert benzenediazonium chloride into benzene?
  - $\text{CH}_3\text{OH}$
  - $\text{H}_3\text{PO}_2$
  - $\text{Br}_2 - \text{H}_2\text{O}$
  - $\text{LiAlH}_4$
- Following are the isomers of molecular formula,  $\text{C}_5\text{H}_{12}$ .
  - 
  - 
  - 
 Decreasing order of their boiling points is
  - $\text{I} < \text{II} < \text{III}$
  - $\text{I} > \text{II} > \text{III}$
  - $\text{II} > \text{I} > \text{III}$
  - $\text{III} > \text{I} > \text{II}$
- 2.5 g of the carbonate of a metal was treated with 100 mL of 1 N  $\text{H}_2\text{SO}_4$ . After the completion of the reaction, the solution was boiled off to expel  $\text{CO}_2$  and was then titrated against 1 N  $\text{NaOH}$  solution. If the equivalent weight of the metal is 20, the volume of alkali that would be consumed is
  - 50 mL
  - 25 mL
  - 75 mL
  - 100 mL
- A polymer formed by coordination polymerisation is
  - low density polythene
  - high density polythene
  - nylon-6
  - dacron.
- A compound which does not give a positive Lassaigne's test for nitrogen is
  - urea
  - hydrazine
  - azobenzene
  - phenyl hydrazine.
- The correct order of increasing ionic character?
  - $\text{BeCl}_2 < \text{MgCl}_2 < \text{CaCl}_2 < \text{BaCl}_2$
  - $\text{BeCl}_2 < \text{MgCl}_2 < \text{BaCl}_2 < \text{CaCl}_2$
  - $\text{BeCl}_2 < \text{BaCl}_2 < \text{MgCl}_2 < \text{CaCl}_2$
  - $\text{BaCl}_2 < \text{CaCl}_2 < \text{MgCl}_2 < \text{BeCl}_2$
- Which of the following metal oxides is antiferromagnetic in nature?
  - $\text{MnO}_2$
  - $\text{TiO}_2$
  - $\text{NO}_2$
  - $\text{CrO}_2$
- In context with the transition elements, which of the following statements is incorrect?
  - In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.
  - In the highest oxidation states, the transition metals show basic character and form cationic complexes.
  - In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.
  - Once the  $d^5$  configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.

12. Which of the following statements is not correct?  
 (a) The efficiency of a solid catalyst depends upon its surface area.  
 (b) Catalyst operates by providing alternate path for the reaction that involves a lower energy of activation.  
 (c) Catalyst lowers the energy of activation of the forward reaction only.  
 (d) Catalyst does not affect the overall enthalpy change of the reaction.
13. There are several criteria of purity of organic compounds. Which is considered to be the best?  
 (a) Melting point  
 (b) Mixed melting point  
 (c) Colour  
 (d) Microscopic examination
14. Predict the product C obtained in the following reaction of 1-butyne.
- $$\text{CH}_3\text{CH}_2-\text{C}\equiv\text{CH} + \text{HCl} \xrightarrow{\text{B}} \xrightarrow{\text{HI}} \text{C}$$
- (a)  $\text{CH}_3-\text{CH}_2-\text{CH}_2-\overset{\text{I}}{\underset{\text{Cl}}{\text{C}}}-\text{H}$
- (b)  $\text{CH}_3-\text{CH}_2-\overset{\text{I}}{\text{CH}}-\text{CH}_2\text{Cl}$
- (c)  $\text{CH}_3-\text{CH}_2-\overset{\text{I}}{\underset{\text{Cl}}{\text{C}}}-\text{CH}_3$
- (d)  $\text{CH}_3-\overset{\text{I}}{\text{CH}}-\text{CH}_2\text{CH}_2\text{I}$
15. When  $[\text{Zn}^{2+}] = [\text{Cu}^{2+}] = 1$ , the electrical potential of Daniell cell is 1.1 V. However,  
 (a) when  $E_{\text{ext}} < 1.1$  V, current flows from Zn to Cu  
 (b) when  $E_{\text{ext}} = 1.1$  V, current flows from Cu to Zn  
 (c) when  $E_{\text{ext}} > 1.1$  V, current flows from Zn to Cu  
 (d) when  $E_{\text{ext}} < 1.1$  V, electrons flow from Cu to Zn.
16. In which of the following the hydration energy is higher than the lattice energy?  
 (a)  $\text{MgSO}_4$  (b)  $\text{RaSO}_4$   
 (c)  $\text{SrSO}_4$  (d)  $\text{BaSO}_4$
17.  $K_c$  for  $A + B \rightleftharpoons C + D$  is 10 at  $25^\circ\text{C}$ . If a container contains 1, 2, 3 and 4 mol per litre of A, B, C and D respectively at  $25^\circ\text{C}$ , then  
 (a) forward reaction should be favoured  
 (b) backward reaction should be favoured  
 (c) the reaction should be at equilibrium  
 (d) none of these.
18. The coordination number of a central metal atom in a complex is determined by  
 (a) the number of ligands around a metal ion bonded by sigma bonds  
 (b) the number of ligands around a metal ion bonded by pi-bonds  
 (c) the number of ligands around a metal ion bonded by sigma and pi-bonds both  
 (d) the number of only anionic ligands bonded to the metal ion.
19. For carbocations,  
 $\text{CH}_3-\text{O}-\overset{+}{\text{C}}\text{H}_2$ ,  $\text{CH}_3-\text{NH}-\overset{+}{\text{C}}\text{H}_2$ ,  $\text{CH}_3-\text{S}-\overset{+}{\text{C}}\text{H}_2$   
 (A) (B) (C)  
 Correct order of stability is  
 (a)  $A > B > C$  (b)  $C > B > A$   
 (c)  $B > A > C$  (d)  $C > A > B$
20. Zn gives  $\text{H}_2$  gas with  $\text{H}_2\text{SO}_4$  and HCl but not with  $\text{HNO}_3$  because  
 (a) Zn acts as an oxidising agent when reacted with  $\text{HNO}_3$   
 (b)  $\text{HNO}_3$  is weaker acid than  $\text{H}_2\text{SO}_4$  and HCl  
 (c) in electrochemical series Zn is above hydrogen  
 (d)  $\text{NO}_3^-$  ion is reduced in preference to hydronium ion.
21. Calculate the energy of first stationary state of  $\text{Li}^{2+}$  if ionisation energy of  $\text{He}^+$  is  $19.6 \times 10^{-18} \text{ J atom}^{-1}$ .  
 (a)  $176.4 \times 10^{-18} \text{ J atom}^{-1}$   
 (b)  $4.9 \times 10^{-18} \text{ J atom}^{-1}$   
 (c)  $8.7 \times 10^{-18} \text{ J atom}^{-1}$   
 (d)  $44.1 \times 10^{-18} \text{ J atom}^{-1}$
22. The dipole moment of *o*, *p* and *m*-dichlorobenzene will be in the order  
 (a)  $o > p > m$  (b)  $p > o > m$   
 (c)  $m > o > p$  (d)  $o > m > p$
23. Fluorine is not tested by Beilstein's test because  
 (a) it does not react with copper  
 (b) copper fluoride is not volatile  
 (c)  $\text{F}_2$  is evolved as a gas  
 (d) none of these.
24. Which of the following is most basic?  
 (a)  $\text{Ce}(\text{OH})_3$  (b)  $\text{Lu}(\text{OH})_3$   
 (c)  $\text{Yb}(\text{OH})_3$  (d)  $\text{Tb}(\text{OH})_3$
25.  $A + \text{Na}_2\text{CO}_3 \rightarrow B + C$   
 $\downarrow$   
 $\text{CO}_2 \rightarrow$  Milky cloud, C  
 The chemical formulae of A, B and C are

