

SAMPLE QUESTION PAPER

BLUE PRINT

Time Allowed : 3 hours

Maximum Marks : 70

S. No.	Chapter	Passage based/ MCQs/A & R (1 mark)	SA-I (2 marks)	SA-II (3 marks)	LA (5 marks)	Total
1.	The Solid State	1(1)	–	1(3)	–	12(23)
2.	Solutions	1(1)	1(2)	–	1(5)	
3.	Electrochemistry	1(1)	–	1(3)	–	
4.	Chemical Kinetics	2(2)	1(2)	–	–	
5.	Surface Chemistry	1(1)	1(2)	–	–	
6.	The <i>p</i> -Block Elements	2(2)	1(2)	–	–	8(19)
7.	The <i>d</i> - and <i>f</i> -Block Elements	1(1)	1(2)	–	1(5)	
8.	Coordination Compounds	1(4)	–	1(3)	–	
9.	Haloalkanes and Haloarenes	1(4)	1(2)	–	–	13(28)
10.	Alcohols, Phenols and Ethers	1(1)	–	1(3)	–	
11.	Aldehydes, Ketones and Carboxylic Acids	2(2)	1(2)	–	1(5)	
12.	Amines	1(1)	1(2)	1(3)	–	
13.	Biomolecules	1(1)	1(2)	–	–	
	Total	16(22)	9(18)	5(15)	3(15)	33(70)

CHEMISTRY

Time allowed : 3 hours

Maximum marks : 70

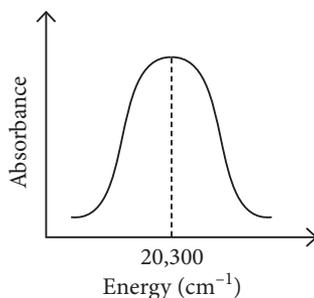
General Instructions : Read the following instructions carefully.

- There are 33 questions in this question paper. All questions are compulsory.
- Section A : Q. No. 1 to 16 are objective type questions. Q. No. 1 and 2 are passage based questions carrying 4 marks each while Q. No. 3 to 16 carry 1 mark each.
- Section B : Q. No. 17 to 25 are short answer questions and carry 2 marks each.
- Section C : Q. No. 26 to 30 are short answer questions and carry 3 marks each.
- Section D : Q. No. 31 to 33 are long answer questions carrying 5 marks each.
- There is no overall choice. However, internal choices have been provided.
- Use of calculators and log tables is not permitted.

SECTION - A (OBJECTIVE TYPE)

1. Read the passage given below and answer the following questions:

The extent to which the set of d -orbitals is split in the electrostatic field produced by the ligands depends upon several factors. Two of the most important factors are the nature of the ligands and the nature of the metal ion. In order to see this effect, consider the complex ion $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$. The Ti^{3+} ion has a single electron in the $3d$ -orbital, and we refer to it as d^1 ion. In the octahedral field generated by six H_2O molecules, the single electron will reside in one of the three degenerate t_{2g} orbitals. Under spectral excitation, the electron is promoted to an e_g orbital giving rise to an absorption spectrum consisting of a single peak that can be represented as shown :



The maximum absorption in the spectrum for $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ occurs at $20,300 \text{ cm}^{-1}$ which is equal to 243 kJ mol^{-1} . This gives the value of Δ_o directly, but only in case of simple d^1 ions. Other complexes containing the Ti^{3+} ion (e.g., $[\text{Ti}(\text{NH}_3)_6]^{3+}$, $[\text{TiF}_6]^{3-}$, etc.) could also be prepared and spectra obtained for these complexes. If this was done, it would be observed that the absorption maximum occurs at a different energy for each complex. Because the maximum corresponds to the splitting of d -orbitals, the ligands could be ranked in terms of their ability to cause the splitting of orbital energies. Such a ranking is known as the spectrochemical series and for several common ligands the following order of decreasing energy is observed, $\text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{Br}^-$. In general, the splitting in tetrahedral fields is only about half as large as that in octahedral fields.

The following questions are multiple choice questions. Choose the most appropriate answer :

- (i) Which of the following ligands is a strong field ligand?
(a) CO (b) H₂O (c) Br⁻ (d) OH⁻
- (ii) Which of the following ligands has lowest Δ_o value?
(a) CN⁻ (b) CO (c) F⁻ (d) NH₃

OR

The visible spectra of salts of the following complexes are measured in aqueous solution for which complex would the spectrum contain absorption with highest E_{\max} values?

- (a) [Co(H₂O)₆]²⁺ (b) [Co(H₂O)₆]³⁺ (c) [Co(NH₃)₆]³⁺ (d) [Co(CN)₆]³⁻
- (iii) Which of the following statements is incorrect for complex [Ti(H₂O)₆]³⁺ ?
(a) [Ti(H₂O)₆]³⁺ is violet in colour.
(b) [Ti(H₂O)₆]³⁺ is an octahedral complex.
(c) Excitation of electron in [Ti(H₂O)₆]³⁺ occurs as, $t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$
(d) The colour of the complex [Ti(H₂O)₆]³⁺ arises due to $d-d$ and $f-f$ transition of the electron.
- (iv) Which of the following order is correct in spectrochemical series of ligands?
(a) Cl⁻ < F⁻ < NO₂⁻ < CN⁻ (b) CN⁻ < Cl⁻ > NO₂⁻ < F⁻
(c) F⁻ > Cl⁻ > NO₂⁻ < CN⁻ (d) F⁻ < Cl⁻ < NO₂⁻ < CN⁻

2. Read the passage given below and answer the following questions :

A nucleophilic substitution reaction that occurs by an S_N1 mechanism proceeds in two steps. In the first step, the bond between the carbon atom and the leaving group breaks to produce a carbocation and most commonly, an anionic leaving group. In the second step, the carbocation reacts with the nucleophile to form the substitution product. The formation of a carbocation is the slow or rate determining step. The rate of S_N1 reactions decrease in the order 3° > 2° > 1°, which is the reverse order observed in S_N2 reactions. In contrast to S_N2 reactions at stereogenic centers, which occur with inversion of configuration, an S_N1 reaction gives a racemic mixture of enantiomers that has no optical rotation.

