# DPP No. # 11 (JEE-ADVANCED)

#### PHYSICAL / INORGANIC CHEMISTRY

Total Marks : 100	Max. Time: 80 min.

Single choice Objective (–1 negative marking) Q.1 to Q.8	(3 marks 2½ min.)	[24, 20]
Multiple choice objective (-1 negative marking) Q.9 to Q.11	(4 marks, 3 min.)	[12, 09]
Assertion and Reason ('-1' negative marking) Q.12 to Q.13	(3 marks 2½ min.)	[06, 05]
Comprehension (-1 negative marking) Q.14 to Q.19	(3 marks 2½ min.)	[18, 15]
Match Listing (-1 negative marking) Q.20	(8 marks, 3 min.)	[08, 08]
Single Digit Subjective Questions (no negative marking) Q.21 to Q.25	(4 marks 2½ min.)	[20, 12½]
Double Digit Subjective Questions (no negative marking) Q.26	(4 marks 2½ min.)	[04, 2½]
Match the column (4 vs 5) (no negative marking) Q.27	(8 marks, 8 min.)	<b>[08. 08]</b>

#### ORGANIC CHEMISTRY

Total Marks: 69 Max. Time: 57 min.

Single choice Objective (–1 negative marking) Q.28 to Q.34	(3 marks 2½ min.)	[21, 17½]
Multiple choice objective (–1 negative marking) Q.35 to Q.36	(4 marks, 3 min.)	[08, 06]
Assertion and Reason ('-1' negative marking) Q.37	(3 marks 2½ min.)	[03, 2½]
Comprehension (-1 negative marking) Q.38 to Q.40	(3 marks 2½ min.)	[09, 7½]
Single Digit Subjective Questions (no negative marking) Q.41 to Q.42	(4 marks 2½ min.)	[08, 05]
Double Digit Subjective Questions (no negative marking) Q.43	(4 marks 2½ min.)	[04, 21/2]
Match the column (4 vs 4) (no negative marking) Q.44	(8 marks, 8 min.)	[08, 08]
Match the column (5 vs 4) (no negative marking) Q.45	(8 marks, 8 min.)	[08, 08]

### PHYSICAL / INORGANIC CHEMISTRY

1. Which of the following is true when equal volume of 0.04 M NaCl solution is mixed with 0.1 M K[Ag(CN) $_2$ ].

Given:  $(K_{inst}[Ag(CN)_2]^-) = 4 \times 10^{-19}$ ,  $K_{sp}(AgCI) = 2.8 \times 10^{-10}$  and  $\sqrt[3]{5} = 1.7$ ).

- (A) More K[Ag(CN)<sub>2</sub>] will be formed.
- (B) AgCI will be precipitated.
- (C) There is no change in concentration of K+
- (D) None of these.
- 2. A solid crystallises as cubic close packing of O<sup>2-</sup> ions. A<sup>x+</sup> ions occupy 25% of the tetrahedral voids and B<sup>y+</sup> ions occupy 50% of the octahedral voids. The suitable values of 'x' and 'y' are :

(A) 
$$x = 1$$
,  $y = 3$ 

(B) 
$$x = 2$$
,  $y = 1$ 

(C) 
$$x = 3$$
,  $y = 2$ 

(D) 
$$x = 1$$
,  $y = 2$ 



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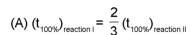
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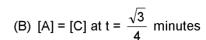
3. For the two reactions

Reaction I :  $A \rightarrow B$ Reaction II :  $C \rightarrow D$ 

following curves are plotted

which of the following is incorrect option:





(D) If both [A]<sub>0</sub> and [C]<sub>0</sub> are 1 M then 
$$(t_{50\%})_1 = \frac{1}{3} (t_{50\%})_1$$

Conc.

**4.** Following data of osmotic prssure ( $\pi$ ) is obtained when different moles  $C_{17}H_{35}COONa$  are mixed in 1L solution at 25°C:

Moles

0

0.01

0.02

0.03

0.04

$$\frac{\pi}{RT}$$
 (moles/liter)

0

0.02

0.04

0.058

0.076

Select the incorrect nature of mixture at different concentration.

