MARKING SCHEME

PRACTICE PAPER - 04

1. (i) (a) Statement (a) is correct. $[Co(CN)_6]^{3-1}$

 $^{0}_{C0}{}^{3^{+}} = 1s^{2}, 2s^{2}, 2p^{6}, 3s^{2}, 3p^{6}, 3d^{6}$

 $_{\mathrm{CN}^-}$ is a strong field ligand and as it approaches the metal ion, the electron must pair up.

The splitting of the d-orbitals into two sets of orbitals in as octahedral complex [Co(CN)₆] ³⁻ may be represented as $t_{2a}^6 e_a^0$.



Here, for d⁶ ions, three electrons first inter orbitals with parallel spin out the remaining may pair up in t_{2q} orbital giving rise to low spin complex (strong ligand) field.

: [Co(CN)₆]³⁻ has no unpaired electrons and will be in low spin configuration.

(ii) (b) Based on spectrochemical series, ligands arranged in increasing order of crystal field strength are as

 $NH_3 < en < CN^- < CO$

iii) (b) For
$$[Cr(H_2O)_6]^{2+}$$
 and $Cr^{2+} = [Ar]_3 d^4$



As H₂O is a weak field ligand, so pairing of electrons does not occur.

CFSE for $[Cr(H_2O)_6]^{2+} = 3(-0.4\Delta_o) + 1(0.6\Delta_o) = -0.6\Delta_o$

 $\Delta_0 \propto Crystal$ Field Stabilisation Energy (CFSE)

 Δ_0^{0} depends on $Z_{\rm eff}$ and for 3*d*-series, $Z_{\rm eff}$ is less than 4d -series.

Hence, Δ_0 of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ From above table.

 $\Delta_0 \text{ of } [\text{Ti}(\text{H}_2\text{O})_6]^{3+} > \Delta_0 \text{ of } [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$ Or

(a) CFSE = $3(-0.4) + 1(0.6) = -0.6\Delta_{0}$

(iv) (c) CFSE for octahedral and tetrahedral complexes are closely related to each other by formula $\Delta_t = \frac{4}{\Omega} \Delta_0$.

where, $\Delta_{o} = CFSE$ for octahedral complex,

 $\Delta_t = CFSE$ for tetrahedral complex

According to question, $\Delta_o = 18000 \text{ cm}^{-1}$

:
$$\Delta_t = \frac{4}{9} \Delta_0 = \frac{4}{9} \times 18000 \text{ cm}^{-1}$$

= 4 × 2000 cm⁻¹
= 8000 cm⁻¹

Hence, correct choice is option (c).

- 2. (i) (d) Conductivity always decreases with decrease in concentration for weak and strong electrolytes. This is explained by the decrease in the number of ions per unit volume that carry current in solution on dilution. Hence, Assertion is incorrect but Reason is correct.
 - (ii) (c) Pure water has small amounts of hydrogen and hydroxyl ions ($\sim 10^{-7}$ M) due to which it has very low conductivity $(3.5 \times 10^{-5} \text{ S m}^{-1})$. Hence, assertion is correct but reason is incorrect.
 - (iii) (d) When electrolytes are dissolved in water, they furnish their own ions in the solution, hence the conductivity increases.

Hence, assertion is incorrect but reason is correct.

(iv) (a) Since, conductivity depends upon the number of ions per unit volume. Therefore, the conductivity of strong electrolytes decreases on dilution due to decrease in number of ions per unit volume.

Hence, both Assertion and Reason are correct but Reason is the correct explanation of Assertion.

Or

(a) Molar conductivity of weak electrolytic solution increases on dilution, because as we add excess water to increase the dilution, degree of dissociation

10. (C)

CH2CONH2 Br₂ NaOH

COOCH₃

Hofmann

reaction

bromamide

CH2NH

increases which leads to increase in the number of ions in the solution. Thus, $\Lambda_{\!m}\,$ show a very sharp increase.

Hence, both Assertion and Reason are correct but Reason is the correct explanation of Assertion.