In these questions (Q.No. i-iv), a statement of assertion followed by a statement of reason is given.

Choose the correct answer out of the following choices :

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.
- (i) **Assertion :** Rate of ethanolysis of 1° halide by S_N2 mechanism is fast.
Reason : Carbocation is stabilised by resonance.
- (ii) **Assertion :** S_N2 reactions do not proceed with retention of configuration.
Reason : S_N2 reactions proceed in single step.

OR

Assertion : In an optically active alkyl halide nucleophilic substitution reaction gives a mixture of enantiomers.

Reason : Reaction occurs by S_N1 mechanism.

- (iii) **Assertion :** 1° allylic halides shows higher reactivity in S_N1 reactions than other 1° alkyl halides.
Reason : Intermediate carbocation is stabilised by resonance.
- (iv) **Assertion :** S_N1 reaction is carried out in the presence of polar protic solvent.
Reason : A polar protic solvent decreases the stability of carbocation due to solvation.

Following questions (Q. No. 3 - 11) are multiple choice questions carrying 1 mark each :

3. An organic compound of molecular formula C_3H_6O did not give a silver mirror with Tollens' reagent but give an oxime with hydroxylamine. It may be
(a) $CH_2=CH-CH_2-OH$ (b) CH_3COCH_3
(c) CH_3CH_2CHO (d) $CH_2=CH-OCH_3$
4. Reactivity of transition elements decreases almost regularly from Sc to Cu because of
(a) lanthanoid contraction (b) regular increase in ionisation enthalpy
(c) regular decrease in ionisation enthalpy (d) increase in number of oxidation states.

OR

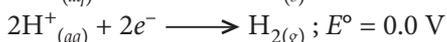
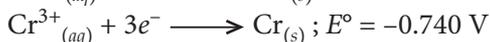
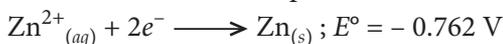
Which pair of compounds shows similar colour?

- (a) Sm^{3+}, Dy^{3+} (b) La^{3+}, Pr^{3+} (c) Pr^{3+}, Pm^{3+} (d) Sm^{3+}, Eu^{3+}
5. The decreasing order of osmotic pressures of 10 g glucose (P_1), 10 g urea (P_2) and 10 g sucrose (P_3) at 273 K when dissolved in 250 mL of water separately is
(a) $P_1 > P_2 > P_3$ (b) $P_2 > P_3 > P_1$ (c) $P_2 > P_1 > P_3$ (d) $P_3 > P_2 > P_1$
6. The ionic radii of Rb^+ and I^- are 1.46 Å and 2.16 Å respectively. The most possible type of structure exhibited by it, is
(a) CsCl type (b) NaCl type (c) ZnS type (d) CaF_2 type.

OR

In a compound, atoms of element Y form *ccp* lattice and those of element X occupy $2/3^{rd}$ of tetrahedral voids. The formula of the compound will be

- (a) X_3Y_4 (b) X_4Y_3 (c) X_2Y_3 (d) X_2Y
7. In the synthesis of ammonia from nitrogen and hydrogen gases, if 6×10^{-2} mole of hydrogen disappears in 10 minutes, the number of moles of ammonia formed in 0.3 minutes is
(a) 1.8×10^{-2} (b) 1.2×10^{-3} (c) 4×10^{-2} (d) 3.6×10^{-2}
8. Hydrogen fluoride is liquid unlike other hydrogen halides because
(a) fluorine atom is smaller in size (b) HF is the weakest acid
(c) fluorine is highly reactive (d) HF molecules form intermolecular H-bonds.
9. The standard reduction potential at 298 K for the following half cell reactions are given below :



Which is the strongest reducing agent?

- (a) $Zn_{(s)}$ (b) $Cr_{(s)}$ (c) $H_{2(g)}$ (d) $Fe^{2+}_{(aq)}$

OR

A 0.05 M KOH solution offered a resistance of 31.6 ohm in a conductivity cell of cell constant 0.367 cm^{-1} at 298 K. What is the equivalent conductance of KOH solution?

- (a) $0.2322 \text{ S cm}^2 \text{ eq}^{-1}$ (b) $2.322 \text{ S cm}^2 \text{ eq}^{-1}$
(c) $23.22 \text{ S cm}^2 \text{ eq}^{-1}$ (d) $232.28 \text{ S cm}^2 \text{ eq}^{-1}$

10. On oxidation with a mild oxidising agent like $\text{Br}_2/\text{H}_2\text{O}$, the glucose is oxidised to
- (a) saccharic acid (b) glucaric acid
(c) gluconic acid (d) valeric acid.
11. Which of the following is not a characteristic of alcohol?
- (a) The $-\text{OH}$ group in alcohols is involved in intermolecular hydrogen bonding.
(b) Their boiling points rise fairly uniformly with rising molecular weight.
(c) Lower members are insoluble in water and organic solvents but the solubility regularly increases with molecular mass.
(d) Lower members have a pleasant smell and, higher members are colourless and tasteless.

OR

1-Propanol in the presence of HBF_4 reacts with diazomethane to give

- (a) di-*n*-propyl ether (b) dimethyl ether
(c) 1-methoxypropane (d) 2-methoxypropane.

In the following questions (Q. No. 12-16), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices :

- (a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

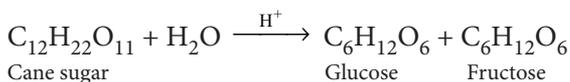
12. **Assertion :** Carboxylic acids do not undergo Friedel — Crafts reaction.