A	B	C
(a) $\text{Ca}(\text{OH})_2$	$\text{NaOH}$	$\text{CaCO}_3$
(b) $\text{NaOH}$	$\text{Ca}(\text{OH})_2$	$\text{CaCO}_3$
(c) $\text{NaOH}$	$\text{CaO}$	$\text{CaCO}_3$
(d) $\text{CaO}$	$\text{Ca}(\text{OH})_2$	$\text{NaOH}$

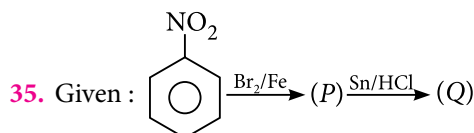
26. Which of the following is true?  
 (a) *tert*-Butoxide is a stronger base as well as stronger nucleophile than ethoxide.  
 (b) *tert*-Butoxide is a weaker base but stronger nucleophile than ethoxide.  
 (c) *tert*-Butoxide is a stronger base, but weaker nucleophile than ethoxide.  
 (d) *tert*-Butoxide and ethoxide are equally strong bases as well as strong nucleophiles.
27. Which one of the following information can be obtained on the basis of Le-Chatelier's principle?  
 (a) Dissociation constant of a weak acid.  
 (b) Entropy change in a reaction.  
 (c) Equilibrium constant of a chemical reaction.  
 (d) None of these.

28. The compound  is used as

- (a) antiseptic (b) antibiotic  
 (c) analgesic (d) pesticide.
29. The average osmotic pressure of human blood is 7.8 bar at 27°C. What is the concentration of an aqueous NaCl solution that could be used in the blood stream?  
 (a) 0.16 mol/litre (b) 0.32 mol/litre  
 (c) 0.60 mol/litre (d) 0.45 mol/litre
30. Ethylene oxide when treated with Grignard reagent yields  
 (a) primary alcohol (b) secondary alcohol  
 (c) tertiary alcohol (d) cyclopropyl alcohol.
31. The third line of the Balmer series, in the emission spectrum of the hydrogen atom, is due to the transition from the  
 (a) fourth Bohr orbit to the first Bohr orbit  
 (b) fifth Bohr orbit to the second Bohr orbit  
 (c) sixth Bohr orbit to the third Bohr orbit  
 (d) seventh Bohr orbit to the third Bohr orbit.
32. Hybridisation in  $\dot{\text{C}}\text{H}_3$ ,  $\overset{+}{\text{C}}\text{H}_3$  and  $\bar{\text{C}}\text{H}_3$  are respectively  
 (a)  $sp^2$ ,  $sp^2$ ,  $sp^3$  (b)  $sp^2$ ,  $sp^3$ ,  $sp^3$   
 (c)  $sp^3$ ,  $sp^3$ ,  $sp^2$  (d)  $sp^3$ ,  $sp^2$ ,  $sp^2$
33. Which one of the following pairs is not correctly matched?

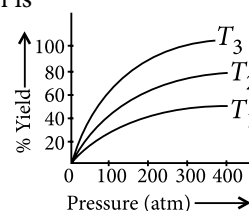
- (a)  $>\text{C}=\text{O} \xrightarrow{\text{Clemmensen's reduction}} >\text{CH}_2$   
 (b)  $>\text{C}=\text{O} \xrightarrow{\text{Wolff-Kishner reduction}} >\text{CHOH}$   
 (c)  $-\text{COCl} \xrightarrow{\text{Rosenmund's reduction}} \text{CHO}$   
 (d)  $-\text{C}\equiv\text{N} \xrightarrow{\text{Stephen reduction}} \text{CHO}$

34. Which of the following acids does not exhibit optical isomerism?  
 (a) Maleic acid (b)  $\alpha$ -amino acids  
 (c) Lactic acid (d) Tartaric acid



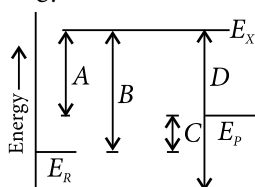
The products P and Q are

- | P                                   | Q                          |
|-------------------------------------|----------------------------|
| (a) <i>p</i> -bromonitrobenzene     | <i>p</i> -bromoaniline     |
| (b) <i>o</i> -bromonitrobenzene     | <i>o</i> -bromoaniline     |
| (c) <i>o,p</i> -dibromonitrobenzene | <i>o,p</i> -dibromoaniline |
| (d) <i>m</i> -bromonitrobenzene     | <i>m</i> -bromoaniline     |
36. The preparation of ammonia by Haber's process is an exothermic reaction. If the precipitation follows the following temperature-pressure relationship for its % yield, then for temperatures  $T_1$ ,  $T_2$  and  $T_3$  the correct option is



- (a)  $T_3 > T_2 > T_1$   
 (b)  $T_1 > T_2 > T_3$   
 (c)  $T_1 = T_2 = T_3$   
 (d) nothing could be predicted.
37. The prefixes *syn* and *anti* are used to denote  
 (a) structural isomers  
 (b) conformational isomers  
 (c) geometrical isomers  
 (d) optical isomers.
38. Half-life period of a first order reaction is 1386 s. The specific rate constant of the reaction is  
 (a)  $0.5 \times 10^{-2} \text{ s}^{-1}$  (b)  $0.5 \times 10^{-3} \text{ s}^{-1}$   
 (c)  $5.0 \times 10^{-2} \text{ s}^{-1}$  (d)  $5.0 \times 10^{-3} \text{ s}^{-1}$
39. The bond order of a molecule is given by  
 (a) the difference between the number of electrons in bonding and antibonding orbitals  
 (b) total number of electrons in bonding and antibonding orbitals