3. (b) In alkaline medium, glycine predominantly exists as an anion. It is shown as follows

 $H_{3}N^{+} - CH_{2} - COO^{-} + OH^{-}$

- 4. (a) $t_{1/2} = \frac{0.0693}{k}$ for first order reaction. So, it is (1) independent of initial concentration. (1)
- 5. (b) Sulphuric acid removes the elements of water from cotton.

Or

(a) Electronic configuration of group 17 elements is ns²np⁵. All these elements have seven electrons in their outermost shell which is one electron short of the next noble gas.

- 6. (c) Ca²⁺ is the strongest reducing agent as its value of reduction potential is the lowest. (1)
- 7. (a) Given figure shows the structure of simple cubic unit cell.

In simple cubic (sc) unit cell, each corner atom is shared between 8 unit cells.

(c) Contribution of each atom per unit cell located at face-centre in a fcc unit cell is 0.5 or $\frac{1}{2}$

8. (a) 5-chlorohexan-2-ol is the IUPAC name of given compound.



(c) Alkenes react with water in the presence of acid as catalyst to form alcohols. In case of unsymmetrical alkenes, the addition reaction takes place in accordance with Markownikoff's rule.

$$CH_3 - CH = CH_2 + H_2O \rightleftharpoons^{H^{\oplus}} H_3C - CH - CH_3$$

Propene $H_3C - CH - CH_3$
OH

Propan-2-ol

9. (b) Primary alcohols contain — CH₂OH group.

So,
$$H_3C - C - CH_2OH$$
 is a primary alcohol.
 $H_3C - C - CH_2OH$ (1)





11. (c) The starting material used for the industrial preparation of phenol is cumene.



Phenol



Benzaidehyde does not have α-hydrogen. On reaction with alkali, it undergoes Cannizzaro reaction.

Hence Assertion is incorrect but Reason is correct. (1)

a On warming an aldehyde with freshly prepared ammoniacal silver nitrate solution (Tollen's reagent), a bright silver mirror is produced due to the formation of silver metal.

The aldehydes are oxidised to corresponding carboxylate anion. The reaction occurs in alkaline medium.

$$_{RCHO}$$
 + 2[Ag(NH₃)₂]⁺ + 3OH⁻ → $_{RCOO^-}$
+ 2Ag ↓ + 2H₂O + 4NH₃
Silver mimor

14. cl Assertion is correct but Reason is incorrect.

- Tetrahedral void is so called because it is surrounded by four spheres tetrahedrally while octahedral void is so called because it is surrounded by six spheres octahedrally. (1)
- 15. d 2- chloro -2 methylbutane is formed when neopentyl alcohol reacts with HCI. The initially formed primary carbocation undergoes rearrangement to form more stable tertiary carbocation.



Therefore, Assertion is incorrect but Reason is correct statement. (1)

16. a In case of haloarenes, the phenyl cation formed as a result of self ionisation will not be stabilised by resonance and therefore S_N 1 mechanism is fued out.

^Terefore, both Assertion and Reason are correct and Peason is correct explanation of Assertion. (1)



- Or (i) In aniline, the electron pair on nitrogen atom is involved in conjugation with ring and is less available for protonation than that in methylamine. Therefore, pK_b value of aniline is more than that of methylamine and aniline is less basic (as higher the pK_b value, weaker is the base). (1)
 - (ii) Ethylamine is soluble in water due to hydrogen bonding.



In aniline due to bulky hydrocarbon part, the extent of hydrogen bonding is less and it is not soluble in water. (1)

18. The amino acids exists as Zwitter ions in aqueous solution. Due to this, dipolar salt like structure amino acids have strong dipole-dipole interactions. Thus, their melting points are higher than corresponding haloacid which do not have salt like character. Secondly, they interact strongly with H₂O due to their salt like character. As a result, polar amino acids dissolve in polar solvents like H₂O. (2)