- (A) Upto 0.02 M concentration, the mixture is true solution.
- (B) After 0.03 M concentration, the mixture is a colloidal.
- (C) At 0.04 M concentration, the mixture is homogenous.
- (D) The critical micelle concentration (CMC) of C<sub>17</sub>H<sub>25</sub>COONa may be 0.03 M.
- 1 mole of a compound Co(NH<sub>3</sub>)<sub>5</sub>Cl<sub>2</sub>Br gives 2 moles of curdy white precipitate, when treated with excess of AgNO<sub>3</sub> solution. Which of the following is incorrect about the compound?
  - (A) The compound may be represented as [Co(NH<sub>2</sub>)<sub>5</sub>Br] Cl<sub>2</sub>.
  - (B) The Van't Hoffs factor (i) is 3, when  $\alpha$  = 1.0
  - (C) The boiling point of 1M aq. solution of  $Co(NH_3)_5Cl_2Br$  should be triple of its value, when it were non-electrolyte.
  - (D) None of these
- 6. Calcium imide on hydrolysis gives gas (B) which on oxidation by bleaching powder gives gas (C). Gas (C) on reaction with magnesium give compound (D) which on hydrolysis gives again gas (B). Identify (B),(C) and (D).

$$(A) NH_2, N_2, Mg_2N_3$$

(C) 
$$N_2, N_2O_5, Mg(NO_3)_2$$

(D) 
$$NH_3$$
,  $NO_2$ ,  $Mg(NO_2)_2$ 

7. 
$$A + H_2O \longrightarrow B + HCI$$

Compound (A), (B) and (C) will be respectively:

- 8.\_ Which of the following fails to react significantly with air at room temperature?
  - (A) Be
- (B) Li
- (C) Ba
- (D) All of these

- 9.\* Which of the following statement(s) is/are correct?
  - (A) Chlorine dioxide (CIO<sub>2</sub>) is powerful oxidising agent but bleaching action is poorer than Cl<sub>2</sub>.
  - (B) CIO<sub>2</sub> in alkaline solution undergoes disproportionation.
  - (C) CIO<sub>2</sub> is diamagnetic in nature.
  - (D) CIO<sub>2</sub> is a yellow gas but deep red liquid.



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- 10.\* The freezing point of a 0.08 molal aqueous solution of NaHSO<sub>4</sub> is -0.372°C. Which of the following is/are correct for the given solution? Assume no hydrolysis and m ≈ M. (K<sub>f</sub> of water = 1.86 K kg/mole)
  (A) 0.2 moles of ions are present in 1 kg solvent.
  (B) Degree of dissociation of HSO<sub>4</sub><sup>-</sup> is 0.6.
  (C) Dissociation constant for the reaction HSO<sub>4</sub><sup>-</sup> ⇒ H<sup>+</sup> + SO<sub>4</sub><sup>2-</sup> is 4 × 10<sup>-2</sup>.
  (D) RLVP of the given solution is 9/2500.
- 11.\* A nonvolatile solute 'X' completely dimerises in water, if the temperature is below −3.72°C and the solute completely dissociates as X → Y + Z, if the temperature is above 100.26°C. In between these temperature, (including both temperature) 'X' is neither dissociated nor associated. One mole of 'X' is dissolved in 1kg water.

Given:  $K_b$  of water = 0.52 K.Kg mol<sup>-1</sup>;  $K_f$  of water = 1.86 K.Kg mol<sup>-1</sup> Which of the following statement(s) is/are true regarding the solution?

- (A) The freezing point of solution is 1.86°C.
- (B) The boiling point of solution is 101.04°C.
- (C) When the solution is cooled to -7.44°C, 75% of water present intially will separate as ice.
- (D) When the solution is heated to 102.08°C,50% of water present intially will escape out as vapor.
- **12. Statement-1**: Knowing  $K_{a_1}$  of  $CO_2$ , pH can be determined of an aqueous solution of  $Na_2CO_3$  of known concentration.

**Statement-2**: Only first hydrolysis of  $CO_3^{2-}$  ion is significant because for most of dibasic acids,  $K_{a_1} >> K_{a_2}$ 

- (A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
- (B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
- (C) Statement-1 is True, Statement-2 is False
- (D) Statement-1 is False, Statement-2 is True
- 13.\_ Statement-1: Salts of Be and Mg do not give flame test.

Statement-2: CaCl, gives apple green colour in flame test.

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

#### Comprehension #1

An ore of a common metal contain a green colored compound 'M' of metal, which dissolves readily in hydrochloric acid. However the metal does not dissolve in dilute hydrochloric acid. The compound 'M' gives effervescence of gas 'X' and produces a blue colored solution of 'P' on treatment with HCl. The gas 'X' is non-combustible colorless and odorless. The gas 'X' reacts with aqueous suspension obtained by adding 'Y' in water to give white precipate of 'Z'. Z on heating gives back X and Y. When gas Q is passed through 'P' a black precipitate of 'R' is obtained. When a gas 'S' is passed through P the blue solution turns deep blue.

**14.** The compound "M" is:

(A)  $MgCO_3$ ,  $Mg(OH)_2$  (B)  $CuFeS_2$  (C)  $CuCO_3$ ,  $Cu(OH)_2$  (D)  $FeCO_3$ 

**15.** Gases 'Q' and 'S' are allowed to enter a long tube of length 100 cm from opposite ends under identical conditions. What is the distance travelled by 'Q' before it meets 'S'?

