SECTION - A

1. (D) $271 \cdot 6 \ S \ cm^2 \ mol^{-1}$

$$\Lambda_m^\circ (CaCl_2) = \Lambda_m^\circ (Ca^{2+}) + 2\Lambda_m^\circ (Cl^-) = 119 + 2 \times 76.3 = 271 \cdot 6 \ S \ cm^2 \ mol^{-1}$$

2. (A) A - methanol , B - Potassium formate

(annizzano reaction)

3. (c) Ascorbic acid

4. (A) Pd - BaSO_4

5. (A) $(CH_3)_3 C - Br$

3° carbocation is highly stable and favours $S_N 1$

6. (B) Manganese

(Mn has $4s^2 \ 3d^5$ configuration → $+2$ to $+7$ oxidation states)

7. (c) $k = Ae^{-E_a/RT}$

8. (A) $CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{N} - CH_3$

9. (c) Tertiary alcohol

10. (B) Slope $= -k$, Intercept $= [R_0]$

$[R] = [R_0] - kt$ for zero order reaction

11. (A) I-(r), II-(p), III-(s), IV-(q)

12. (A) $(n-1) d^{1-10} ns^{1-2}$

13. (D) Assertion (A) is false, but Reason (R) is true

p-nitrophenol is more acidic than phenol.

14. (A) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct

explanation of the Assertion (A).

15. (C) Assertion (A) is true, but Reason (R) is false.
Fructose is a reducing sugar as it reduces Fehling solution and Tollen's reagent (by tautomerisation in basic medium to form aldehydic-glucose)

16. (C) Assertion (A) is true, but Reason (R) is false.
When cell external opposing potential is more than 1.1V cell acts like an electrolytic cell.

4

SECTION-B

17. (a) The sum of exponents (or powers) to which concentration of various reactants is raised, in the expression of rate law for a chemical reaction, is called order of reaction and indicates the dependence of reaction rate on reactant concentration.

Eq for reaction $A + B \rightarrow$ Products

if rate $= k[A]^x[B]^y$, order of reaction with respect to A and B is x and y respectively. Overall order of reaction is $x+y$.

(b) The minimum amount of energy required to overcome the potential barrier of a chemical reaction to bring about the reaction of reactants to form an unstable intermediate and then convert into products, is called activation energy (Ea)

As per Arrhenius equation, $k = Ae^{-Ea/RT}$, lower the activation energy, more favoured is the reaction. This is achieved by use of catalyst.

Ea is measured in $J\,mol^{-1}$ (SI)

Potential energy

Reactant

Product

intermediate

Ea

Reaction coordinate
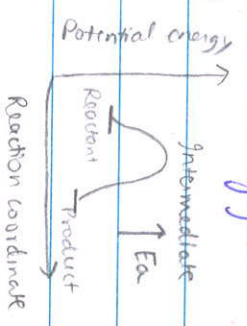
18. Given, $w_2 = 18$, $w_2 = 18$ g, $M_2 = ?$, $W_1 = 200$ g $= 200/1000 = 0.2$ kg

$T_f = 272.07$ K $T_f°$ for water $= 273.15$ K $K_f = 1.86$ K kg mol^{-1}

For depression of freezing point, we use due to non-volatile solute, we use

$$\Delta T_f = K_f \cdot m$$

$$T_f° - T_f = K_f \times \frac{w_2}{M_2 \times w_1}$$

$$\left(\text{Molality } m = \frac{\text{Moles of solute}}{\text{Mass (kg) of solvent}} \right)$$

$$(273.15 - 272.07)\,K = 1.86 \frac{K\,kg}{mol} \times \frac{18\,g}{M_2 \times 0.2\,kg}$$

$$1.08 = \frac{1.86 \times 18}{M_2 \times 0.2} \qquad \therefore M_2 = \frac{1.86 \times 18}{1.08 \times 0.2} = 155 \text{ g mol}^{-1}$$

Molecular mass of solute is 155 g mol^{-1}

19. (a) CH_3-CH_2-I undergoes S_N2 reaction at a faster rate than CH_3-CH_2-Br because C—I bond enthalpy is lower and also because $I^{\ominus}$ is a better leaving group (and nucleophile) than $Br^{\ominus}$ so its bond cleavage on attack of nucleophile by S_N2 is faster and more favoured.