19. Let a = 100, a - x = 100 - 30 = 70, t = 40 min

For first order reaction,

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} = \frac{2.303}{40} \log \frac{100}{70}$$
$$= \frac{2.303}{40} \log \frac{10}{7} = \frac{2.303}{40} \log 1.428$$
$$= \frac{2.303}{40} \times 0.1548$$
$$k = 8.91 \times 10^{-3} \min^{-1}$$

Also,
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.91 \times 10^{-3} \text{ min}^{-1}} = 77.78 \text{ min}$$

 $t_{1/2} = 77.78 \text{ min}$ (2)

20. (i) The conversion of aniline into benzyl alcohol can be carried out in the following manner :



(ii) The conversion of benzene to *m*-bromophenol can be carried out in the following manner :



- (i) Noble gases being monoatomic have no interatomic forces except weak dispersion forces and therefore, they are liquefied at very low temperatures. Hence, they have low boiling points.
 - (ii) In SF₆, the six F atoms sterically protect the sulphur atom from attack by water due to steric hindrance. Further, F does not have *d*-orbitals to accept the electrons donated by H_2O molecules. As a result of these two reasons, SF₆ does not undergo hydrolysis. (1)

Or

- (i) Halogens have the smallest size in their respective periods and therefore, have high effective nuclear charge. As a result, they readily accept one electron to acquire the stable electronic configuration of the nearest noble gas. In other words, large amount of energy is released when a halogen atom accepts an electron to form the corresponding halide ion and thus, halogens have maximum negative electron gain enthalpies.
- (ii) The thermal stability of hydrides decreases on moving down the group. This is due to the decrease in the bond dissociation enthalpy (H-*E*) of hydrides on moving down the group where E = O, S, Se, Te. (1)

- **22.** The compounds in which small atoms like H, C, N, etc. occupy interstitial sites in the crystal lattice are called interstitial compounds. These compounds are well known for transition metals because small atoms can easily occupy the position in the voids present in the crystal lattices of transition metals.
- **23.** When $FeSO_4$ and $(NH_4)_2SO_4$ solution are mixed in 1_{11} molar ratio, Mohr's salt (a double salt) is formed.

$$\begin{aligned} \operatorname{FeSO}_{4}(aq) &+ (\operatorname{NH}_{4})_{2}\operatorname{SO}_{4}(aq) &\longrightarrow \\ &\operatorname{FeSO}_{4} \cdot (\operatorname{NH}_{4})_{2}\operatorname{SO}_{4} \cdot \operatorname{6H}_{2} \\ &\operatorname{FeSO}_{4} \cdot (\operatorname{NH}_{4})_{2}\operatorname{SO}_{4} \cdot \operatorname{6H}_{2} \\ &+ 2\operatorname{NH}_{4}^{+}(aq) + 2\operatorname{SO}_{4}^{2-}(aq)_{+ \operatorname{6H}_{3}} \end{aligned}$$

Because Fe^{2+} ions are formed on dissolution of $M_{Ohr'_3}$ salt, its aqueous solution gives the test of $Fe^{2+}_{ion_3}$. But when CuSO₄ is mixed with ammonia, following reaction occurs,

 $\begin{array}{l} \text{CuSO}_4(aq) + 4\text{NH}_3(aq) \longrightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4 \\ \text{This complex does not produce } \text{Cu}^{2^+} \text{ ion, so the} \\ \text{solution of } \text{CuSO}_4 \text{ and } \text{NH}_3 \text{ does not give the test of} \\ \text{Cu}^{2^+} \text{ ion.} \end{array}$

24. Given, $O + e^- \longrightarrow O^-$; $\Delta_{e_g} H = -141 \text{ kJ mol}^{-1}$ $O + 2e^- \longrightarrow O^{2-}$; $\Delta_{e_g} H = +702 \text{ kJ mol}^{-1}$

As it is obvious from the given data, the formation of divalent anion needs more energy as compared to monovalent anion where energy is released. Yet the number of oxides with -2 oxidation state of oxygen is more evident.