(A) 50 cm

- (B) 41.4 cm
- (C) 46.5 cm
- (D) 59 cm
- 16. Which of the following is used as raw material in Solvay's process to produce CO<sub>2</sub>?

(A) M

(B) Y

(C) Z

(D) R

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### Comprehension # 2

Two liquids A and B mix to form an ideal binary liquid solution, On adding non volatile solid solute C to the solution, A starts polymerising into a hexamer non volatile soluble solid 'A<sub>6</sub>' following zero order kinetics, with a rate constant = 10<sup>-1</sup> moles/ min. If initially 10 moles of A and 20 moles of B were taken to form liquid solution and 5 moles of C were added then answer the following questions based on above information and data given below: [Data: vapor pressure of pure A = 100 torr, vapor pressure of pure B = 90 torr]

- 17. The vapor pressure of the solution 1 hrs. after solid C is added will be given by:
  - (A)  $\frac{220}{3}$  torr

- (B) 98 torr (C)  $\frac{2200}{29}$  torr (D)  $\frac{2200}{24}$  torr
- 18. Which of the following statements is incorrect regarding the above process?
  - (A) The vapor pressure will keep on decreasing initially.
  - (B) The vapor pressure will become constant 100 min. after addition of C.
  - (C) Two hours after addition of C, the vapor pressure will become 72 torr.
  - (D) Four hours after addition of C, the vapor pressure will become 67.5 torr.
- 19. If C is not added so there is no polymerisation of A, then mol fraction of A in vapour phase will be:
  - (A) 5/14
- (B) 9/14
- (C) 1/3
- (D) 2/3
- 20. The standard reduction potential data at 25°C is given below.

 $E^{o}$  (Fe<sup>3+</sup>.Fe<sup>2+</sup>) = + 0.77 V;

 $E^{\circ}$  (Fe<sup>2+</sup>.Fe) = -0.44 V;

 $E^{\circ}$  (Cu<sup>2+</sup>.Cu) = + 0.34 V;

List I

 $E^{\circ}(Cu^{+}.Cu) = + 0.52 \text{ V};$ 

E° (Cu²+.Cu) = + 0.34 V; E° (O<sub>2</sub>(g) + 4H+ + 4e<sup>-</sup>  $\rightarrow$  2H<sub>2</sub>O) = + 1.23 V; E° (O<sub>2</sub>(g) + 2H<sub>2</sub>O + 4e<sup>-</sup>  $\rightarrow$  4OH) = + 0.40 V E° (Cr²+ Cr) = -0.74 V; E° (Cr²+ Cr) = -0.91 V

 $E^{\circ} (Cr^{3+}.Cr) = -0.74 \text{ V};$ 

 $E^{\circ}$  (Cr<sup>2+</sup>.Cr) = -0.91 V

List II

Match E<sup>o</sup> of the rebox pair in List I with the values given in List II and select the correct answer using the code given below the lists:

P.	E <sup>o</sup> (Fe <sup>3+,</sup> Fe)						- 0.36	V	
Q.	E° (4H <sub>2</sub> O <del>←</del> 4H+ 4OH-)					2.	-0.4 V	,	
R.	$E^{\circ}$ (Cu <sup>2+</sup> + Cu $\rightarrow$ 2Cu <sup>+</sup> )					3.	-0.04	V	
S.	E <sup>o</sup> (Cr <sup>3+</sup> , Cr <sup>+2</sup> )						-0.83	V	
Codes:									
	Р	Q	R	S		Р	Q	R	S
(A)	4	1	2	3	(B)	2	3	4	1
(C)	1	2	3	4	(D)	3	4	1	2

- 21. Find the number of molecules which are planar:
  - (a)  $CIF_3$  (b)  $SF_6$  (c)  $XeF_6$  (g)  $H_2S$  (h)  $NH_3$  (i)  $PH_3$

- (I) OCI<sub>2</sub>

22. (B) + whit ppt. Yellow particles soluble in dil. mineral acid

Find the sum of number of  $p\pi - p\pi$  and  $p\pi - d\pi$  bonds in trimer of 'C'.

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23. A metal 'A' exists in the bcc structure having uncovered length along the edge equal to 1.2 Å. If molar mass of the metal is 307.2 gm/mole then calculate density of the crystal in g/mL.