Reason : Carboxyl group is *meta*-directing group.

13. **Assertion :** Fluorine combines with sulphur to form SF_6 but no other halogen forms hexahalide with sulphur.

Reason : The reactivity of halogens increases as the atomic number increases.

14. **Assertion :** The reaction,



is a first order reaction.

Reason : Change in concentration of H_2O is negligible.

15. **Assertion :** Hofmann degradation of benzamide gives aniline.

Reason : Hofmann bromamide degradation reaction can be used for descending amine series.

16. **Assertion :** In physical adsorption, enthalpy of adsorption is very low.

Reason : In physical adsorption, attraction between gas molecules and solid surface is due to weak van der Waals' forces.

OR

Assertion : In the coagulation of a negative sol the flocculating power is in the order : $\text{Al}^{3+} > \text{Ba}^{2+} > \text{Na}^+$.

Reason : Greater the valence of the flocculating ion added, greater is its power to cause precipitation.

SECTION - B

The following questions Q.No. 17-25 are short answer type and carry 2 marks each.

17. The freezing point of pure nitrobenzene is 278.8 K. When 2.5 g of unknown substance is dissolved in 100 g of nitrobenzene, the freezing point of solution is found to be 276.8 K. If the freezing point depression constant for nitrobenzene is 8 K kg mol^{-1} , what is the molar mass of unknown substance?

OR

A solution of glucose ($C_6H_{12}O_6$) in water is labelled as 10% by weight. What would be the molality of the solution? (Molar mass of glucose = 180 g mol^{-1})

18. (a) Amino acids show amphoteric behaviour. Why?
(b) Write one difference between α -helix and β -pleated structures of proteins.
19. Which halogen will produce O_2 and O_3 as passed through water and why?

OR

Account for the following :

- (i) H_2S has lower boiling point than H_2O .
(ii) Reducing character decreases from SO_2 to TeO_2 .

20. Account for the following :
- (i) The pK_b of aniline is more than that of methylamine.
(ii) Gabriel phthalimide synthesis is the preferred method for synthesizing primary amines.
21. (i) In the transition series, starting from lanthanum ($_{57}La$), the next element hafnium ($_{72}Hf$) has an atomic number of 72. Why do we observe this jump in atomic number?
(ii) $Ce(IV)$ is a good analytical reagent. Why?
22. Explain why :
- (i) Alkyl halides, though polar, are immiscible with water.
(ii) Tertiary halides are least reactive towards S_N2 reactions.
23. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is a first order reaction.
(i) After 55 seconds at 400 K the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.
(ii) Calculate the pressure of Cl_2O_7 after 100 seconds of decomposition at this temperature.
24. Two moles of organic compound 'A' on treatment with a strong base gives two compounds 'B' and 'C'. Compound 'B' on dehydrogenation with Cu gives 'A' while acidification of 'C' yields carboxylic acid 'D' with molecular formula of CH_2O_2 . Identify the compounds A, B, C and D and write all chemical reactions involved.

OR

- (a) Give reason why aldehydes are more reactive than ketones towards nucleophilic reagents.
(b) Why pH of reaction should be carefully controlled while preparing ammonia derivatives of carbonyl compounds ?

25. Explain the following:
- (i) Physisorption is multi-layered, while chemisorption is mono-layered.
(ii) True solution does not show Tyndall effect.

SECTION - C

Q.No. 26-30 are short answer type II carrying 3 marks each :

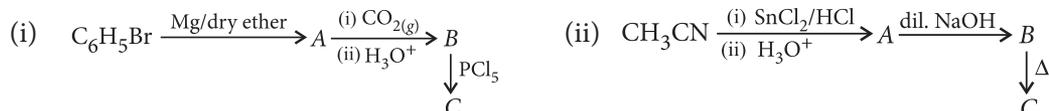
26. (a) Propanamine and *N,N*-dimethylmethanamine contain the same number of carbon atoms, even though propanamine has higher boiling point than *N,N*-dimethylmethanamine. Why?
(b) Illustrate the following reactions giving suitable example in each case :
(i) Ammonolysis
(ii) Acetylation of amines

- (iii) Cr^{2+} is a stronger reducing agent than Fe^{2+} .
- (iv) Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.
- (v) Cr^{2+} is reducing agent and Mn^{3+} oxidising agent while both have d^4 configuration.

32. (a) An organic compound (A) which has characteristic odour, on treatment with NaOH forms two compounds (B) and (C). Compound (B) has the molecular formula $\text{C}_7\text{H}_8\text{O}$ which on oxidation with CrO_3 gives back compound (A). Compound (C) is the sodium salt of the acid. Compound (C) when heated with soda lime yields an aromatic hydrocarbon (D). Deduce the structures of (A), (B), (C) and (D). Write chemical equations for all reactions taking place.
- (b) Account for the following :
- (i) Aromatic carboxylic acids do not undergo Friedel-Crafts reaction.
 - (ii) pK_a value of 4-nitrobenzoic acid is lower than that of benzoic acid.

OR

- (a) Write the structures of compounds A, B and C in each of the following reactions :



- (b) A ketone A ($\text{C}_4\text{H}_8\text{O}$), which undergoes a haloform reaction gives compound B on reduction. B on heating with sulphuric acid gives a compound C which forms monozonide D. D on hydrolysis in presence of zinc dust gives only acetaldehyde E. Identify A, B, C, D and E. Write the reactions involved.
33. (a) Boiling point of water at 750 mm Hg is 99.63°C . How much sucrose is to be added to 500 g of water so that it boils at 100°C ? (Molal elevation constant for water is $0.52 \text{ K kg mol}^{-1}$.)
- (b) The freezing point of a solution containing 50 cm^3 of ethylene glycol in 50 g water is found to be -34°C . Assuming ideal behaviour, calculate the density of ethylene glycol. (K_f for $\text{H}_2\text{O} = 1.86 \text{ K kg mol}^{-1}$)

OR

- (a) Define the term, 'osmosis'. What is the advantage of using osmotic pressure as compared to other colligative properties for the determination of molar masses of solutes in solutions?
- (b) (i) What happens when red blood corpuscles (RBC) are placed in
- (a) 0.5% NaCl solution
 - (b) 1% NaCl solution?
- (ii) 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?