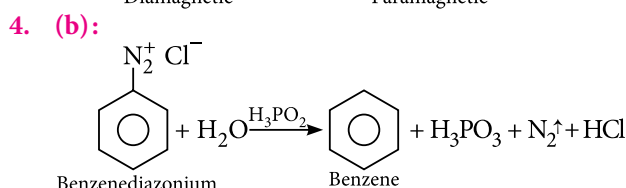
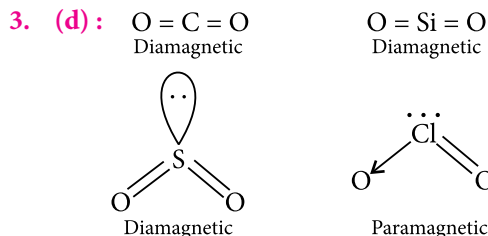
- (c) twice the difference between the number of electrons in bonding and antibonding orbitals  
 (d) half the difference between number of electrons in bonding and antibonding orbitals.
40. The order of increasing freezing points for the solutions of following solutes :  
 $C_2H_5OH$ ,  $Ba_3(PO_4)_2$ ,  $Na_2SO_4$ ,  $KCl$  and  $Li_3PO_4$
- (a)  $Ba_3(PO_4)_2 < Na_2SO_4 < Li_3PO_4 < C_2H_5OH < KCl$   
 (b)  $Ba_3(PO_4)_2 < C_2H_5OH < Li_3PO_4 < Na_2SO_4 < KCl$   
 (c)  $C_2H_5OH < KCl < Na_2SO_4 < Ba_3(PO_4)_2 < Li_3PO_4$   
 (d)  $Ba_3(PO_4)_2 < Li_3PO_4 < Na_2SO_4 < KCl < C_2H_5OH$
41. Impure nickel is purified by  
 (a) the Mond's carbonyl process  
 (b) electrolytic refining  
 (c) the van-Arkel process  
 (d) the zone refining process.
42. Which process is suitable for the purification of aniline?  
 (a) Vacuum distillation  
 (b) Steam distillation  
 (c) Fractional distillation  
 (d) Fractional crystallisation
43. In the accompanied diagram,  $E_R$ ,  $E_P$  and  $E_X$  represent the energy of the reactants, products and activated complex respectively. Which of the following is the activation energy for the backward reaction?



- (a) A      (b) B      (c) C      (d) D
44. 1.00 g of a non-electrolyte solute (molar mass  $250 \text{ g mol}^{-1}$ ) was dissolved in 51.2 g of benzene. If the freezing point depression constant,  $K_f$  of benzene is  $5.12 \text{ K kg mol}^{-1}$ , the freezing point of benzene will be lowered by  
 (a) 0.2 K                      (b) 0.4 K  
 (c) 0.3 K                      (d) 0.5 K
45. What formal charges are present in the molecule  $C_6H_5C \equiv N - O$ ?  
 (a) N is - 1 and C is + 1  
 (b) N is + 1 and C is - 1  
 (c) O is - 1 and C is + 1  
 (d) O is - 1 and N is + 1

## SOLUTIONS

1. (b): Higher the stability constant of ligand, lesser is the dissociation of complex and more is its stability. Hence, stronger is the ligand.
2. (d): Compound (d) has two dissimilar chiral carbon atoms hence has maximum stereoisomers. (In option (c) one meso form will exist).



5. (b): The *n*-alkanes have the most extended structure and larger surface area in comparison to branched chain isomers having compact structure (as the shape approaches that of a sphere in the branched chain isomers). Thus, intermolecular forces are weaker in branched chain isomers, therefore, they have lower boiling points in comparison to straight chain isomers *i.e.*, higher the branching, lower the boiling point, hence, the order is I > II > III.

6. (a): Equivalent weight of metal carbonate =  $20 + 30 = 50$   
 $2.5 \text{ g of metal carbonate} = \frac{2.5}{50} = 0.05 \text{ eq.}$   
 Number of equivalents of  $H_2SO_4$  that would react = 0.05  
 Number of equivalents of  $H_2SO_4$  taken =  $\frac{100 \times 1}{1000} = 0.1$   
 Number of equivalents of  $H_2SO_4$  which remains unreacted =  $0.1 - 0.05 = 0.05 \text{ eq.}$   
 $\therefore$  Number of equivalents of alkali consumed = 0.05 eq.  
 $\text{meq.} = \text{Normality} \times \text{Volume (in mL)}$   
 $\therefore 1.0 \times V = 0.05 \times 1000$   
 $V = \frac{0.05 \times 1000}{1.0} = 50 \text{ mL}$

7. (b): High density polythene is obtained by coordination polymerisation.
8. (b): Lassaigne's test for nitrogen fails if the nitrogen containing compound does not contain carbon.

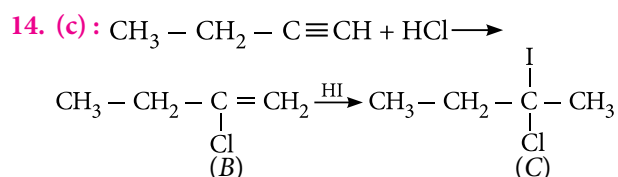
9. (a): Ionic character of compounds of metals increases down the group.

10. (a):  $\text{MnO}_2$  is antiferromagnetic in nature.

11. (b): When the transition metals are in their highest oxidation state, they no longer have tendency to give away electrons, thus they are not basic but show acidic character and form anionic complexes.

12. (c): Catalyst affects the energy of activation of both forward as well as backward reaction.

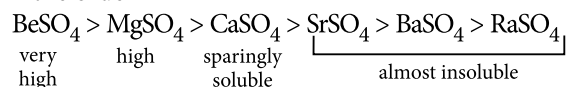
13. (b)



According to Markownikoff's rule, during hydrohalogenation to unsymmetrical alkene, the negative part of the addendum adds to less hydrogenated (*i.e.* more substituted) carbon atom.

15. (c)

16. (a): When hydration energy exceeds lattice energy, the compound becomes soluble in water. The solubility of alkaline earth metal sulphates decreases in the order



The solubilities of  $\text{BeSO}_4$  and  $\text{MgSO}_4$  are due to high energy of solvation of smaller  $\text{Be}^{2+}$  and  $\text{Mg}^{2+}$  ions.

17. (a): For the reaction  $A + B \rightleftharpoons C + D$

$$Q = \frac{[C][D]}{[A][B]} = \frac{3 \times 4}{1 \times 2} = 6$$

But  $K_c = 10$ ; as  $Q < K_c$  thus forward reaction should occur.

18. (a): The number of atoms of the ligands that are directly bound to the central metal atom or ion by coordinate bonds is known as the coordination number of the metal atom or ion.

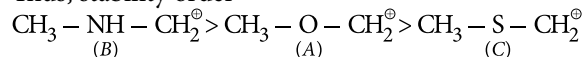
Coordination number of metal = number of  $\sigma$  bonds formed by metal with ligands.

19. (c): Due to resonance effect stability of carbocation increases as

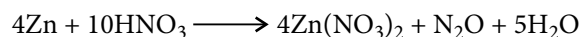
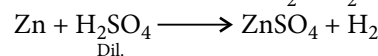


As compared to O electronegativity of nitrogen is lesser. Thus, cation B is more stable than A and C is least stable due to absence of resonance effect.

Thus, stability order



20. (d):  $\text{Zn} + 2\text{HCl} \longrightarrow \text{ZnCl}_2 + \text{H}_2$



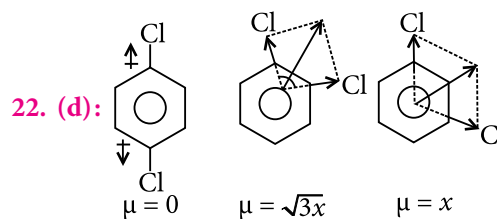
Thus,  $\text{NO}_3^-$  ions are reduced to  $\text{N}_2\text{O}$  whereas in first two reactions  $\text{H}^+$  is reduced to  $\text{H}_2$ .