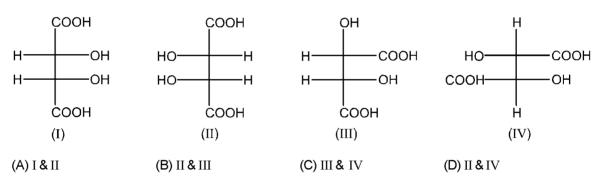
[Use : 
$$N_A = 6 \times 10^{23}$$
 and  $\sqrt{3} = 1.7$ ]

- **24.** Total number of isomers (including stereoisomers) for the complex  $[Pd(NH_3)(H_2O)(NO_2)_2]$  are :
- 25. How many of the following elements have  $\Delta_r H^o > 0$  at 298 K?  $O_2$  (g), Monoclinic sulphur, Diamond, Red phosporous,  $O_3$  (g),  $Cl_2$  (g), Rhombic sulphur,  $Br_2$  (g),  $O_3$  (g),  $O_4$  (g), Liquid sodium,  $O_4$  (g),  $O_4$
- **26.** The equilibrium partial pressure of  $N_2O_4(g)$  and  $NO_2(g)$  are 4 and 2 atm, respectively. Now, at constant temperature, the equilibrium pressure of system is increased to 60 atm. The new equilibrium partial pressure of  $N_2O_4(g)$  becomes :

<b>27</b> .		Column-l		Column-II
	(A)	Mohr's salt (aq.) + Na <sub>2</sub> O <sub>2</sub>	(p)	Colored solution
	(B)	AgNO <sub>3</sub> + NaN <sub>3</sub>	(q)	White and insoluble product posssible
	(C)	Chrome alum(aq.) + Na <sub>2</sub> O <sub>2</sub>	(r)	Colored and insoluble product possible
	(D)	Pb <sub>3</sub> O <sub>4</sub> + HNO <sub>3</sub>	(s)	Colorless solution
		3 4 3	(t)	evolution of gas possible on heating.

#### **ORGANIC CHEMISTRY**

28. Which of the following structures are superimposable?



29. The main positions of electrophilic attack for the given reactions are respectively.

30. The reactant X & Y of following reactions are

$$X + Y \xrightarrow{OH^{-}} OH^{-}$$

$$(A) \bigcirc CHO + CH_{3}CHO$$

$$(B) \bigcirc C-CH_{3} + CH_{3}-C-CH_{3}$$

$$(C) \bigcirc C-CH_{3} + HCHO$$

$$(D) \bigcirc C-CH_{3} + CH_{3}-C-H$$

31. Observe the following reaction I and II  $k_1$ ,  $k_2$ ,  $k_2$  and  $k_2$  are rate constants. Select the correct option.

(I) 
$$< \frac{(CH_3CH_2)_3N:}{[k_1']} CH_3 - I \xrightarrow{(k_1)} N:$$

(II) 
$$\leftarrow \frac{(CH_3CH_2)_3N:}{[k_2']} CH_3 - CH - CH_3 \xrightarrow[]{(k_2)} N:$$

- (A)  $k_1 > k_1'$
- (B)  $k_2 < k_2'$
- (C)  $k_1 < k_2$
- (D)  $k_1' < k_2'$

32. The product of the following reaction does not show positive test with

$$\begin{array}{c|c}
C \\
\hline
C \\
CH_{3}
\end{array}
\xrightarrow{NH_{3}}
\xrightarrow{Br_{2}/NaOH}
\xrightarrow{\Delta}$$
 product.

- (A) (CHCl<sub>3</sub> + KOH)/ $\Delta$  (Carbyl amine test)
- (B)  $HNO_2$ , OH $OH^-$ ( $\beta$ -naphthol test)
- (C) Ph-SO, CI/NaOH (Hinsberg test)
- (D) Neutral FeCl<sub>3</sub> Test

**33.** CCI<sub>3</sub>–CH=O reacts with chlorobenzene in presence of sulphuric acid & produces :

The reagents x and y are respectively:

- (A)  $Br_2 / CCI_4$ ,  $H_2 / Ni$
- (C) Na / NH $_3$  ( $\ell$ ), Br $_2$  / CCI $_4$

- (B) HBr, HBr
- (D) Br<sub>2</sub> / CCl<sub>4</sub>, Lindlar's hydrogenation

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- **35.** Select the correct statements out of the following:
  - (A)  $\beta$ -D(+) glucopyranose is more stable than  $\alpha$ -D(+) glucopyranose.
  - (B) Sucrose is laevorotatory sugar.
  - (C) Although fructose is a ketone but it gives positive Tollen's test.
  - (D) Starch contains  $\alpha$ -glycosidic linkage whereas cellulose contains  $\beta$ -glycosidic linkage.
- **36.** 2-Phenylbutan-2-ol can be prepared by :

(A) PhMgBr + 
$$\xrightarrow{\text{O}}$$
  $\xrightarrow{\text{ether}}$   $\xrightarrow{\text{H}^{\oplus}}$ 

(B) CH<sub>3</sub>MgBr + Ph—C—C<sub>2</sub>H<sub>5</sub> 
$$\xrightarrow{\text{ether}}$$
  $\xrightarrow{\text{H}^{\oplus}}$ 

(C) 
$$C_2H_5MgBr + Ph-C-CH_3 \xrightarrow{ether} H^{\oplus}$$

(D) 
$$CH_3CH_2CH_2MgBr + PhCHO \xrightarrow{ether} H^{\oplus}$$

37. Statement-1: Nitration of benzene and hexadeuterobenzene occurs almost at the same rate.

**Statement-2**: Cleavage of C – H bond takes faster than C – D bond.

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

#### Comprehension #3

Compound (X) ( $C_8H_7N$ ) on treatment with cold  $SnCl_2/dil.HCl$  (aqueous), produces Y ( $C_8H_8O$ ). (Y) on heating with sodium acetate in acetic anhydride followed by acidification forms (Z) ( $C_{10}H_{10}O_2$ ). All these compounds (X,Y,Z) on oxidation under severe conditions form a diacid which gives only one mononitro isomer in nitrating mixture.