SOLUTIONS

1. (i) (a)

(ii) (c) : Because F^- is a weak field ligand.

OR

(d) : $[Co(CN)_6]^{3-}$ complex would contain absorption with highest E_{max} value because according to spectrochemical series, the crystal field splitting energy of CN^- ion is very high.

(iii) (d)

(iv) (a)

2. (i) (c) : The ethanolysis of 1° halide generally proceeds via S_N2 mechanism. In case if it proceeds via S_N1 mechanism, the intermediate carbocation is unstable, since it has no adjacent carbon atom for resonance.

(ii) (b)

OR

(a)

(iii) (a)

(iv) (c) : Polar protic solvents increase the stability of carbocation due to solvation.

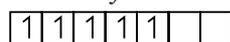
3. (b)

4. (b)

OR

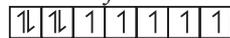
(a) : ${}_{62}Sm : [Xe] 4f^6 5d^0 6s^2$

${}_{62}Sm^{3+} : [Xe] 4f^5 5d^0 6s^0$



${}_{66}Dy : [Xe] 4f^{10} 5d^0 6s^2$

${}_{66}Dy^{3+} : [Xe] 4f^9 5d^0 6s^0$



Same no. of unpaired electrons are present in f -orbital. Thus, exhibit same colour.

5. (c) : All solutes are non-electrolytes.

\therefore Osmotic pressure, $P = \frac{wRT}{M \times V}$

$\therefore P \propto \frac{w}{M}$

$M_{glucose} = 180, M_{urea} = 60, M_{sucrose} = 342$

$P_1 = \frac{10}{180}, P_2 = \frac{10}{60}, P_3 = \frac{10}{342}$

\therefore The decreasing order of osmotic pressure is, urea > glucose > sucrose or $P_2 > P_1 > P_3$.

6. (b) : $r_{Rb^+} = 1.46 \text{ \AA}$

$r_{I^-} = 2.16 \text{ \AA} \quad \frac{r_+}{r_-} = 0.676$

As radius ratio lies in between 0.414 – 0.732, so, possible structure is NaCl type.

OR

(b) : Number of Y atoms per unit cell in ccp lattice (N) = 4

Number of tetrahedral voids = $2N = 2 \times 4 = 8$

Number of tetrahedral voids occupied by X = $2/3^{rd}$ of the tetrahedral void = $2/3 \times 8 = 16/3$

Hence, the formula of the compound will be, $X_{16/3}Y_4 = X_4Y_3$

7. (b) : $N_2 + 3H_2 \rightarrow 2NH_3$

$-\frac{[H_2]}{\Delta t} = \frac{3[NH_3]}{2 \Delta t}$

or $\frac{[NH_3]}{\Delta t} = -\frac{2[H_2]}{3 \Delta t} = \frac{2}{3} \times \frac{6 \times 10^{-2}}{10}$

$\Delta[NH_3] = 0.4 \times 10^{-2} \times 10 = 4 \times 10^{-2}$

In 10 min, no. of moles of $NH_3 = 4 \times 10^{-2}$

then in 0.3 min = $\frac{4 \times 10^{-2} \times 0.3}{10} = 1.2 \times 10^{-3}$

8. (d) : HF molecules are associated due to intermolecular H-bonding and thus exist as liquid.

9. (a) : Zn has lowest reduction potential value and it will be easily oxidised. Therefore, it acts as strongest reducing agent.

OR

(d) : $\kappa = \frac{1}{R} \times \frac{l}{a} = \frac{1}{31.6} \times 0.367$

$\Lambda_{eq} = k \times \frac{1000}{\text{Normality}}$

KOH is univalent, $KOH \rightarrow K^+ + OH^-$

Hence, its molarity = normality

$\therefore \Lambda_{eq} = \frac{0.367}{31.6} \times \frac{1000}{0.05} = 232.28 \text{ S cm}^2 \text{ eq}^{-1}$

10. (c) : $CH_2OH(CHOH)_4CHO \xrightarrow[\text{[O]}]{Br_2/H_2O} CH_2OH(CHOH)_4COOH$
Glucose Gluconic acid

11. (c)

OR

(c) : $CH_3CH_2CH_2OH + CH_2N_2 \xrightarrow[\Delta]{HBF_4} CH_3CH_2CH_2OCH_3 + N_2 \uparrow$
1-Propanol 1-Methoxypropane

12. (b) : Carboxylic acids do not undergo Friedel-Crafts reaction because the $-\text{COOH}$ group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.

13. (c) : The reactivity of halogens decreases as the atomic number increases.

14. (a) : Such reactions are called pseudo first order reactions.

15. (a) : In this reaction the amine so formed contains one carbon less than that present in the amide.

16. (a) : Physical adsorption is an exothermic process but its enthalpy of adsorption is quite low (20 - 40 kJ mol^{-1}). This is because the attraction between gas molecules and solid surface is only due to weak van der Waals' forces.

OR

(a) This is known as Hardy-Schulze rule.