(b) Increasing order of boiling points for given alkanes and haloalkanes can be determined on the basis of their increasing molecular mass, as follows —

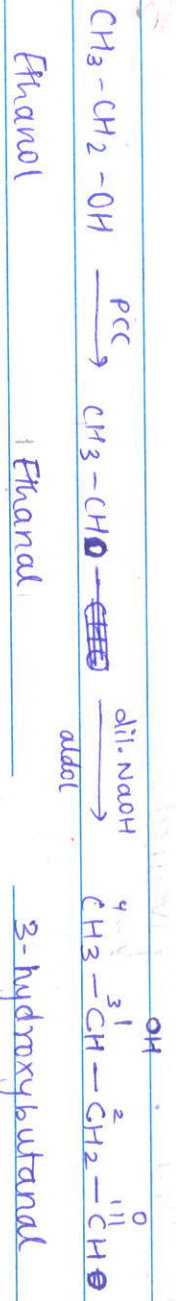Butane < 1-chlorobutane < 1-bromobutane < 1-iodobutane

20. (b)

(i) Toluene can be converted to benzoic acid by side-chain oxidation using $KMnO_4-KOH$ (or $KMnO_4$ in acidic medium) or some other strong oxidising agent.
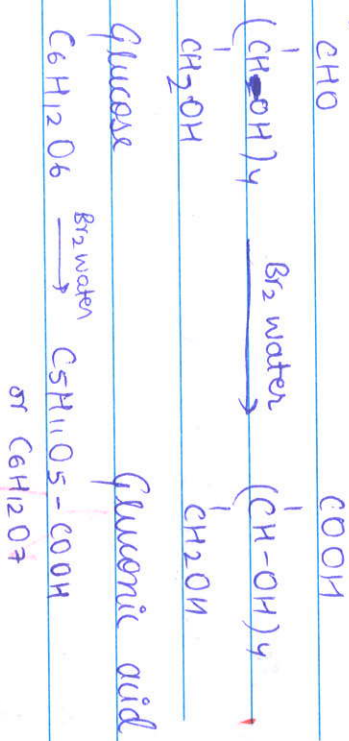

Toluene   Benzoic acid
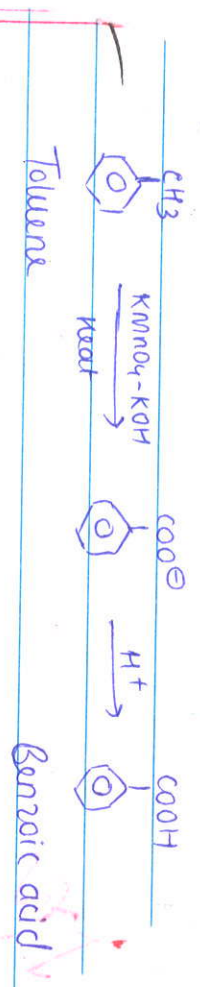
(ii) To convert ethanol to 3-hydroxybutanal, we first oxidise it to
ethanal using mild oxidising agents like PCC (pyridinium chlorochromate)
or then and then by aldol reaction on mild conditions using dil. NaOH

$$CH_3-CH_2-OH \xrightarrow{PCC} CH_3-CHO \xrightarrow[aldol]{dil.\ NaOH} \overset{OH}{\underset{4}{C}H_3-\overset{|}{\underset{3}{C}H}-\overset{}{\underset{2}{C}H_2}-\overset{O}{\underset{1}{C}H\!\!}}$$

Ethanol   Ethanal   3-hydroxybutanal

21. (a) Glucose reacts with bromine water, a mild oxidising agent to form
gluconic acid, which confirms the presence of aldehyde group (-CHO)
in glucose. Chemical equation is —

$$\begin{array}{c} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array} \xrightarrow{Br_2\ water} \begin{array}{c} COOH \\ | \\ (CH-OH)_4 \\ | \\ CH_2OH \end{array}$$

     glucose   gluconic acid

$$C_6H_{12}O_6 \xrightarrow{Br_2\ water} C_5H_{11}O_5-COOH$$
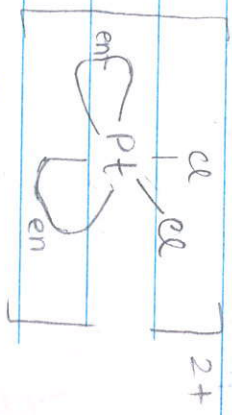$$or\ C_6H_{12}O_7$$