The reason is that their crystal lattice is more stable due to stronger electrostatic forces of attraction involving divalent oxygen than the oxides in which oxygen is monovalent in nature. (3)

Or

(i) Bartlett (1962) prepared a red compound of formula $O_2^+[PtF_6]^-$, dioxygenyl hexafluoroplatinate (V). He argued that the first ionisation energy of oxygen O_2 (= 1180 kJ mol⁻¹) was almost identical with that of xenon (= 1170 kJ mol⁻¹). He thought that if oxygen could form such compounds, xenon should also form similar compounds. He prepared Xe⁺PtF_6^- by mixing PtF_6 with xenon.

 $Xe + PtF_6 \longrightarrow Xe^+[PtF_6]^-$

- (ii) (a) Xenon is used for filling radio and television tubes.
 - (b) Liquid helium is used as a cryogenic agent for carrying experiments at low temperatures.
 - (c) Neon is used for filling in sodium vapour lamps and electric discharge tubes used for making decorative tubes for advertisement.

25. Given, cell edge length,
$$a = 250 \text{ pm} = 250 \times 10^{-10} \text{ cm}$$

pensity = 8 g cm⁻³
For bcc cell, number of atoms, $Z = 2$
Molar mass, $M = ?$
We know that, density, $d = \frac{Z \cdot M}{a^3 \cdot N_A}$
or 8g cm⁻³ = $\frac{2 \times M}{(250 \times 10^{-10} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}$
or $M = \frac{(250 \times 10^{-10} \text{ cm})^3 (6.022 \times 10^{23} \text{ mol}^{-1})}{2} \times 8$
 $= \frac{9.409 \times 8}{2} = 37.64 \text{ g mol}^{-1}$
For bcc unit cell, $4r = \sqrt{3}a$
Radius, $r = \frac{\sqrt{3} \cdot a}{4} = \frac{1.732 \times 250}{4} = 108.25 \text{ pm}$ (1)

26. Wurtz-Fittig reaction When aryl halide is heated with alkyl halide in the presence of sodium in dry ether, halogen atom is replaced by alkyl group and alkylarene is formed. This reaction is called Wurtz-Fittig reaction.



(ii) Fittig reaction When haloarenes react with sodium in the presence of dry ether, two aryl groups are joined together and diphenyl is formed. This reaction is called Fittig reaction.



(iii) Swarts reaction The synthesis of alkyl fluorides is achieved by heating an alkyl bromide/chloride in the presence of AgF, Hg₂ F₂, CoF₂ or SbF₃. This reaction is known as Swarts reaction.

$$R - Br + AgF \longrightarrow R - F + AgBr$$

$$H_{3}C - Br + AgF \longrightarrow H_{3}C - F + AgBr$$
(1)
$$Or$$
(i)
$$CH_{3}CH_{2}CI \xrightarrow{KCN} CH_{3}CH_{2}CN \xrightarrow{2H_{2}O/H^{+}}$$
Ethyl chloride
$$Ethyl nitrile$$
(A)
$$CH_{3}CH_{2}CH_{2}Br \xrightarrow{Alc.KOH} CH_{3}CH = CH_{2}$$
(B)
$$(ii) CH_{3}CH_{2}CH_{2}Br \xrightarrow{Alc.KOH} CH_{3}CH = CH_{2}$$
(B)
$$(iii) CH_{3}CH_{2}CH_{2}Br \xrightarrow{Alc.KOH} CH_{3}CH = CH_{2}$$

$$(A)$$

$$(B)$$

$$(B)$$

$$(B)$$

$$(B)$$

$$(CH_{3}CH_{2}CH_{2}Br \xrightarrow{Alc.KOH} CH_{3}CH = CH_{2}$$

$$(CI)$$

$$(B)$$

$$(CI)$$

$$(B)$$

$$(CI)$$

27. Initial millimoles of CH₃COOH = $100 \times 0.50 = 50$

Final millimoles of CH₃COOH = $100 \times 0.49 = 49$ Millimoles adsorbed = 50 - 49 = 1