17. Given, $w_1 = 2.5 \text{ g}$

$$\Delta T_f = 278.8 - 276.8 = 2 \text{ K}$$

$$w_2 = 100 \text{ g}, K_f = 8 \text{ K kg mol}^{-1}$$

$$\Rightarrow \Delta T_f = K_f \times \frac{w_1}{M_1} \times \frac{1000}{w_2}$$

$$\Rightarrow 2 = 8 \times \frac{2.5}{M_1} \times \frac{1000}{100}$$

$$\Rightarrow M_1 = 4 \times 2.5 \times 10 \Rightarrow M_1 = 10 \times 10$$

$$\therefore M_1 = 100 \text{ g mol}^{-1}$$

OR

Mass of solution = 100 g

Mass of solute = 10 g

Mass of solvent = 100 - 10 = 90 g

$$= \frac{90}{1000} \text{ kg} = 0.09 \text{ kg}$$

$$\text{Number of moles of solute, } n = \frac{10}{180} = 0.055 \text{ mol}$$

$$\text{Molality } (m) = \frac{0.055 \text{ mol}}{0.09 \text{ kg}} = 0.61 \text{ m}$$

18. (a) : As amino acids have both acidic (carboxy group) and basic (amino group) in the same molecule, they react with both acids and bases. Hence, they show amphoteric behaviour.

(b) In α -helix structure, intramolecular H-bonding takes place whereas in β -pleated structure, intermolecular H-bonding takes place.

19. F_2 is highly reactive and has greater affinity for hydrogen. Therefore, it decomposes water at low temperature and even in dark liberating oxygen and ozone.



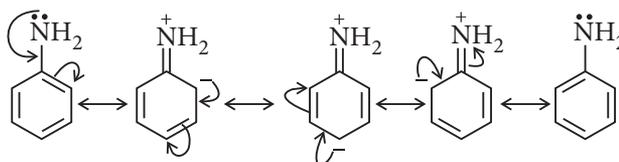
OR

(i)	H_2O	>	H_2S
Boiling point	373 K		213 K

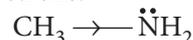
The abnormally high boiling point of H_2O is due to strong intermolecular H-bonding. Since, all other elements have much lower electronegativity than oxygen, they do not undergo H-bonding.

(ii) The +6 oxidation state of S is more stable than +4 therefore, SO_2 acts as a reducing agent. Further, since the stability of +6 oxidation state decreases from S to Te therefore, the reducing character of the dioxides decreases while their oxidising character increases. Thus, TeO_2 acts as an oxidising agent.

20. (i) In case of aniline, the lone pair of electrons on the N-atom is delocalized with the π -electrons of the benzene ring, making the lone pair of electrons on nitrogen less available for protonation.



On the other hand, in methylamine the electron-releasing methyl group increases the electron density around nitrogen, thereby increasing the availability of the lone pair of electrons.



Therefore, aniline is a weaker base than methylamine and hence, its $\text{p}K_b$ value is higher than that of methylamine.

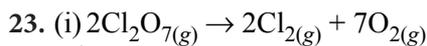
(ii) Gabriel phthalimide synthesis is the only method used to make primary amines because it is not possible to alkylate potassium phthalimide with either $(\text{CH}_3)_2\text{CH}-\text{X}$ or $(\text{CH}_3)_3\text{C}-\text{X}$.

21. (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° 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.

22. (i) Only those compounds which can form hydrogen bonds with water are miscible with it. Alkyl halides, though polar due to the presence of electronegative halogen atom, are immiscible since they cannot form hydrogen bonds.

(ii) Tertiary halides are least reactive toward S_N2 reactions because bulky groups hinder the approach of nucleophile.



For 1st order reaction,

$$k = \frac{2.303}{t} \log\left(\frac{P_0}{P}\right) = \frac{2.303}{55} \log\left(\frac{0.062}{0.044}\right) = 6.2 \times 10^{-3} \text{ s}^{-1}$$

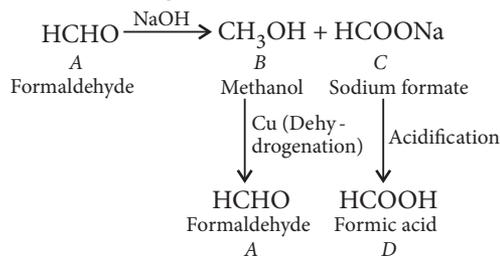
(ii) $k = \frac{2.303}{t} \log\left(\frac{P_0}{P}\right)$

Here $k = 6.2 \times 10^{-3} \text{ s}^{-1}$, $t = 100 \text{ s}$, $P_0 = 0.062 \text{ atm}$

$$\therefore 6.2 \times 10^{-3} = \frac{2.303}{100} \log\left(\frac{0.062}{P}\right)$$

$$\text{or } \log \frac{0.062}{P} = \frac{6.2 \times 10^{-3} \times 100}{2.303} \Rightarrow P = 0.033 \text{ atm}$$

24. Since the molecular formula of D is CH_2O_2 , thus, D is HCOOH (formic acid). D is obtained by the acidification of C , so, C is sodium formate (HCOONa). Thus, A must be formaldehyde (as it undergoes Cannizzaro reaction with a strong base).



Thus, $A = \text{Formaldehyde (HCHO)}$

$B = \text{Methanol (CH}_3\text{OH)}$

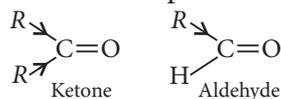
$C = \text{Sodium formate (HCOONa)}$

$D = \text{Formic acid (HCOOH)}$

OR

(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.



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

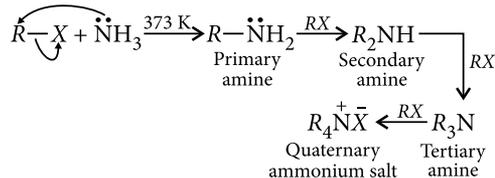
(b) In strongly acidic medium ammonia derivatives being basic will react with acids and will not react with carbonyl compound. In basic medium, OH^- will attack carbonyl group. Therefore, pH of a reaction should be carefully controlled.

25. (i) Physical adsorption occurs due to intermolecular attractive forces between the adsorbate and adsorbent. If the size of the adsorbent pores is close to the size of adsorbate molecules, multilayer adsorption takes place, *i.e.*, adsorption takes place until all the pores are filled with adsorbate molecules, whereas in chemisorption chemical bonds are formed between adsorbate and adsorbent molecules. Therefore, it is monolayered.