**38.** What is structure of (X):

$$C\equiv N$$
  $CH_3$ 

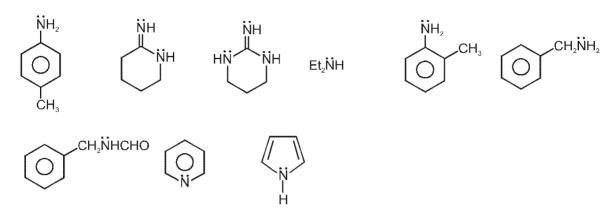
$$(D) \bigcirc CH_2C \equiv N$$

- **39.** What is not true about (Y):
  - (A) It cannot gives fehling solution test
  - (C) It gives Tollen's test positive
- (B) It gives lodoform test positive
- (D) It gives 2, 4-DNP test positive
- **40.** The reductive ozonolysis products of (Z) are :

41. 
$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{H^{\oplus}} [F] \xrightarrow{Br_2/CCl_4} C_5H_{10}Br_2 (G)$$

How many total products of (G) are formed?

**42.** How many of the following are stronger bases than aniline?



- **43.** 3–Amino–2,3–dimethyl butan–2–ol when treated with NaNO<sub>2</sub>/HCl gives product (X). (X) on treatment with LiAlH<sub>4</sub> forms (Y). (Y) on heating with conc. H<sub>2</sub>SO<sub>4</sub> forms (Z). Calculate the molecular weight of (Z).
- **44.** Match list I (reaction) with II (products) and then select the correct answer from the codes given below the lists:

List I

- (A) Phenol + NaOH + CH<sub>3</sub>I
- (B) Phenol + NaOH +CHCl<sub>3</sub>
- (C) Phenol + Phthalic anhydride + conc. H<sub>2</sub>SO<sub>4</sub>
- (D) Phenol + CO<sub>2</sub> + NaOH

List II

- (p) Phenolphthalein
- (q) Salicylic acid
- (r) Anisole
- (s) Salicylaldehyde

45. Column-l

$$(A) \bigcirc OH^{\Theta}$$

(C) 
$$\xrightarrow{\text{HNO}_3+\text{H}_2\text{SO}_4}$$

Column-II

- (p) Aromatic ring substitution
- (q) Nucleophilic addition
- (r) Condensation reaction
- (s) Formation of more than one organic products

## Solution of DPP # 11

TARGET: JEE (ADVANCED) 2015 Course: VIJETA & VIJAY (ADP & ADR)

### **CHEMISTRY**

### PHYSICAL / INORGANIC CHEMISTRY

1. After mixing

$$[NaCl] = 0.02 M$$
 ;  $K[Ag(CN)_2] = 0.05 M$ .

$$[Ag(CN)_2]^- \Longrightarrow Ag^+ + 2CN^- + 4 \times 10^{-19}$$

x is going to be very small in comparison to 0.05 as  $K_{inst}$  is very small.

So, 
$$4 \times 10^{-19} = \frac{x \times (2x)^2}{0.05 - x} = \frac{4x^3}{0.05}$$

$$\Rightarrow \qquad x^3 = 5 \times 10^{-21} \quad \Rightarrow \qquad x \simeq 1.7 \times 10^{-7}$$

$$Q_{so}$$
 of AgCI = 1.7 × 10<sup>-7</sup> × 0.02 = 3.4 × 10<sup>-9</sup> > 2.8 × 10<sup>-10</sup>

Hence, AgCl will be precipitated.

Further, [Ag(CN),] dissociates on dilution and [K+] is halved on dilution.

2.  $O^{2-}$  ion = 4 [ccp lattice]

$$A^{x+} = 8 [TV] \frac{1}{4} = 2.$$
 ;  $B^{y+} = 4[OV] \frac{1}{2} = 2.$ 

$$\Rightarrow$$
 By charge balancing.

$$2x + 2y - 8 = 0$$
 So,  $x + y = 4$ .