21. (d):  $E_1$  *i.e.*, I.E. of  $\text{He}^+ = E_1$  of  $\text{H} \times 2^2$

$E_1$  *i.e.*, I.E. of  $\text{Li}^{2+} = E_1$  of  $\text{H} \times 3^2$

$$\frac{E_1 \text{ of } \text{Li}^{2+}}{E_1 \text{ of } \text{He}^+} = \frac{9}{4}$$

$$E_1 \text{ of } \text{Li}^{2+} = \frac{9}{4} \times 19.6 \times 10^{-18} \\ = 44.1 \times 10^{-18} \text{ J atom}^{-1}$$



In *p*-dichlorobenzene, two C-Cl dipoles cancel each other

$\therefore \mu = 0$ .

In *o*-dichlorobenzene, the two C-Cl dipoles (say  $x$ ) are inclined at an angle of  $60^\circ$ . Therefore, according to parallelogram law of forces, the resultant

$$= \sqrt{x^2 + x^2 + 2x^2 \times \cos 60^\circ} \\ = \sqrt{x^2 + x^2 + 2x^2 \times 1/2} = \sqrt{3x^2} = \sqrt{3}x$$

In *m*-dichlorobenzene, the two dipoles are inclined to each other at an angle of  $120^\circ$ , therefore, resultant

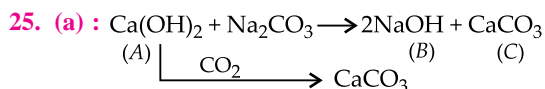
$$= \sqrt{x^2 + x^2 + 2x^2 \times \cos 120^\circ} \\ = \sqrt{x^2 + x^2 + 2x^2 \times (-1/2)} = \sqrt{x^2} = x$$

Thus, the decreasing order of dipole moments is  $o > m > p$ .

23. (b): Fluoride cannot be detected by this test because the  $\text{CuF}_2$  formed loses fluorine only at a molten stage above  $950^\circ\text{C}$ , which is difficult to be attained in the lab *i.e.*, it is not volatile and hence, the presence of fluoride cannot be detected by this test.

24. (a):  $\text{Ce}(\text{OH})_3$  is the strongest base. As the size of the lanthanide ions decreases from  $\text{Ce}^{3+}$  to  $\text{Lu}^{3+}$ , the covalent character of  $M - \text{OH}$  bond increases and hence, the basic strength decreases.

Thus,  $\text{Ce}(\text{OH})_3$  is most basic while  $\text{Lu}(\text{OH})_3$  is least basic.



26. (c)

27. (d) : According to Le-Chatelier's principle, if a system at equilibrium is subjected to change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect. So, it can predict only the direction of equilibrium.

28. (c) : The given compound is aspirin which is used as an analgesic.

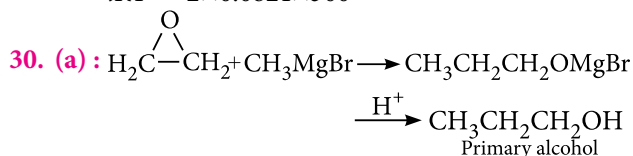
29. (a) :  $\pi = 7.8 \text{ bar} = 7.8 \text{ atm}$  (1 bar = 1 atm)

$$T = 273 + 27 = 300 \text{ K}$$

$i = 2$  (for NaCl)

$$\pi = iCRT$$

$$C = \frac{\pi}{iRT} = \frac{7.8}{2 \times 0.0821 \times 300} = 0.16 \text{ mol/L.}$$



31. (b) : For Balmer series,  $n_1 = 2$

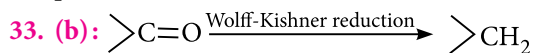
For  $n^{\text{th}}$  line in any series,  $n_2 = n_1 + n$

$\therefore$  For 3<sup>rd</sup> line in Balmer series  $n_2 = 2 + 3 = 5$ .

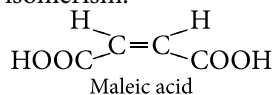
32. (a) :  $\dot{\text{C}}\text{H}_3$  (methyl free radical) has planar structure with  $sp^2$  hybridisation of 'C' atom. The odd electron is present in unhybridised  $2p_z$  orbital.

$\overset{+}{\text{C}}\text{H}_3$  (methyl carbonium ion) also has trigonal planar structure ( $sp^2$ ).

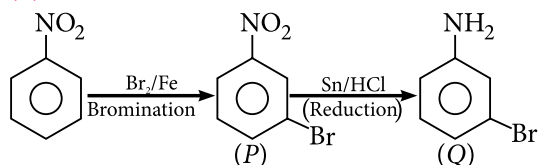
$\overset{-}{\text{C}}\text{H}_3$  (methyl carbanion) has tetrahedral structure ( $sp^3$ ) and one of the hybrid orbital contains the lone pair of electrons.



34. (a) : Maleic acid shows geometrical isomerism and not optical isomerism.



35. (d) :



$-\text{NO}_2$  group is a deactivating and  $m$ -directing group so it directs the incoming  $\text{Br}^-$  ion to the  $m$ -position thereby leading to the formation of bromonitrobenzene. Upon reduction with  $\text{Sn}/\text{HCl}$ , the  $-\text{NO}_2$  group reduces to  $-\text{NH}_2$  i.e., the final product is  $m$ -bromoaniline.

36. (b) : For exothermic reactions as temperature increases yield decreases thus

$$T_1 > T_2 > T_3$$

37. (c) : *Syn* and *anti* prefixes are used to denote geometrical isomers involving either  $\text{C}=\text{N}$  or  $\text{N}=\text{N}$  bond.

38. (b) : Given,  $t_{1/2} = 1386 \text{ s}$

For a first order reaction,

$$t_{1/2} = \frac{0.693}{k} \quad (k = \text{rate constant})$$

$$\Rightarrow 1386 = \frac{0.693}{k}$$

$$\Rightarrow k = 5 \times 10^{-4} \text{ s}^{-1} = 0.5 \times 10^{-3} \text{ s}^{-1}$$

39. (d) : Bond order (B.O.) =  $\frac{1}{2}(N_b - N_a)$ .

40. (d) :  $\Delta T_f \propto i$

$i$  for  $\text{C}_2\text{H}_5\text{OH} = 1$

$i$  for  $\text{KCl} = 2$

$i$  for  $\text{Ba}_3(\text{PO}_4)_2 = 5$

$i$  for  $\text{Na}_2\text{SO}_4 = 3$

$i$  for  $\text{Li}_3\text{PO}_4 = 4$

Thus, depression in freezing point will be in order:

$\text{C}_2\text{H}_5\text{OH} < \text{KCl} < \text{Na}_2\text{SO}_4 < \text{Li}_3\text{PO}_4 < \text{Ba}_3(\text{PO}_4)_2$

Thus, freezing point will be in the order

$\text{Ba}_3(\text{PO}_4)_2 < \text{Li}_3\text{PO}_4 < \text{Na}_2\text{SO}_4 < \text{KCl} < \text{C}_2\text{H}_5\text{OH}$

41. (a)

42. (b) : Aniline is steam volatile.