Moles adsorbed $=\frac{1}{1000}$

Number of molecules adsorbed

$$= \frac{1}{1000} \times 6.023 \times 10^{23}$$

$$= 6.023 \times 10^{20}$$
Area per molecule
$$= \frac{\text{Total surface area}}{\text{Number of molecules}}$$

$$= \frac{3.01 \times 10^2}{6.023 \times 10^{20}} = 5 \times 10^{-19} \text{ m}^2$$
(3)

$$\begin{array}{c} CH_{3}CH_{2}CHO + 2[Ag(NH_{3})_{2}]^{+} + 3OH^{-} \longrightarrow \\ Propanal \\ CH_{3}CH_{2}COO^{-} + 2Ag \downarrow + 4NH_{3} + 2H_{2}O \\ Silver mirror \\ CH_{3}COCH_{3} \xrightarrow{\text{Tollen's reagent}} No silver mirror \\ Propanone \end{array}$$

(b) lodoform test Acetophenone being a methylketone, on treatment with NaOI (12 / NaOH) gives yellow precipitate of iodoform but benzophenone does not.

$$\begin{array}{ccc} C_{6}H_{5}COCH_{3}+3NaOI \longrightarrow C_{6}H_{5}COONa+CHI_{3} \downarrow\\ Acetophenone & & lodoform \\ C_{6}H_{5}COC_{6}H_{5} \longrightarrow No \ ppt. \\ Benzophenone & (1) \end{array}$$

Di-tert-butyl ketone < tert-butylmethyl ketone < acetone < acetaldehyde.

(1)

(1)

29. (i) The order of given reaction is one.

(ii) For first order reactions,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{(3.0 \text{ h})}$$

or
$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

or
$$\log \frac{[A]_0}{[A]} = \frac{k \times t}{2.303}$$
,
 $\log \frac{[A]_0}{[A]} = \frac{0.693}{3 \text{ h}} \times \frac{8 \text{ h}}{2.303} = 0.8024$
 $\frac{[A]_0}{[A]} = \text{antilog } 0.8024 = 6.345$
 $[A]_0 = 1\text{ M};$
 $[A] = \frac{[A]_0}{6.345} = \frac{1 \text{ M}}{6.345} = 0.1576 \text{ M}$
(1)

After 8 h, sucrose left = 0.1576 M

Or (i) Pseudo first order reaction The reaction which is bimolecular but has order one, is called pseudo first order reaction, e.g. acidic hydrolysis of ester.

$$CH_{3}COOC_{2}H_{5} + H_{2}O \xrightarrow{H^{+}} CH_{3}COOH + C_{2}H_{5}OH$$
(1)

(ii) Given, $t_{1/2} = 37.9 \sec$ Initial concentration = $[R]_0$ Concentration after time, $t = \frac{[R]_0}{4}$

[because 3/4th of the PH₃ is decomposed]

(a)
$$t = 1 \min = 60 \sec k = \frac{0.693}{37.9} = 0.0183 \sec^{-1}$$

 $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$
 $60 = \frac{2.303}{0.0183} \log \frac{[R]_0}{[R]}$
or $\log \frac{[R]_0}{[R]} = \frac{60 \times 0.0183}{2.303} = 0.4768$
 $\frac{[R]_0}{[R]} = \text{antilog } 0.4768 \Rightarrow \frac{[R]_0}{[R]} = 2.997$
Let the initial amount $[R_0]$ is 100
 $\frac{100}{2.997} = [R]$
 $[R] = 33.3\%$ (1)
(b) $k = \frac{0.693}{t_{1/2}} = \frac{0.693}{37.9} \sec^{-1}$
 $t = \frac{2.303}{k} \log \frac{[R]_0}{[\frac{[R]_0}{4}]} = \frac{2.303}{37.9} \log 4$
 $2.303 \times 37.9 \times 0.6020$

$$t = \frac{2.303 \times 37.9 \times 0.6020}{0.693} = 75.82 \sec$$
(1)

(1)

(1)

(1)

3

30. (i) Hydrolysis of cyclohexyl methyl bromide by aq. NaOH gives cyclohexyl methanol.