(ii) Tyndall effect is not observed in true solution as the diameter of dispersed particles is much smaller as compared to wavelength of the light used.

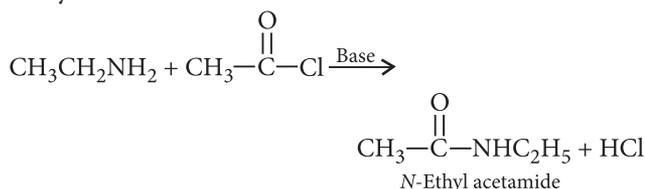
26. (a) Primary amines (R-NH_2) have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N). So, primary amines boil at a higher temperature than tertiary amines.

(b) (i) **Ammonolysis** : Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.



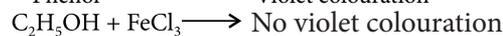
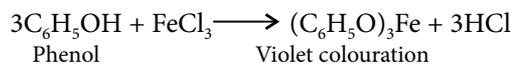
(ii) **Acetylation of amines** : The process of introducing

an acetyl group ($\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-$) into a molecule is called acetylation.

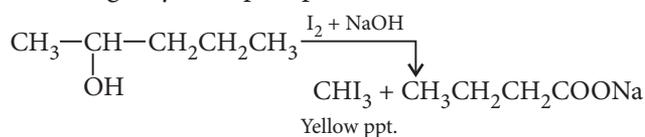


27. (a) Phenol undergoes electrophilic substitution reaction more easily than benzene due to strong activating effect of $-\text{OH}$ group attached to benzene ring.

(b) (i) Phenol gives a violet colouration with FeCl_3 solution while ethanol does not.

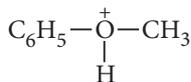


(ii) On adding I_2 and NaOH , 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.



OR

- (i) Acid dehydration of 2° and 3° alcohols give alkenes rather than ethers, due to steric hindrance, as elimination completes over substitution and as a consequence, alkenes are easily formed. The method is suitable for the preparation of ethers giving primary alkyl groups only.
- (ii) Protonation of anisole (phenylmethyl ether) gives methyl phenyl oxonium ion.



In this ion, the stronger bond is O—C₆H₅. Therefore, attack by I⁻ ion exclusively breaks the weaker O—CH₃ bond forming methyl iodide and phenol. The phenol formed does not react further to give aryl halides.

(iii) Ethanol has higher boiling point because of strong intermolecular hydrogen bonding whereas in methoxymethane, molecules are held by dipole-dipole interaction.

28. (i) As 27 g of Al will contain 6.023 × 10²³ atoms
∴ 8.1 g Al will contain

$$= \frac{6.023 \times 10^{23}}{27} \times 8.1 \text{ atoms} = 1.8069 \times 10^{23} \text{ atoms}$$

In fcc, 4 atoms are present in one unit cell

- ∴ 1.8069 × 10²³ atoms will be present in

$$\frac{1.8069 \times 10^{23}}{4} = 4.517 \times 10^{22} \text{ unit cells}$$

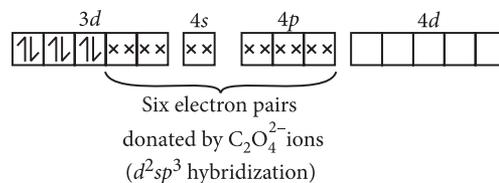
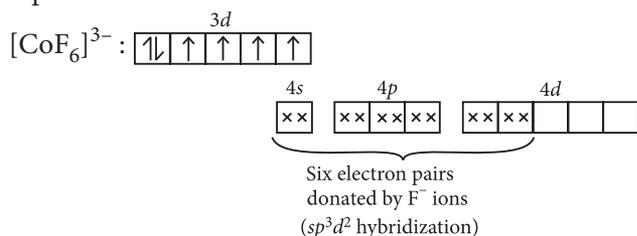
- (ii) Number of atoms in 0.5 mol hcp lattice
= 0.5 × 6.022 × 10²³ = 3.011 × 10²³

- ∴ Number of octahedral voids = Number of atoms
= 3.011 × 10²³

- Number of tetrahedral voids = 2 × Number of atoms
= 2 × 3.011 × 10²³ = 6.022 × 10²³

- Total number of voids = Number of octahedral voids
+ Number of tetrahedral voids
= 3.011 × 10²³ + 6.022 × 10²³ = 9.033 × 10²³ voids

29. Formation of [CoF₆]³⁻ and [Co(C₂O₄)₃]³⁻ can be represented as :



- (i) [Co(C₂O₄)₃]³⁻ is diamagnetic as all the electrons are paired.

(ii) [Co(C₂O₄)₃]³⁻ is more stable as C₂O₄²⁻ is a chelating ligand and forms chelate rings.

(iii) [CoF₆]³⁻ is outer orbital complex as it undergoes sp³d² hybridization using the outer 4d-orbital.

(iv) [Co(C₂O₄)₃]³⁻ is low spin complex due to absence of any unpaired electron.