43. (a) : For backward reaction, activation energy is the energy difference between product and activated complex.

$$44. (b) : m = \frac{1000 \times K_f \times w}{W \times \Delta T} \quad \text{or} \quad 250 = \frac{1000 \times 5.12 \times 1}{51.2 \times \Delta T}$$

$$\therefore \Delta T = \frac{1000 \times 5.12 \times 1}{51.2 \times 250} = 0.4 \text{ K}$$

45. (d) : For nitrogen, formal charge =  $5 - \frac{1}{2}(8) = +1$

For oxygen, formal charge =  $6 - 6 - \frac{1}{2}(2) = -1$ .

□□

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# PRACTICE QUESTIONS ON Assertion & Reason

# AIIMS

TIME TO THINK SMART!

❖ PHYSICAL CHEMISTRY ❖ ORGANIC CHEMISTRY  
❖ INORGANIC CHEMISTRY

**Directions :** In the following questions, a statement of Assertion is followed by a statement of Reason. Mark the correct choice as :

- If both assertion and reason are true and reason is the correct explanation of assertion.
- If both assertion and reason are true but reason is not the correct explanation of assertion.
- If assertion is true but reason is false.
- If both assertion and reason are false.

## PHYSICAL CHEMISTRY

- Assertion:** The cell potential of mercury cell is 1.35 V which remains constant.  
**Reason :** In mercury cell, the electrolyte is a paste of HgO and ZnO.
- Assertion :** The transition of electrons  $n_3 \rightarrow n_2$  in H atom will emit greater energy than  $n_4 \rightarrow n_3$ .  
**Reason :**  $n_3$  and  $n_2$  are closer to nucleus than  $n_4$ .
- Assertion :** If more and more solute is added to a solvent, the freezing point of the solution keeps on becoming higher and higher.  
**Reason :** Presence of large amount of the solid solute does not allow the solution to freeze.
- Assertion :** van der Waals' equation explains the behaviour of ideal gases.  
**Reason :** Ideal gases can only be compressed.
- Assertion:** In an electrochemical cell, concentration of the anodic half-cell increases while that of cathodic half-cell decreases when the two electrodes are joined by a wire.  
**Reason :** At anodic half-cell metal oxidises to metal ion dissolving the ion in the solution thus, its concentration increases at anode and decreases at cathode due to reduction of metal ions.

- Assertion :** Most probable velocity is the velocity possessed by maximum fraction of molecules at the same temperature.  
**Reason :** On collision, more and more molecules acquire higher speed at the same temperature.
- Assertion :** The molecules on the surface have lesser energy.  
**Reason :** During adsorption, the surface of solid is in a state of relaxation.
- Assertion :** Enthalpy of formation of O<sub>2</sub> molecule at 298 K and 1 atm pressure is zero.  
**Reason :** Enthalpy of formation of all the elements at STP is zero.
- Assertion :** If the solubility of AgCl in water is  $1.5 \times 10^{-10}$ , then its solubility in 0.01M NaCl aqueous solution is  $1.5 \times 10^{-8}$  M.  
**Reason :** NaCl dissociates completely so  $[Cl^-] = 0.01$  M.
- Assertion :** In caesium chloride crystals, Cs<sup>+</sup> ions adopt *bcc* arrangement.  
**Reason :** For *bcc* arrangement, number of tetrahedral sites is double the number of atoms in the packing.

## ORGANIC CHEMISTRY

- Assertion:** In the Friedel-Crafts acylation of benzene, the attacking electrophile is an acyl carbocation ( $RCO^+$ ).  
**Reason :** The reaction of benzene with  $CH_3CH_2CH_2Cl$  in presence of  $AlCl_3$  gives *n*-propylbenzene.
- Assertion :** Vinylic halides are reactive towards nucleophilic substitution reactions.  
**Reason :** Reactivity is due to the polarity of carbon halogen bond.



- 13. Assertion :** Hydration of 3, 3-dimethyl-1-butene with acid gives 2,3-dimethyl-2-butanol.  
**Reason :** Hydration of alkenes with acids occur through carbanion formation.
- 14. Assertion :** Ketones do not react with monohydric alcohols but do so with dihydric alcohols to give cyclic ketals.  
**Reason :** Ketal formation is used to protect the carbonyl group in organic synthesis.
- 15. Assertion :** Formic acid is a reducing agent.  
**Reason :** Formic acid is used as preservative for fruits.
- 16. Assertion :** Oxidation of 1-nitro naphthalene gives *o*-nitro phthalic acid whereas 1-amino naphthalene on oxidation gives phthalic acid.  
**Reason :** An amino group attached to the benzene ring makes it resistant to oxidation whereas nitro group makes the benzene ring susceptible to oxidation.
- 17. Assertion :** Chemical substances which are used to check pregnancy in women are called antifertility drugs.  
**Reason :** Antifertility drugs are also called birth control drugs or oral contraceptives.
- 18. Assertion :** Orlon is used as synthetic fibres.  
**Reason :** The monomer of orlon is vinyl chloride.
- 19. Assertion :** Chloroform and benzene form a pair of miscible liquids and they are separated by fractional distillation.  
**Reason :** Boiling point of benzene is less than that of chloroform.
- 20. Assertion :** Amino acids mostly exist as dipolar ions.  
**Reason :** The dipolar structure of amino acids is known as zwitterion or internal salt.
- 23. Assertion :** Decreasing order of van der Waals' radii is : Cl > N > O > H.  
**Reason :** van der Waals' radii increase as the number of energy level increases and decrease as nuclear charge increases.
- 24. Assertion :** Geometry of SF<sub>4</sub> molecule can be termed as distorted tetrahedron, a folded square or see-saw.  
**Reason :** Four fluorine atoms surround or form bond with sulphur molecule.
- 25. Assertion :** Sodium reacts with oxygen to form Na<sub>2</sub>O<sub>2</sub> whereas potassium reacts with oxygen to form KO<sub>2</sub>.  
**Reason :** Potassium is more reactive than sodium.
- 26. Assertion :** The maximum and minimum oxidation number of sulphur are - 2 and +6 respectively.  
**Reason :** SO<sub>2</sub> behaves both as an oxidising as well as reducing agent. However, SO<sub>3</sub> can only as an oxidising agent.
- 27. Assertion :** There is a dip in the melting point of Mn in the first transition series.  
**Reason :** It has high enthalpy of atomization.
- 28. Assertion :** A nearly tetrahedral arrangement of the orbitals about the oxygen atom allows each water molecule to form hydrogen bonds with as many as four neighbouring water molecules.  
**Reason :** In ice each water molecule form four hydrogen bonds as each molecule is fixed in the space.
- 29. Assertion :** BF<sub>3</sub> molecule has zero dipole moment.  
**Reason :** F is electronegative and B - F bonds are polar in nature.