3. (A) t 100% =  $\frac{a}{k}$ 

$$\frac{(t_{100\%})I}{(t_{100\%})II} = \frac{a_I}{a_{II}} \times \frac{k_{II}}{k_I} = \frac{1}{0.5} \times \frac{1/\sqrt{3}}{\sqrt{3}} = \frac{2}{3}$$

(B) 
$$a - x = -k_A t + a$$
 or  $(1 - x) = -\sqrt{3} t + 1$  or  $x = +\sqrt{3} t$ 

similarly 
$$0.5 - y = -\frac{1}{\sqrt{3}}t + 0.5 \text{ or } y = \frac{t}{\sqrt{3}}$$

$$[A] = [C]$$

$$1 - x = 0.5 - y$$

$$1 - \sqrt{3} t = 0.5 - \frac{t}{\sqrt{3}}$$

$$0.5 = t \left( \sqrt{3} - \frac{1}{\sqrt{3}} \right)$$
;  $t = \frac{\sqrt{3}}{4} \text{ min.}$ 

(D) 
$$\frac{(t_{50\%})I}{(t_{50\%})II} = \frac{a_I}{a_{II}} \cdot \frac{k_{II}}{k_I} = \frac{\frac{1}{\sqrt{3}}}{\sqrt{3}} = \frac{1}{3}$$

4. 
$$\pi = iCRT$$

$$\frac{\pi}{RT}$$
 = iC

$$C_{17}H_{35}g COONa \rightarrow CH_3COO^- + Na^+$$

$$\begin{array}{ccc}
1 & 0 & 0 \\
1 - \alpha & \alpha & \alpha
\end{array}$$

$$i = \frac{1+\alpha}{1} = 2$$

$$\pi_1 = 0.02$$

$$\pi_{2} = 0.04$$

$$(\pi_3^2)_{\text{Theo.}} = 0.06 \text{ and } (\pi_3^2)_{\text{exp.}} = 0.058$$
  
 $(\pi_3^2)_{\text{exp.}} < (\pi_3^2)_{\text{Theo.}}$  So. association.

$$(\pi_3)_{\text{exp.}} < (\pi_3)_{\text{Theo}}$$
 So. association.

So here at this point micelle formation has taken place and colloid has been formed. We can say at 0.04 M concentrate mixture will be heterogeneous.

6. (a) 
$$Ca(NH) + 2H_{2}O \longrightarrow Ca(OH)_{2} + NH_{3} (g)$$

$$2NH_{3} + 3CaOCI_{3} \longrightarrow N_{2}(g) + 3CaCI_{2} + 3H_{2}O$$

$$(B) \qquad (C)$$

$$N_{2}(g) + 3Mg \longrightarrow Mg_{3}N_{2}$$

$$(C) \qquad (D)$$

$$Mg_{3}N_{2} + 6H_{2}O \longrightarrow 3Mg(OH)_{2} + 2NH_{3}$$

$$(D) \qquad (B)$$

7. (B) 
$$PCI_5(A) + H_2O \longrightarrow POCI_3(B) + 2HCI$$
  
 $POCI_3(B) + 3H_2O \longrightarrow H_3PO_4(C) + 3HCI$ 

- Due to less reactivity of Be. 8.\_
- 9. CIO<sub>2</sub> is powerful oxidising agent, also strong chlorinating agent. Its bleaching power is almost 30 times stronger than Cl<sub>2</sub>. In alkaline solution undergoes disproportionation



unpaired electron that`s why paramagnetic

10.\* NaHSO<sub>4</sub> 
$$\longrightarrow$$
 Na<sup>+</sup> + HSO<sub>4</sub><sup>-</sup> 0.08 0 0 (0.08) (0.08)

Suppose the degree of dissociation of  $HSO_a^-$  is  $\alpha$ 

$$HSO_4^- \iff H^+ + SO_4^{2-}$$
  
At eq.  $C(1-\alpha)$   $C\alpha$   $C\alpha$ 

$$\Rightarrow$$
 [H<sup>+</sup>] = 0.08  $\alpha$ 

$$[SO_4^{-2}] = 0.08 \alpha$$

$$[HSO_{4}^{-}] = 0.08 (1 - \alpha)$$

Total ions present = 0.08 + 0.08 (1 –  $\alpha$ ) + 0.08  $\alpha$  + 0.08  $\alpha$  $= 0.16 \pm 0.08 \alpha$ 

$$i = \frac{0.16 + 0.08\alpha}{0.08} = (2 + \alpha)$$

$$\Delta T_r = K_r \times m \times i$$

$$0.372 = (2 + \alpha) \times 1.86 \times 0.08$$

$$\Rightarrow$$
  $\alpha = 0.5$ 

$$\Rightarrow K_{\text{dissociation}} = \frac{C\alpha^2}{1-\alpha} = \frac{0.08 \times \left(\frac{1}{2}\right)^2}{1/2} = 0.04 \qquad \qquad \text{RLVP} = x_{\text{solute}} \qquad = \frac{0.2}{0.2 + \frac{1000}{18}} = \frac{9}{2509}$$