30. (i) $E_{\text{cell}}^{\circ} = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^{\circ} - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 1.44 - 0.68 = 0.76 \text{ V}$

$$E_{\text{cell}}^{\circ} = \frac{0.059}{1} \log K_C \quad [n=1]$$

$$\therefore 0.76 = 0.059 \log K_C \quad \text{or} \quad \log K_C = \frac{0.76}{0.059} = 12.8814$$

$$\text{or} \quad K_C = 7.6 \times 10^{12}$$



$$\begin{aligned} \therefore E_{\text{OP}} &= E_{\text{OP}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2}} \\ &= 0 - \frac{0.059}{2} \log \frac{[0.02]^2}{2} \end{aligned}$$

$$E_{\text{OP}(\text{H}_2/\text{H}^+)} = +0.109 \text{ V}$$



$$\begin{aligned} \therefore E_{\text{OP}} &= E_{\text{OP}}^{\circ} - \frac{0.059}{2} \log_{10} \frac{P_{\text{Cl}_2}}{[\text{Cl}^-]^2} \\ &= -1.36 - \frac{0.059}{2} \log \frac{10}{[0.1]^2} \end{aligned}$$

$$\therefore E_{\text{OP}(\text{Cl}^-/\text{Cl}_2)} = -1.4485 \text{ V}$$

OR

(i) Given, $\Lambda_{\text{Ba}(\text{OH})_2}^{\circ} = \lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{OH}^-}^{\circ} = 523.28 \dots \text{(i)}$

$\Lambda_{\text{BaCl}_2}^{\circ} = \lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{Cl}^-}^{\circ} = 280.00 \dots \text{(ii)}$

$\Lambda_{\text{NH}_4\text{Cl}}^{\circ} = \lambda_{\text{NH}_4^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ} = 129.80 \dots \text{(iii)}$

we have to calculate, $\Lambda_{\text{NH}_4\text{OH}}^{\circ} = \lambda_{\text{NH}_4^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ} = ?$

Multiply eqn. (iii) by 2 and then subtract it from eqn. (ii).

$$\lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{Cl}^-}^{\circ} - 2\lambda_{\text{NH}_4^+}^{\circ} - 2\lambda_{\text{Cl}^-}^{\circ} =$$

$$\lambda_{\text{Ba}^{2+}}^{\circ} - 2\lambda_{\text{NH}_4^+}^{\circ} = 280 - 2 \times 129.80 = 20.4 \dots \text{(iv)}$$

Now subtract eqn. (iv) from eqn. (i)

$$\lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{OH}^-}^{\circ} - \lambda_{\text{Ba}^{2+}}^{\circ} + 2\lambda_{\text{NH}_4^+}^{\circ}$$

$$2\lambda_{\text{NH}_4^+}^{\circ} + 2\lambda_{\text{OH}^-}^{\circ} = 523.28 - 20.4 = 502.88$$

$$\therefore \Lambda_{\text{NH}_4\text{OH}}^{\circ} = \frac{502.88}{2} = 251.44 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

(ii) Normality of a solution is given by the number of equivalent per dm^3 (or per litre) of the solution. Therefore, concentration of the given solution = 0.12 equiv/dm^3
conductivity of the solution, $(\kappa) = 0.024 \text{ S cm}^{-1}$

Then,

(a) The equivalent conductivity is given by,

$$\Lambda_{eq} = \frac{1000\kappa}{C_{eq}} = \frac{1000 \times 0.024}{0.12} \text{ S cm}^2 \text{ equiv}^{-1}$$

$$= 200 \text{ S cm}^2 \text{ equiv}^{-1}$$

(b) The given electrolyte is of the type A^+B^- . This means that each cation (or anion) carries a charge equivalent to the charge carried by one electron. So, $Z = 1$.

$$\text{Then, } \Lambda_m = 1 \times \Lambda_{eq} = 1 \times 200 \text{ S cm}^2 \text{ mol}^{-1}$$

$$= 200 \text{ S cm}^2 \text{ mol}^{-1}$$

31. (a) Oxoanion of chromium in which it shows +6 oxidation state equal to its group number is $\text{Cr}_2\text{O}_7^{2-}$ (dichromate ion).

(b) (i) Scandium ($Z = 21$), atom has incompletely filled d -orbitals ($3d^1$) in its ground state, so it is regarded as transition element. On the other hand, zinc ($Z = 30$) atom has completely filled d -orbitals ($3d^{10}$) in its ground state as well as most common oxidation state of +2.

(ii) Electrode potential (E°) value is the sum of three factors :

- Enthalpy of atomisation ; $\Delta_a H$ for $\text{Cu}_{(s)} \rightarrow \text{Cu}_{(g)}$
- Ionisation enthalpy ; $\Delta_i H$ for $\text{Cu}_{(g)} \rightarrow \text{Cu}_{(g)}^{2+}$
- Hydration enthalpy ; $\Delta_{hyd} H$ for $\text{Cu}_{(g)}^{2+} \rightarrow \text{Cu}_{(aq)}^{2+}$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration. Therefore, $E^\circ_{M^{2+}/M}$ for Cu is positive.

(c) Transition elements can use their ns and $(n-1)d$ orbital electrons for bond formation. Therefore, they show variable oxidation states.

For example, Sc has $ns^2(n-1)d^1$ electronic configuration. If it utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons from its ns and $(n-1)d$ subshell then its oxidation state = +3.

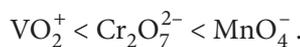
Among the $3d$ series manganese (Mn) exhibits the largest number of oxidation states from +2 to +7 because it has maximum number of unpaired electrons.



OR

(i) The ions in which the central metal atom is present in the highest oxidation state will have the highest oxidising power. In VO_2^+ , vanadium is present in the +5 oxidation state, while in $\text{Cr}_2\text{O}_7^{2-}$ ion, Cr is present in the +6 oxidation state. Similarly, in MnO_4^- , Mn is present in the +7 oxidation state. Thus, as the oxidation

state of the central atom increases, the oxidising power of oxoanions increases in the order :



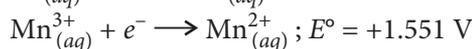
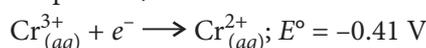
(ii) Third ionization enthalpy of Mn is very high because the third electron has to be removed from the stable half-filled $3d$ -orbitals [$\text{Mn}^{2+} (Z = 25) = 3d^5$].

(iii) Cr^{2+} is a stronger reducing agent than Fe^{2+} .