(b)(i) Thymine(T) is present in DNA
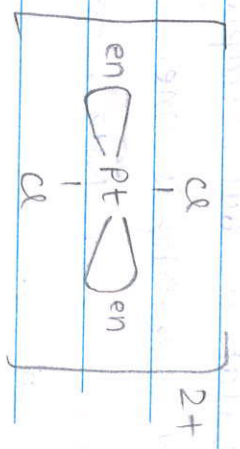(ii) Uracil(U) is present in RNA
(Both are nitrogenous pyrimidine bases)

22. (a) $[Pt(en)_2 Cl_2]^{2+}$ has 2 geometrical isomers; cis and trans -

Cis - isomer
optically active

Trans - isomer
Optically inactive

($\bigtriangleup$ en - en -
didentate ligand)

(b) On the basis of crystal field theory for d^4 ion, if $\Delta o < P$ it means the energy crystal field splitting energy (CFSE) $\sim \Delta o$ is insufficient to cause pairing of electrons into t_{2g} orbitals and hence fourth electron in filling d orbitals, enters e_g orbital. This occurs when the ligand is a weak field ligand forming high spin complex. Electronic configuration will be $t_{2g}^3 e_g^1$.

9

(c) A ligand that can donate or share its ⇄ electrons to the central metal atom or ion, through only one of its atoms per molecule, #aH is known as a unidentate ligand. Such ligands in a coordination entity do not undergo chelation but simply ligate to central atom or ion through a single bond. Denticity is one.

Examples are Cl^-, $\overset{..}{N}H_3$, $H_2\overset{..}{O}$ in which bonding occurs through Cl, N, O atoms respectively.

23.

For cell at 25°C given by

$Sn \mid Sn^{2+} (0.001 M) \parallel H^+ (0.01 M) \mid H_2(g)$ (1bar) $\mid Pt(s)$

$E°(Sn^{2+}|Sn) = -0.14V$ $E°(H^+/H_2) = 0V$

Half-cell equations are :

(cathode (reduction) : $2H^+ (0.01M) + 2e^- \rightarrow H_2(g)$ (1bar)

Anode (oxidation) : $Sn \rightarrow Sn^{2+} (0.001M) + 2e^-$

Net equation : $2H^+ (0.01M) + Sn \rightarrow H_2(g)$ (1bar) $+ Sn^{2+} (0.001M)$

$E°_{cell} = E°_{(H^+/H_2)} - E°_{(Sn^{2+}/Sn)}$ $(E°_{cathode} - E°_{anode})$

$= 0 - (-0.14V) = +0.14V$
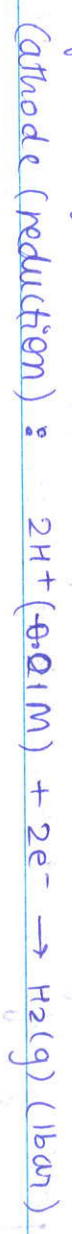
As per Nernst equation, $E_{cell} = E°_{cell} - \dfrac{2.303 RT}{nF} \log \dfrac{[Sn^{2+}][H_2]}{[H^+]^2 [Sn]}$, $n = 2$

$E_{cell} = E°_{cell} - \dfrac{0.059}{2} \log \dfrac{[Sn^{2+}]}{[H^+]^2}$

$$E_{cell} = 0.14 - \frac{0.059}{2} \log \frac{(0.001)}{(0.01)^2} = 0.14 - \frac{0.059}{2} \log 10$$