Corporate Office: CG Tower, A-46 & 52, IPIA, Near City Mall, Jhalawar Road, Kota (Raj.)-324005

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11.\* (A) 
$$\triangle T_b = iK_b \times m$$
  
= 0.52 × 1 = 0.52

 $T_b = 100.52$ °C So it will dissociate

hence 
$$\Delta T_b = i K_b m = 1.04$$

 $T_b = 101.04K$ 

(B) 
$$\Delta T_r = iK_r \times m = 1 \times 1.86 \times 1 = 1.86$$
;  $T_r = -1.86$ °C and X will not get dimerise

(C) 
$$7.44 = \frac{1}{2} \times 1.86 \times \frac{1}{W_A} \times 1000$$

(C)  $7.44 = \frac{1}{2} \times 1.86 \times \frac{1}{W_A} \times 1000$ ;  $W_A = 125 \text{ gm}$  So weight of ice seprate = 1000 - 125 = 875

% of ice seprate= 
$$\frac{875}{1000} \times 100 = 87.5\%$$

(D) 
$$2.08 = 2 \times 0.52 \times \frac{1}{W_{\Delta}} \times 100$$

$$W_{\Delta} = 500 \text{ gm}$$

So 500 gm i.e. 50% of H<sub>2</sub>O will evaporation

**14.** 
$$CuCO_3$$
.  $Cu(OH)_2$  +  $HCI \longrightarrow CuCl_2(aq)$  +  $CO_2$   $\uparrow$  (blue) (P) (X)

Cu + HCl → No dissolution

$$CaO + H_2O \longrightarrow Ca(OH)_2 \xrightarrow{+CO_2} CaCO_3 \downarrow (Z)$$

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$

$$CuCl_2$$
 +  $H_2S \longrightarrow CuS \downarrow (black)$ 
 $(gas Q)$  (R)

$$CuCl_2$$
 +  $NH_3 \longrightarrow [Cu(NH_3)_4]Cl_2$  (deep blue)  
(gas S)

**15.** 
$$Q = H_2 S$$
 ,  $S = NH_3$ 

Let distance travelled by  $H_aS = x$ 

$$\Rightarrow \frac{x}{100-x} = \frac{\sqrt{17}}{\sqrt{34}} \Rightarrow \frac{x}{100-x} = \frac{1}{\sqrt{2}} \Rightarrow \sqrt{2} x = 100-x \Rightarrow (\sqrt{2} + 1) x = 100$$

$$\Rightarrow x = \frac{100}{(\sqrt{2} + 1)} = 41.4 \text{ cm}$$

## Comp # 17 to 18

17. 
$$n_A = 10 \text{ mole}$$
  $n_B = 20 \text{ mole and } n_C = 5 \text{ mole.}$ 
 $P_A^0 = 100 \text{ torr}$ ,  $P_B^0 = 90 \text{ torr}$ 
 $6A \rightarrow A_6 \text{ (s)}$ 
 $10 \qquad 0$ 

$$P_{A}^{\circ} = 100 \text{ torr}, \quad P_{B}^{\circ} = 90 \text{ to}$$

$$\stackrel{\text{A}}{6} \rightarrow A_6^{\text{B}}(s)$$

$$10-x$$
  $\frac{x}{6}$ 

$$x = Kt = 10^{-1} \times 60 = 6$$

after 1 hrs 
$$\Rightarrow$$
 A = 4, B = 20, ; Solute = C +  $\frac{x}{6}$  = 5 + 1 = 6 ; P° =  $P_A^{\circ} x_A + P_B^{\circ} x_B$ 

$$P^{\circ} = 100 \times \frac{4}{24} + \frac{20}{24} \times 90 = 16.66 + 75$$

$$P^{o} = 91.66 \text{ torr}$$
  $\frac{P^{o} - P^{s}}{P^{s}} = \frac{n}{N} \Rightarrow \frac{91.66 - P^{s}}{P^{s}} = \frac{6}{24} = \frac{1}{4} \Rightarrow 73.33 \text{ torr} = \frac{220}{3}$ 

$$\begin{array}{ccc}
6A & \rightarrow & A_6 \\
10 & & 0
\end{array}$$

$$0 & & \frac{10}{6}$$

$$A = 0$$
,  $B = 20$  Solute =  $5 + \frac{10}{6} = 6.66$ 

After 100 min.