### INORGANIC CHEMISTRY

- 21. Assertion :** Isomorphous substances form crystals of same shape and can grow in saturated solution of each other.  
**Reason :** They have similar constitution and chemical formulae.
- 22. Assertion :** Zinc is obtained from the roasted or calcined ore (ZnO) by heating with calculated quantity of coal or coke in a reverberatory furnace, when C reduces the metal oxide to free metal.  
**Reason :** The process of extracting the metal by reduction of its oxide ore with carbon is called smelting.
- 30. Assertion :** The degree of complex formation in actinides decreases in the order M<sup>4+</sup> > MO<sub>2</sub><sup>2+</sup> > M<sup>3+</sup> > MO<sub>2</sub><sup>+</sup>.  
**Reason :** Actinides form complexes with π-bonding ligands such as alkyl phosphines and thioethers.

### SOLUTIONS

1. (b) : The overall reaction in a mercury cell is given as :  

$$\text{Zn}_{(s)} + \text{HgO}_{(s)} \rightarrow \text{ZnO}_{(s)} + \text{Hg}_{(l)}$$
 The cell potential remains constant during its life as the overall reaction does not involve any ion in solution whose concentration may change during its life time.

2. (a) : The difference between the energies of adjacent energy levels decreases as we move away from the nucleus. Thus in H atom

$$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 \dots$$

3. (d) : The freezing point keeps on becoming lower and lower when more and more solute is added to a solvent. Depression in freezing point is a colligative property as it depends on the number of particles present in solution, so solution will freeze more rapidly on adding large amount of solute.

4. (d) : van der Waals' equation

$$\left( P + \frac{an^2}{V^2} \right) (V - nb) = nRT \text{ (for } n \text{ mol of gas) explains}$$

the behaviour of real gases, where  $a$  and  $b$  are van der Waals' constants, whose values depend on the nature of the gas. Real gases can be compressed.

5. (a)

6. (c) : On collision, some molecules are speeded up while others are slowed down.

7. (d) : The molecules on the surface, have higher energy than those inside.

The surface of a solid or a liquid is in a state of strain or tension on account of the unbalanced or residual forces.

8. (c) : Enthalpy of formation of the most stable allotrope of the element is taken as zero.

9. (b) : NaCl dissociates completely and so in 0.01 M NaCl solution,  $[Cl^-] = 0.01$  M.

If  $s$  is the solubility of AgCl in  $\text{mol L}^{-1}$  then  $[Ag^+] = [Cl^-] = s \text{ mol L}^{-1}$

and hence total  $[Cl^-] = s + (0.01) \text{ mol L}^{-1} \approx 0.01 \text{ mol L}^{-1}$

$$\therefore K_{sp} = [Ag^+][Cl^-] = s(0.01)$$

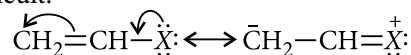
$$\therefore s = \frac{1.5 \times 10^{-10}}{0.01} = 1.5 \times 10^{-8} \text{ mol L}^{-1}$$

10. (c) : Number of tetrahedral sites is double the number of atoms in the packing for a closed packed arrangement ( $hcp$  and  $ccp$ ) and not for  $bcc$ .

11. (c) : In the reaction of benzene with  $CH_3CH_2CH_2Cl$  in presence of  $AlCl_3$ , attacking species is secondary carbocation  $CH_3\overset{+}{C}HCH_3$  and not primary carbocation  $CH_3CH_2\overset{+}{C}H_2$ . Therefore, the product obtained is isopropyl benzene.

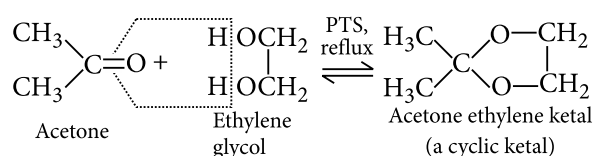
12. (d) : Vinylic halides are unreactive towards nucleophilic substitution reactions because of resonance

effect. Resonance gives rise to partial double bond character to the carbon-halogen bond making it stronger and therefore more difficult to cleave than a  $C_{sp^3} - X$  bond. It also reduces the polarity of the carbon-halogen bond thereby making heterolysis difficult.



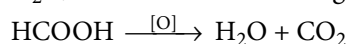
13. (c) : Hydration of alkenes by acids occur through carbocation intermediate. The initially formed carbocation ( $2^\circ$ ) being less stable rearranges to the more stable carbocation ( $3^\circ$ ), which in turn gives 2, 3-dimethyl-2-butanol.

14. (b) :

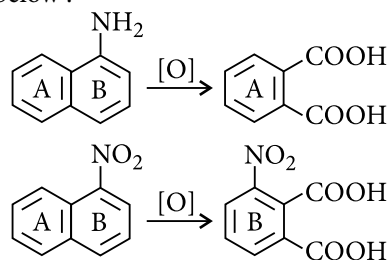


The ketals can be decomposed back to the original ketone by treatment with acid.

15. (b) : Formic acid is readily oxidised to  $CO_2$  and  $H_2O$ , and thus acts as a strong reducing agent.



16. (c) : An amino group increases the electron density in the benzene ring to which it is attached thereby making it susceptible to oxidation while a nitro group decreases the electron density in the benzene ring to which it is attached thereby making it resistant to oxidation. Instead, the other benzene ring gets oxidised giving  $o$ -nitrophenolic acid as shown below :

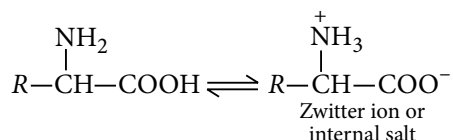


17. (b)

18. (c) : The monomer of orlon is acrylonitrile.

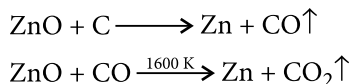
19. (c) : Chloroform (b.pt.  $60^\circ C$ ) and benzene (b.pt.  $80^\circ C$ ) can be separated by fractional distillation since the difference in boiling points is very less.

20. (b): The  $-\text{COOH}$  group and  $-\text{NH}_2$  group of amino acids neutralise each other involving the transfer of a proton from the  $-\text{COOH}$  group to the  $-\text{NH}_2$  group within the molecule. So, amino acids largely exist as dipolar ions.



21. (a): Examples of isomorphous compounds are  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{SeO}_4$  (valency of S, Cr, Se=6) and  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (valency of Zn, Mg, Fe = 2).

22. (b): The reactions involved are:



23. (a): As number of energy shells for H, O, N and Cl is 1, 2, 2 and 3 respectively so van der Waals' radius of H is the smallest and Cl is the biggest. Both O and N have two energy levels but the nuclear charge on O (+8) is higher than that of N (+7). Thus, the van der Waals' radius of N is bigger than that of O.  
So, the decreasing order is:  $\text{Cl} > \text{N} > \text{O} > \text{H}$ .

24. (b):  $\text{SF}_4$  has five electron pairs whose arrangement should be trigonal bipyramidal according to VSEPR theory. Two structures are possible.