$$= 0.14 - \frac{0.059 \times 1}{2} \quad (\log 10 = 1)$$

$$= 0.14 - 0.0295$$

$$= 0.1105 \, V \approx 0.11 \, V$$
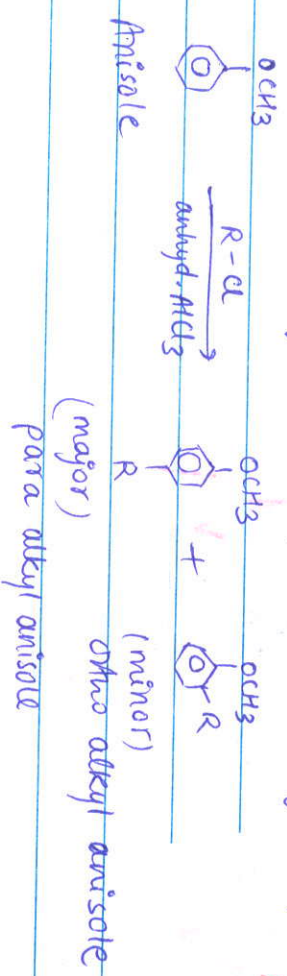
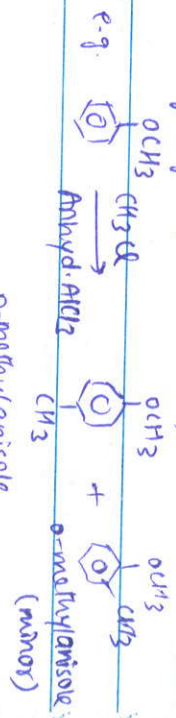Emf of given cell is 0.11 V

24. (b) Williamson ether synthesis

$$R-X + R'O^{\ominus} \, Na^{\oplus} \longrightarrow R-O-R' + NaX$$

R, R' — alkyl/n groups   X → halide (Cl, Br, I)

$$CH_3-Br + C_2H_5-O^{\ominus}Na^{\oplus} \longrightarrow CH_3-O-C_2H_5 + NaBr$$

— bromomethane /   ethyl methyl ether
   methylbromide

(c) Friedel crafts alkylation of anisole gives para product (major) ~~and~~ and ortho (minor)

'R-alkyl group - CH3 etc.'

e.g.

p-methylanisole
(major)

+

o-methylanisole
(minor)

(d) Riemer—Tiemann reaction

Phenol

intermediate

o-hydroxybenzaldehyde
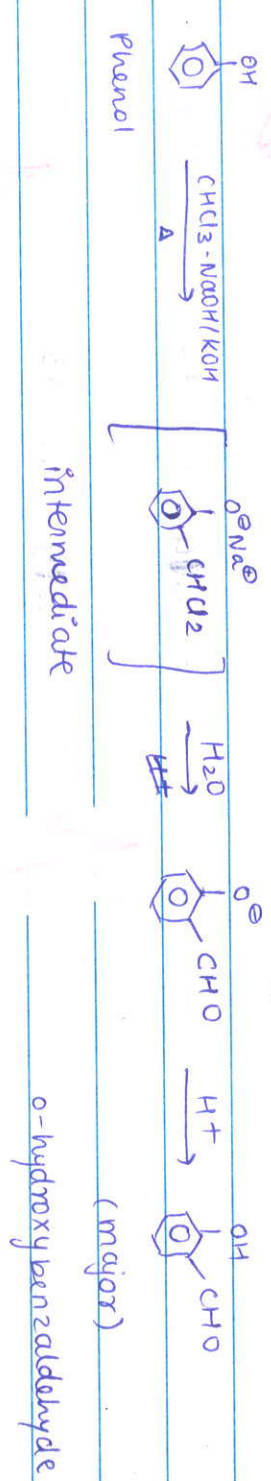
25. (a) (i) Addition of NaHCO₃

It gives brisk effervescence in case of benzoic acid due to CO_2 evolution by an acid-base reaction. No effervescence is observed with phenol as it is not sufficiently acidic for the reaction.
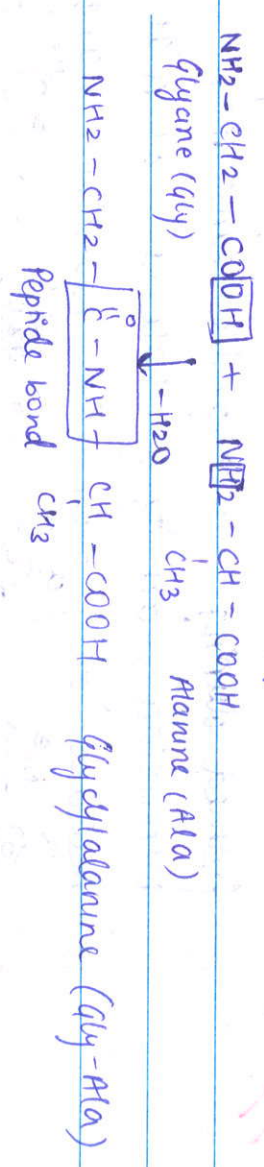
(ii) Addition of Tollen's Reagent

It produces silver mirror in case of reaction with propanal (an aldehyde) while no reaction occurs with propanone (a ketone)

We can also use fehling solution which gives positive test with propanal marked by brick red precipitate formation.