$$\frac{p^o - P^s}{P^s} = \frac{n}{N} \Rightarrow \frac{90 - P^s}{P^s} = \frac{6.66}{20}$$

$$P_s = 67.5 \text{ torr}$$

20. (P) 
$$E_{Fe^{3+}, Fe}^{o} = Fe^{3+} \xrightarrow{+0.77V} Fe^{2+} \xrightarrow{-0.44V} Fe$$

$$xV \qquad n = 3$$

$$\Rightarrow$$
 1 × 0.77 + 2 × (-0.44) = 3 × x

$$\Rightarrow$$
  $x = -\frac{0.11}{3} \text{ V} \simeq -0.04 \text{ V}.$ 

(Q) 
$$4H_2O \rightleftharpoons 4H^+ + 4OH^-$$
  
 $2H_2O \longrightarrow O_2 + 4H^+ + 4e^- - 1.23 V$   
 $+ O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- + 0.4 V$ 

(R) 
$$E^{o}_{(Cu2+ + Cu \rightarrow 2Cu+)}$$
  $Cu^{2+} \xrightarrow{xV} Cu^{+} \xrightarrow{-0.52V} Cu$   $+ 0.34V, \quad n = 2$ 

$$x \times 1 + 0.52 \times 1 = 0.34 \times 2$$
  
  $x = 0.16 \text{ V}.$ 

$$\Rightarrow Cu^{2+} + e^{-} \longrightarrow Cu^{+} \qquad 0.16 \text{ V}$$

$$+ Cu \longrightarrow Cu^{+} + e^{-} \qquad -0.52 \text{ V}$$

$$- Cu^{2+} + Cu \longrightarrow 2Cu^{+} \qquad -0.36 \text{ V}$$

(S) 
$$E^{\circ}_{(Cr^{3+}, Cr^{2+})}$$
  $Cr^{3+} \xrightarrow{n=1} Cr^{2+} \xrightarrow{-0.91V} Cr \xrightarrow{n=2} Cr \xrightarrow{-0.74V}$   $r = 3$   $r = 3$   $r = 3$ 

$$x \times 1 + 2 \times (-0.91) = 3 \times (-0.74)$$
  
 $x - 1.82 = -2.22$ 

$$\Rightarrow$$
 x = -0.4 V

**23.** 
$$a-2r=1.2 \text{ Å and } \sqrt{3} \text{ a} = 4r$$
 ;  $a-2 \times \frac{\sqrt{3}}{4} \text{ a} = 1.2 \text{ Å}$ 

$$a\left(1-\frac{\sqrt{3}}{2}\right) = 1.2 \text{ Å}$$
  $a = 8 \text{ Å}$ ;  $d = \frac{2 \times 307.2}{6 \times 10^{23} \times (8 \times 10^{-8})^3} = 2 \text{ g/mL}$ 

**24.** (A) 
$$(NO_2)(NO_2) \rightarrow cis + trans$$
 (B)  $(ONO)(NO_2) \rightarrow 3$  (C)  $(ONO)(ONO) \rightarrow cis + trans$ 

**25.** Monoclinic sulphur, Diamond, 
$$O_3(g)$$
,  $Br_2(g)$ ,  $O(g)$ ,  $I_2(\ell)$ , Liquid sodium.

$$K = \frac{P_{NO_2}^2}{P_{N_2O_4}} = 1$$
; Let  $p_{N_2O_4} = x$ ,  $p_{NO_2} = 60 - x$ 

$$\Rightarrow \frac{(60-x)^2}{x} = 1 \qquad \Rightarrow \qquad 3600 + x^2 - 120 x - x = 0$$

$$x^2 - 121 x + 3600 = 0$$
;  $x = 52.73$ ;  $x = 53$  atm

#### **ORGANIC CHEMISTRY**

32. 
$$\begin{array}{c}
O \\
C \\
C \\
CH_{3}
\end{array}$$

$$\begin{array}{c}
O \\
NH_{3} \\
\Delta
\end{array}$$

$$\begin{array}{c}
Br_{2}/NaOH \\
\Delta
\end{array}$$

$$\begin{array}{c}
C \\
CH_{3}
\end{array}$$

34. 
$$Ph - C \equiv C - Ph \xrightarrow{Na(NH_3(\ell))} Ph \xrightarrow{Ph} C = C \xrightarrow{H} Br_2 \xrightarrow{CCl_4} H \xrightarrow{Ph} Br$$

Both benzene ring have nearly same electron density so attack of E<sup>+</sup> occur at same rate.

41. 
$$CH_{3}-CH_{2}-CH=CH-CH_{3}$$
 (cis + trans)  $\xrightarrow{Br_{2}}$   $CH_{3}-CH_{2}-\overset{*}{C}H-\overset{*}{C}H-CH_{3}$  (d $\ell$  + d $\ell$ )  $\begin{vmatrix} & & & & & & & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & & \\ & & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$ 

$$CH_3$$

45. (A) 
$$OH^{\Theta}$$

$$CH=O$$

$$CH=O$$

$$CH=O$$

$$CH=O$$

$$CH=O$$

$$CH=O$$

$$CH_3CH=O/OH^{\Theta}$$

$$Aldol condansation$$

$$CH=O$$

$$CH=O$$