(ii) Hydrolysis of 1-bromopentane by aq. NaOH
$$\xrightarrow{\text{Heat}}_{S_{n}2}$$
 $\xrightarrow{\text{CH}_2\text{OH}}_{H_{abr}}$
(ii) Hydrolysis of 1-bromopentane by aq. NaOH give (I)
pentan-1-ol.
CH_3CH_2CH_2CH_2CH_2-Br + NaOH $\xrightarrow{\text{Heat}}_{S_{n}2}$
 $CH_3(CH_2)_4$ -OH + NaBr
 $Pentan-1-ol$ (I)
1. (i) The spin only magnetic moment is given by
 $\mu = \sqrt{n(n+2)}$
Thus, $\sqrt{n(n+2)} = 1.8$
Squaring both sides,
 $n(n+2) = 3.24$
 $n^2 + 2n = 3$
 $n^2 + 2n - 3 = 0$
 $n^2 + 3n = n - 3 = 0$

$$(n-1)(n+3)=0$$

 \Rightarrow *n* = 1, but *n* \neq - 3 is not possible,

It means that one unpaired electron is present, i.e. $_{\mbox{i}}$ is copper.

Thus,
$$2\operatorname{Cu}_{(A)} 2\operatorname{H}_2\operatorname{SO}_4 + \operatorname{O}_2 \longrightarrow 2\operatorname{Cu}_{(B)} 2\operatorname{Cu}_4 + 2\operatorname{H}_2 \operatorname{O}_{(B)}$$

 $2\operatorname{Cu}_{(B)} 2\operatorname{Cu}_4 + 4\operatorname{KI}_{(C)} \longrightarrow 2\operatorname{K}_2\operatorname{SO}_4 + 2\operatorname{Cu}_2$
 $(B) 2\operatorname{Cu}_2 \longrightarrow 2\operatorname{Cu}_2 \operatorname{H}_2$
 $(D) (2)$

- (ii) (a) Transition elements are those which, have partly filled *d*-orbitals. Since, neither the atoms nor ions of Zn, Cd and Hg have partly filled *d*-orbitals, they are normally not regarded as transition metals.
 - (b) Compounds of transition metals are coloured due to *d*-*d* transition. (1)
 - (c) Electronic configuration of Mn^{2+} is $3d^{5}$ which is half-filled and hence stable. So, 3rd ionisation enthalpy is very high, i.e., 3rd electron cannot be lost easily. In case of Fe^{2+} , electronic configuration is $3d^{6}$. Thus, it can lose one electron easily to give the stable configuration $3d^{5}$. (1)

Or

- (i) Europium in + 2 oxidation state shows stable electronic configuration, i.e. $[Xe]4t^7 5d^06s^0$. (2)
- (ii) (a) E values for Cr³⁺ / Cr²⁺ is negative (-0.41) and for Mn³⁺ / Mn²⁺ is positive (+1.57 V). Thus, Cr²⁺ can undergo oxidation and therefore, acts as a reducing

agent. On the other hand, Mn (III) can undergo reduction, and therefore, it acts as an oxidising agent

- (b) In the presence of complexing agents, cobalt (1)gets oxidised from +2 to +3 state because Co (III) is more stable than Co (II) (1)
- After loss of ns electrons d¹-electron can easily (C) be lost to give a stable configuration. Therefore, the elements having d¹ configuration are either reducing or undergo disproportionation. (1)

CH3COOH В (H_SO4) Ester

32. ^A-Thus, A is an alcohol.