(b) $CH_3CHF.CH_2.COOH$ is a stronger acid than $CH_2FCH_2CH_2COOH$ due to the fact that fluorine is closer $\underset{\text{distance}}{\overset{\text{by}}{\times}}$ to $-COOH$ group in the former, so by its stronger inductive $(-I)$ effect, it disperses and stabilises the negative charge on $-COO^\ominus$ [carboxylate] ion formed.

26. (a) Amino acids which are not synthesised in our body and need to be consumed from diet (external source) are called essential amino acids and are important for the body growth, development and functioning. Examples are isoleucine, arginine, valine etc. (There are 10 essential amino acids known).

(b) Amino acids are joined to each other to form polypeptides or proteins by peptide bond which is essentially an amide bond $\left(-\overset{\overset{O}{\|}}{C}-NH-\right)$ formed by combination of $-NH_2$ group of one molecule and $-COOH$ of another, of same or different type of amino acid, with elimination of a water molecule.

for example, $NH_2-CH_2-\boxed{COOH} + \boxed{NH_2}-CH-COOH \xrightarrow{-H_2O}$
$\qquad\qquad$ Glycine (Gly) $\quad\;\; \underset{CH_3}{|}$
$\qquad\qquad\qquad\qquad\qquad$ Alanine (Ala)

$NH_2-CH_2-\boxed{\overset{O}{\overset{\|}{C}}-NH}-\underset{CH_3}{\underset{|}{CH}}-COOH$ Glycylalanine (Gly-Ala)
$\qquad\qquad$ Peptide bond

(c) When a native protein (having well-defined biological existence and structure) is subjected to change in external physical conditions, or temperature, like temperature, or chemical changes like change in pH, the hydrogen bonds between & polypeptide chains are broken and disturbed causing uncoiling of helical structure. This is called denaturation of proteins. It changes only secondary and tertiary structure of proteins, while its primary structure is intact. Coagulation of egg white and curdling of milk are examples of denaturation.

27. (a) IUPAC name of compound is 3-bromo-1-chlorocyclohex-1-ene

(However, if substituent was preferred over double bond, name would have been 1-bromo-3-chlorocyclohex-2-ene but that is not right by lowest sum rule).
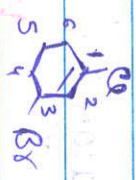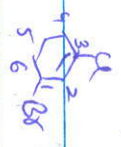
(b) —NO₂ is an electron-withdrawing group which stabilises the negative charge formed during nucleophilic substitution reactions, by its —M effect, thus increasing reactivity of haloarenes when at their ortho and para positions, because only then the negative charge reaches them through resonance.

(carbanion
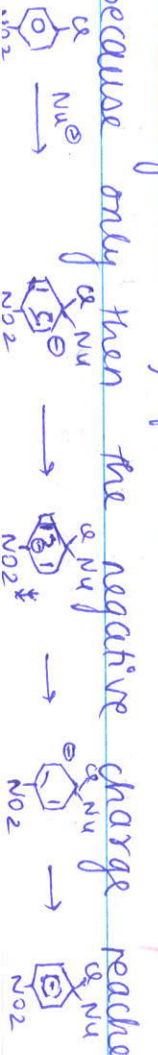
(c) When ethyl chloride is treated with alcoholic potassium hydroxide, dehydrohalogenation or β-elimination occurs and ethene is formed. Reaction is favoured on heating.

$$CH_3 - CH_2 - Cl \xrightarrow{\text{alc. KOH}} CH_2 = CH_2 + HCl$$

ethyl chloride   ethene

$$\left(\because \begin{array}{c} CH_2 - CH_2 \\ | \\ H \quad Cl \end{array} \xrightarrow{-Hcl} CH_2 = CH_2 \right)$$

$$\boxed{\begin{array}{c} H \\ Cl \end{array}}$$

28. For first order reaction, $t = \dfrac{2 \cdot 303}{K} \log \dfrac{[R_0]}{[R]}$ at time t with concentration [R]

For reaction being 99.9% complete, $[R] = \dfrac{0.1\%}{[R_0]} \neq [R_0] \times 10^{-3}$