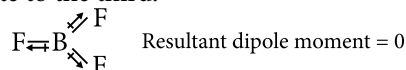
lone pair in the axial position (three *l.p.-b.p.* repulsion at  $90^\circ$ )      lone pair in the equatorial position (two *l.p.-b.p.* repulsions)

25. (b):  $\text{K}^+$  being larger in size than  $\text{Na}^+$  has a weaker positive field around it which cannot prevent the conversion of peroxide ion ( $\text{O}_2^{2-}$ ) to superoxide ion ( $\text{O}_2^-$ ).
26. (b): Since oxidation number of S in  $\text{SO}_2$  is +4, so, it can be either increased or decreased (minimum O.N. of S is -2 and maximum O.N. of S is +6). Therefore,  $\text{SO}_2$ , behaves both as an oxidising as well as a reducing agent. On the contrary, the oxidation number of S in  $\text{SO}_3$  is +6 which can only be decreased. Therefore,  $\text{SO}_3$  can act only as an oxidising agent.

27. (c): Mn has exactly half-filled *d*-orbitals so its electronic configuration is stable. Electrons are held tightly by the nucleus and this results in less delocalisation of electrons and therefore, metallic bond is weaker than the previous element.

28. (a): At any given instant in liquid water at room temperature, each water molecule forms hydrogen bonds with an average 3.4 other water molecules. The liquid water molecules are disorganized and are in continuous motion so hydrogen bonds are constantly and rapidly broken and formed. In ice  $\text{H}_2\text{O}$  molecules are, however fixed in the space lattice.

29. (b):  $\text{BF}_3$  is  $sp^2$  hybridized. Dipole moment is a vector quantity. The three bond moments give a net sum of zero, as the resultant of any two is equal and opposite to the third.



30. (b): Higher the charge on the metal ion, smaller is the ionic size and more is the complex forming ability. Thus, the degree of complex formation decreases in the order  $M^{4+} > \text{MO}_2^{2+} > M^{3+} > \text{MO}_2^+$ . The higher tendency of complex formation of  $\text{MO}_2^{2+}$  as compared to  $M^{3+}$  is due to high concentration of charge on metal atom *M* in  $\text{MO}_2^{2+}$ .

□□

### EXAM DATES 2016

JEE Main	:	3 <sup>rd</sup> April (offline), 9 <sup>th</sup> & 10 <sup>th</sup> April (online)
VITEEE	:	6 <sup>th</sup> to 17 <sup>th</sup> April
MGIMS	:	17 <sup>th</sup> April
AMU (Engg.)	:	24 <sup>th</sup> April
Kerala PET	:	25 <sup>th</sup> & 26 <sup>th</sup> April
Kerala PMT	:	27 <sup>th</sup> & 28 <sup>th</sup> April
APEAMCET	:	29 <sup>th</sup> April
(Engg. & Med.)		
AIPMT	:	1 <sup>st</sup> May
COMED K	:	8 <sup>th</sup> May
Karnataka CET	:	4 <sup>th</sup> & 5 <sup>th</sup> May
BITSAT	:	14 <sup>th</sup> to 28 <sup>th</sup> May
WB JEE	:	17 <sup>th</sup> May
JEE Advanced	:	22 <sup>nd</sup> May
AIIMS	:	29 <sup>th</sup> May
AMU (Med.)	:	1 <sup>st</sup> June
JIPMER	:	5 <sup>th</sup> June

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**Q1. How can we calculate the change in the molar Gibbs' energy if we**

- (i) treat liquid water as an incompressible fluid and
- (ii) treat water vapour as a perfect gas.

*-Geeta Rastogi, Surat (Gujarat)*

**Ans.** Gibbs' energy,  $G$  is given as :

$$G = H - TS$$

For infinitesimal change in each property, we have

$$dG = dH - TdS - SdT \quad \dots(i)$$

As we know,

Enthalpy is related to internal energy ( $U$ ) as :

$$H = U + PV$$

Then,

$$dH = dU + PdV + VdP$$

For a closed system, where there is no non-expansion work,

$$dU = TdS - PdV$$

Then, equation (i), becomes

$$\begin{aligned} dG &= (TdS - PdV) + PdV + VdP - TdS - SdT \\ dG &= VdP - SdT \quad \dots(ii) \quad (\text{At constant composition}) \end{aligned}$$

The change in molar Gibbs' energy is obtained by integrating equation (ii) at constant temperature,

$$G_m(P_f) - G_m(P_i) = \int_{P_i}^{P_f} V_m dP$$

This equation, gives the variation of molar Gibbs' energy with pressure.

Now,

(i) When liquid water is treated as incompressible fluid the molar volume becomes independent of the pressure then,

$$V_m = \text{constant}$$

Therefore,

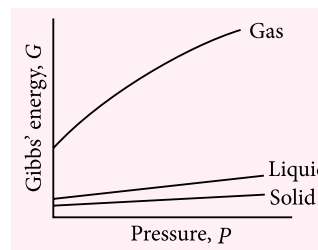
$$\begin{aligned} G_m(P_f) - G_m(P_i) &= V_m \int_{P_i}^{P_f} dp \\ &= V_m(P_f - P_i) \end{aligned}$$

(ii) When water vapour is treated as perfect gas,  $V_m$  varies with pressure and it is given as :

$$V_m = \frac{RT}{P} \quad (\text{Ideal gas equation})$$

Therefore,

$$\begin{aligned} G_m(P_f) - G_m(P_i) &= \int_{P_i}^{P_f} \frac{RT}{P} dP = RT \int_{P_i}^{P_f} \frac{dP}{P} \\ &(\because R \text{ and } T \text{ are constant}) \\ &= RT \ln \left( \frac{P_f}{P_i} \right) \end{aligned}$$



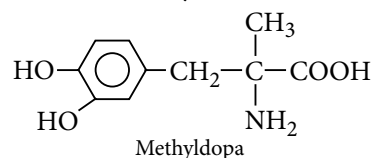
**Q2. What are Chiral drugs? Why are they so important?**

*-Tanya Mehra, (Bangaluru)*

**Ans.** Chiral drugs are the drugs that contain a single enantiomer rather than a racemate.

Chiral drugs are important in pharmaceutical industry as in many drugs the enantiomers have distinctly different effects. Then, stereoselective synthesis plays the role in the preparation of enantiomerically pure drugs.

The antihypertensive drug methyl dopa (aldomet) owes its effect exclusively to the S-isomer.



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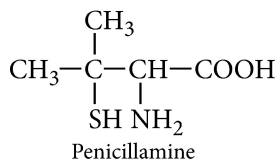


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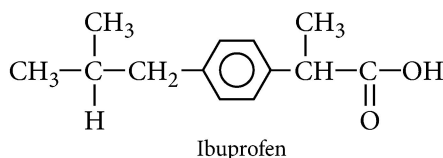
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The *S*-isomer of penicillamine is a highly potent therapeutic agent for primary chronic arthritis, whereas, *R*-isomer of penicillamine has no therapeutic action and is highly toxic.