0

$$A \xrightarrow{\text{Mild exidation}} C \xrightarrow{50\% \text{KOH}} A \xrightarrow{\text{A} + D} A_{\text{Alcohol}}$$

Thus, C und $D \xrightarrow{\text{PCI}_5} \xrightarrow{\text{NH}_3} E \xrightarrow{-\text{H}_2\text{O}} \text{HCN}$

Thus, E is H-C-NH2, because on dehydration, it gives HCN (with intermediate HCOCI)

0

$$\begin{array}{c} O & O \\ \parallel & \parallel \\ CH_3 - C - OH + CH_3 OH & \xrightarrow{H_2SO_4} CH_3 - C - OCH_3 \\ (A) & \xrightarrow{(B)} \\ Methyl \ acetate \\ CH_3 OH & \xrightarrow{Mild \ oxidation} HCHO \\ (A) & (C) \end{array}$$

$$\begin{array}{c} (A) \\ HCHO \\ (C) \end{array} \xrightarrow{KOH} HCOOH + CH_3OH \\ (D) \\ HCOOH \xrightarrow{PCl_5} H - C - Cl \xrightarrow{NH_3} H - C \\ (D) \\ HCOOH \xrightarrow{PCl_5} H - C - Cl \xrightarrow{NH_3} H - C \\ (D) \\ HCOOH \\ (D) \\ HCOOH \\ (E) \\ HCOOH \\ (E) \\ HCOOH \\ (E) \\ (E$$





: 100 g water has 5.6 g of Ba(OH)₂ · 8H₂O :.1000 g water will have $Ba(OH)_2 \cdot 8H_2O = 56g$ Number of moles of Ba(OH)₂ · 8H₂O = $\frac{56}{315}$

 $= 0.178 \, mol$

Thus, molality of Ba(OH)₂ = 0.178 m
Ba(OH)₂
$$\longrightarrow$$
 Ba²⁺ + 2OH⁻
Molality of OH⁻ ions = 2 × molality of Ba(OH)₂
= 2 × 0.178 = 0.356 m (2½)
Or (i) Suppose, the molar mass of solute = M g mol⁻¹
Number of moles of solute $(n_2) = \frac{30}{M}$ mol
Number of moles of H₂O
 $(n_1) = \frac{90 \text{ g}}{18 \text{ g mol}^{-1}} = 5 \text{ mol}$
 $p_1 = 2.8 \text{ kPa}$
 $\frac{p_1^{\circ} - p_1}{p_1^{\circ}} = \frac{n_2}{n_1 + n_2}$
 $\Rightarrow \frac{p_1^{\circ} - 2.8}{p_1^{\circ}} = \frac{30/M}{5 + 30/M}$ (1)
or $1 - \frac{2.8}{p_1^{\circ}} = \frac{30/M}{5 + 30/M}$
or $\frac{2.8}{p_1^{\circ}} = 1 - \frac{30/M}{5 + 30/M} = \frac{5}{5 + 30/M}$
or $\frac{p_{12}^{\circ}}{2.8} = \frac{5 + 30/M}{5} = 1 + \frac{6}{M}$...(i)(1)
On adding 18 g of water, $n(H_2O) = 6 \text{ mol}$
 $(= 5 + 1 = 6 \text{ mol})$

Then, $p_1' = 2.9 \text{ kPa}$ $\therefore \quad \frac{p_1^{\circ} - 2.9}{p_1^{\circ}} = \frac{30 / M}{6 + 30 / M}$ or $1 - \frac{2.9}{p_1^\circ} = \frac{30 / M}{6 + 30 / M}$ $\frac{2.9}{p_1^\circ} = 1 - \frac{30 / M}{6 + 30 / M}$ or $=\frac{6}{6+30/M}$ $\frac{p_1^\circ}{2.9} = \frac{6+30\,/M}{6} = 1 + \frac{5}{M}$ or ...(ii) (1) On dividing Eq. (i) by Eq. (ii), we get $\frac{2.9}{2.8} = \frac{1+6/M}{1+5/M}$ or $2.9\left(1+\frac{5}{M}\right) = 2.8\left(1+\frac{6}{M}\right)$ or 2.9 + $\frac{14.5}{M}$ = 2.8 + $\frac{16.8}{M}$ \Rightarrow M = 23 u (1) (ii) Putting M = 23 in Eq. (i), we get $\frac{p_1^\circ}{2.8} = 1 + \frac{6}{23} = \frac{29}{23}$ $p_1^\circ = \frac{29}{23} \times 2.8 = 3.53 \text{ kPa}$ or (1)