For time $t_9 = \dfrac{2 \cdot 303}{K} \log \dfrac{[R_0]}{[R_0] \times 10^{-3}} = \dfrac{2 \cdot 303}{K} \log 10 = \dfrac{2 \cdot 303 \times 3 \log 10}{K} = \dfrac{2 \cdot 303 \times 3}{K} \quad (log\, 10 = 1) \quad \textemdash ①$

For reaction being 50% complete, $[R_2] = [R_0] \times 50\% = [R_0]/2$

Time $t_{1/2} = \dfrac{2 \cdot 303}{K} \log \dfrac{[R_0]}{[R_0]/2} = \dfrac{2 \cdot 303 \log 2}{K} = \dfrac{2 \cdot 303 \times 0 \cdot 3010}{K} \quad (log\, 2 = 0 \cdot 3010) \quad \textemdash ②$

From ① and ②, $\dfrac{t_9}{t_{1/2}} = \dfrac{3}{0 \cdot 3010} \cong 10 \qquad t_9 = 10\, t_{1/2}$

Hence time required for 99.9% completion of reaction is 10 times the half-life of a first order reaction.
Hence, proved.

SECTION - D

29. (a) In $[CoF_6]^{3-}$, Co^{3+} exists with F^- ions forming outer orbital complex.

$_{27}Co^{3+}$ has electronic configuration $[Ar] 3d^6$ as follows -

Co^{3+}:

↑↓	↑	↑	↑	↑	

   3d⁶   4s⁰
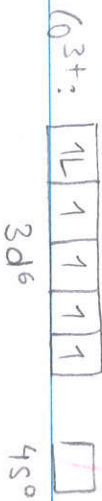
Since pairing is not possible due to insufficient strength of fluorine (weak field ligand), 4 unpaired electrons are present in Co^{3+} making it <u>paramagnetic</u>.

(b) Coordination number of Co in $[Co(en)_2Cl_2]^+$ is 6 as it is ligated with $2Cl^-$ (unidentate) and $2 en(NH_2-CH_2-CH_2-NH_2)$ (bidentate) ligands.

Hence total coordination number is $2\times1 + 2\times2 = 6$.

(c) (i) IUPAC name of $[Pt(NH_3)_2Cl_2]^{2+}$ is diamminedichloroplatinum (IV) ion or diammine dichlorido platinum (IV) ion

(ii) $[Co(NH_3)_6]^{3+}$ is an <u>inner</u> orbital complex as NH₃ being a strong field ligand causing pairing of (4) unpaired electrons in d^6 configuration of Co^{3+} (making it d^2sp^3 hybridisation).

30. (a) function of salt bridge in a galvanic cell is to connect the electrolytes of the two half cells and act as a bridge for movement of ions between them for continuity of the circuit internally.

and completion

(b) Galvanic cell behaves as an electrolytic cell when external opposing voltage exceeds the potential of cell. Thus, electrical energy is used to bring about non-spontaneous chemical reaction. There is reversal of current.

(c) No, copper sulphate cannot be stored in a pot made of zinc as Cu^{2+} gets reduced to Cu and Zn of pot gets oxidised to Zn^{2+}.

$E°cell = E°_{Cu^{2+}/Cu} - E°_{Zn^{2+}/Zn} = 0.34 - (-0.76) = +1.1V$

Positive $E°cell$ indicates that this reaction is feasible and shall occur on account of copper having a positive reduction potential and zinc's oxidation being favoured as well.

SECTION-E

31. (a) Zinc is not regarded as a transition element as it has fully filled d^{10} configuration as both Zn atom $[Ar] 4s^2 3d^{10}$ and Zn^{2+} ion $([Ar] 3d^{10})$ which is its only stable ion. As per IUPAC, our elements having incompletely filled d-subshell in ground state or stable oxidation state only are transition elements, so zinc is not one.

(d) Transition elements are good catalysts as they can show variable oxidation states due to presence of (n-1) d electrons besides ns electrons and provide large surface area to bind with reactants forming intermediates and lowering activation energy to form products.

Examples is finely divided iron used in Haber's process to manufacture ammonia.

(e) Compounds of transition metals generally contain are coloured as they have such cations that have incomplete d subshell with d electrons making d-d transitions absorbing visible light and appearing in complementary colour.

Variable oxidation states impart them various colours.

(f) K_2MnO_4 is paramagnetic as it has Mn^{6+} having 1 d electron (unpaired) while $KMnO_4$ is diamagnetic as it has Mn^{7+} having 0 d electron and remaining subshells are fully filled.