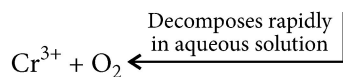
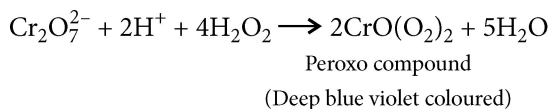
The anti-inflammatory agent ibuprofen is marketed as a racemate even though only the *S*-enantiomer is the active agent. The *R*-isomer of ibuprofen has no anti-inflammatory action and is slowly converted to the *S*-isomer in the body. A formulation of ibuprofen is solely based on the *S*-isomer however, would be more effective than the racemate.



**Q 3.** Does pH affect the reaction between dichromate ion and hydrogen peroxide? If yes, then how? Explain.

–*Sonali Arya, Agra (U.P.)*

**Ans.** Dichromate ion reacts with hydrogen peroxide in acidic medium to give different products at different pH.



In less acidic solutions,  $\text{K}_2\text{Cr}_2\text{O}_7$  and  $\text{H}_2\text{O}_2$  give violet coloured diamagnetic salts. These are thought to contain  $[\text{CrO}(\text{O}_2)(\text{OH})]^-$  (though not known).

In alkaline solution with 30%  $\text{H}_2\text{O}_2$ , a red-brown compound  $\text{K}_3\text{CrO}_8$  is formed.  $\text{K}_3\text{CrO}_8$  contains tetraperoxo species  $[\text{Cr}(\text{O}_2)_4]^{3-}$  and  $\text{Cr}(+V)$ .

**Q 4.** While explaining Schottky defect, why it is said that equal number of cations and anions are missing from the crystal lattice which is actually not applicable for  $\text{CaCl}_2$  that also shows this defect?

–*Sathish Shastry*

**Ans.** Schottky defect in a crystalline solid is the stoichiometric defect which consists of a pair of 'holes' in the crystal lattice *i.e.*, one positive ion and one negative ion are absent. This definition is generally applicable for ionic compounds that constitute monovalent cations and anions. However, for a ionic salt of type  $\text{MX}_2$  like  $\text{CaCl}_2$ , one vacant cationic site and two vacant anionic sites are there. Though, it is generally defined for ionic salts but this defect is also applicable for a metal crystal lattice. Thus, the appropriate way to define Schottky defect is as follows:

A missing atom in a metallic or covalent network crystal or a missing formula unit of ions in an ionic crystal is known as Schottky defect.

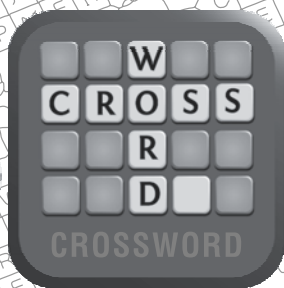


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## ACROSS

1. A polymorph of quartz. (12)
3. The theory which mainly deals with the geometry and magnetic properties of the complex was developed by \_\_\_\_\_. (7)
5. One of the allotropic forms of pure iron. (9)
8. The more stable shape of SF<sub>4</sub>. (12)
9. The process that occurs without change of enthalpy. (11)
11. The molecular fragments obtained after disconnection of an organic compound. (8)
12. Mercuric sulphide is used as a \_\_\_\_\_. (8)
16. Ligand used in organic synthesis for enantioselective transformations. (5)
17. The scientist who introduced the term isotope. (5)
19. Device used to measure the intensity of flame colouration. (17)
20. The temperature at which antiferromagnetic substance changes to paramagnetic. (4)
23. Another name of non stoichiometric solid compounds. (11)
25. In 1935, Yukawa introduced a meson theory which accounts for the stability of \_\_\_\_\_. (7)
26. An electrically neutral molecule, whose name is derived from sugar beets (*Beta vulgaris*). (7)
27. The process that take place when vapour pressure of both the solid and liquid form of a substance are equal. (8)
28. The temperature above which gas shows heating effect on expansion while below it gas cools on expansion. (9)
29. The reagent used for the conversion of alkene into diol which further gets oxidised to aldehyde or ketone. (7)

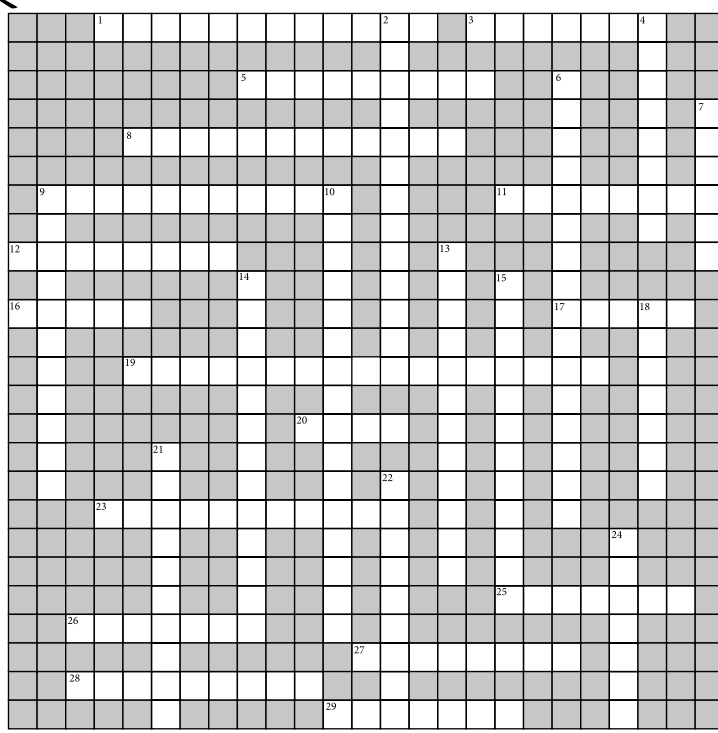
## DOWN

2. Phenomenon used to distinguish between a colloidal and true solution. (13)
4. Substance identified by Dustan's test. (8)
6. Chemical name of Sindri fertilizer. (16)
7. Rearrangement which involves conversion of hydroxamic acid into an isocyanate via intermediate of its *o*-acyl derivative. (6)

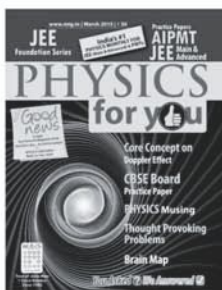
9. The element formed after  $\alpha$ -emission. (11)
10. The selective reactivity of one functional group in the presence of others is called. (16)
13. Common name of prop-1-ene-1,2,3-tricarboxylic acid found in sugarcane and beetroot. (12)
14. H<sub>4</sub>C<sub>4</sub>B<sub>2</sub>H<sub>2</sub> is a pentagonal pyramidal \_\_\_\_\_. (13)
15. The process of separation of colloidal sol into liquid phases. (12)
18. The commercial name of solid CO<sub>2</sub> which is used as refrigerant. (7)
22. Graph of entropy of a substance against temperature. (9)
21. Polyethylene glycol polymers used in ointment bases as water soluble ingredient. (10)
24. The reactive intermediate that appears after electrophilic substitution of benzene. (7)



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