$E^\circ_{\text{Cr}^{3+}/\text{Cr}^{2+}}$ is negative (-0.41 V) whereas $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ is positive ($+0.77 \text{ V}$). Thus, Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+} . Hence, Cr^{2+} is stronger reducing agent than Fe^{2+} .

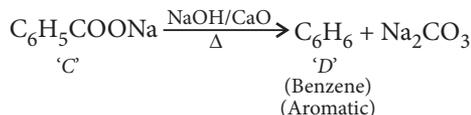
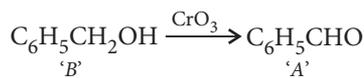
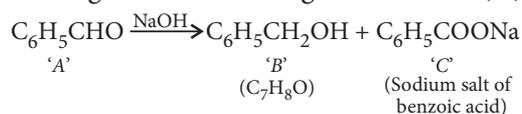
(iv) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3^{rd} electron cannot be lost easily. In case of Fe^{2+} , electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(v) (i) E° values for the $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples are,



These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising agent.

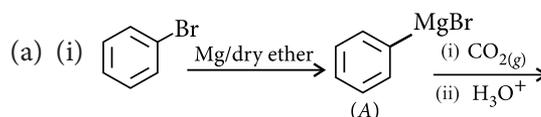
32. (a) Benzaldehyde has a characteristic odour. Reaction of 'A' with NaOH appears to be Cannizzaro reaction which gives 'B' (benzyl alcohol) and 'C' (sodium salt of benzoic acid). Oxidation of alcohols gives aldehydes. Sodium salt of benzoic acid on heating with soda lime gives benzene (D).

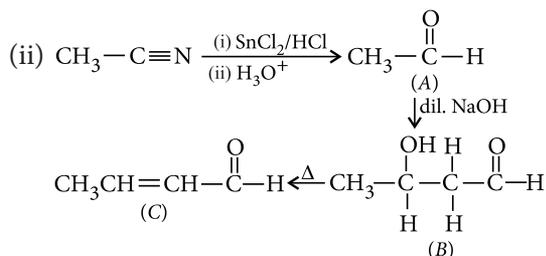
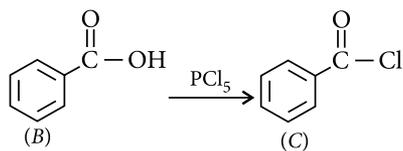


(b) (i) Due to presence of electron withdrawing group ($-\text{COOH}$) in aromatic carboxylic acids, they do not undergo Friedel-Crafts reaction.

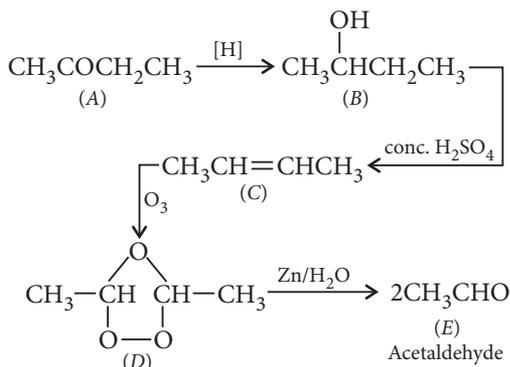
(ii) Due to presence of strong electron withdrawing group ($-\text{NO}_2$), 4-nitrobenzoic acid is more acidic than benzoic acid and therefore, $\text{p}K_a$ value is lower.

OR

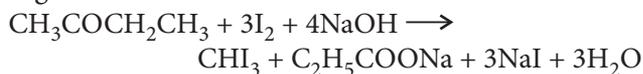




(b) Chemical reactions occur as,



A gives haloform reaction as :



33. (a) Elevation in boiling point (ΔT_b)
 $= 100 - 99.63 = 0.37^\circ\text{C}$

Mass of solvent (water), $w_1 = 500$ g

Mass of solute, $w_2 = ?$

Molar mass of solvent, $M_1 = 18$ g mol⁻¹

Molar mass of solute, ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$), $M_2 = 342$ g mol⁻¹

Applying the formula, $\Delta T_b = K_b \times \frac{w_2 \times 1000}{M_2 \times w_1}$

$$\text{or, } w_2 = \frac{M_2 \times w_1 \times \Delta T_b}{1000 \times K_b} = \frac{342 \times 500 \times 0.37}{1000 \times 0.52} = 122 \text{ g}$$

(b) Given: $V_{\text{ethylene glycol}} = 50 \text{ cm}^3$, $W = 50$ g

$K_f = 1.86 \text{ K kg mol}^{-1}$, $m = 62$ g/mol (ethylene glycol)

$\Delta T_f = 34^\circ\text{C}$, $w = 50 \times d$ g (ethylene glycol)

$$\text{We know, } \Delta T_f = \frac{1000 \times K_f \times w}{m \times W}$$

$$\text{Substituting values, } 34 = \frac{1000 \times 1.86 \times 50 \times d}{62 \times 50}$$

$$\therefore d = 1.133 \text{ g/cm}^3$$

OR

(a) The net spontaneous flow of the solvent molecules from the solvent to the solution or from a less concentrated solution to more concentrated solution through a semi-permeable membrane is called osmosis.

The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and its magnitude is large even for very dilute solution.

(b) (i) (a) The cells will swell or even burst due to haemolysis because 0.5% NaCl solution is hypotonic *w.r.t.* salt concentration in blood plasma.

(b) The cells will shrink due to plasmolysis, because 1% solution of NaCl is hypertonic *w.r.t.* salt concentration in blood plasma.

(ii) Molar mass of heptane (C_7H_{16}) = 100 g mol^{-1}

Molar mass of octane (C_8H_{18}) = 114 g mol^{-1}

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

$$\text{Number of moles of octane} = \frac{35.0 \text{ g}}{114 \text{ g mol}^{-1}} = 0.31 \text{ mol}$$

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

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

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

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

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