Mn^{6+} : [Ar] 3d¹ Mn^{7+} : [Ar]

(g) $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

(oxidising nature of $Cr_2O_7^{2-}$ ion in acidic medium with Cr changing $+6 \rightarrow +3$)

32. (a)(i) The process in which external pressure greater than osmotic pressure is applied on solution side to make the flow of solvent molecules from solution to solvent side (opposite to their own concentration gradient of solvent molecules) across a semipermeable membrane is called reverse osmosis. It is helpful in water purification systems.

(ii) Solubility of gas in liquid decreases with crease in temperature (as K_H increases and $p = K_H x$ as per Henry's law). Hence amount of dissolved gases (oxygen) in water is more in cold water than hot water, so aquatic species find it more comfortable in the former. This is an important consequence of Henry's law.

(iii) Given, $W_2 = 2g$ $M_2 = 180\ g\ mol^{-1}$ $W_1 = 100g$ $M_1 = 18.9\ mol^{-1}$ (water)

$P^0 = 32.8\ mmHg$ at $303K$, $P = ?$

By relative lowering of vapour pressure due to non-volatile solute glucose

RWP = mole fraction of solute

$$\frac{P^0 - P}{P^0} = n_2 = \frac{W_2/M_2}{W_1/M_1 + W_2/M_2}$$

here $W_1 >> W_2$ hence may be neglected

$$\frac{32.8 - P}{32.8} = \frac{\frac{2}{180}}{\frac{100}{18} + \frac{2}{180}} = \frac{0.2}{100 + 0.2} \approx \frac{0.2}{100.2} \approx \frac{0.2}{100} = 0.002$$

$\dfrac{W_1}{M_1}$ $\dfrac{W_2}{M_2}$

$32.8 - P = 32.8 \times 0.002 = 0.0656$

$P = 32.8 - 0.0656 = 32.7344 \approx 32.73\ mmHg$

Vapour pressure of solution is $32.73\ mmHg$.

33.(a) Amide A has high degree of unsaturation, hence should be benzamide.
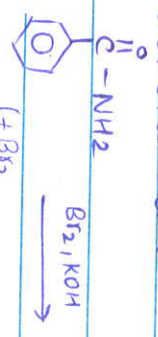
33.(b)(i) A - Benzamide

B - Aniline
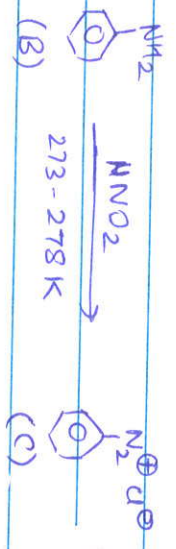
C - Benzene diazonium chloride (or benzene diazonium ion)
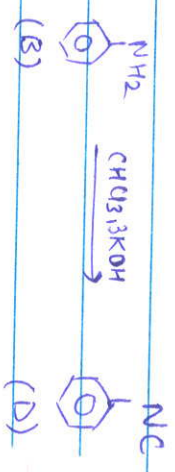
D - Benzene isocyanide (Isocyanobenzene)

E - Benzene

Reactions are —

$$\underset{\text{(A)}}{\overset{\overset{\displaystyle O}{\parallel}}{\underset{\text{C}-NH_2}}}$$
$\xrightarrow[\substack{(+Br_2 \\ +4KOH)}]{Br_2,\ KOH}$
$\underset{\text{(B)}}{\overset{NH_2}{\bigcirc}}$
$(+2K_2CO_3 + 2KBr)$

(B) Hoffmann Bromamide Degradation

$\underset{\text{(B)}}{\overset{NH_2}{\bigcirc}}$
$\xrightarrow[273-278\ K]{NNO_2}$
$\underset{\text{(C)}}{\overset{N_2^{\oplus}Cl^{\ominus}}{\bigcirc}}$ Diazotisation

$\underset{\text{(B)}}{\overset{NH_2}{\bigcirc}}$
$\xrightarrow{CHCl_3 KOH}$
$\underset{\text{(D)}}{\overset{Nc}{\bigcirc}}$ Carbylamine or isocyanide test

$\underset{\text{(C)}}{\overset{N_2^{\oplus}Cl^{\ominus}}{\bigcirc}}$
$\xrightarrow{C_2H_5OH}$
$\underset{\text{(E)}}{\bigcirc}$