CBSE Class 12 Chemistry 2026 — Set 1 — Answer Key

English Medium

Time Allowed: 3 Hours

General Instructions:

1. This is an answer key — each question is shown with its correct answer and a step-by-step explanation.
2. Questions appear in the original paper order.

Q.1

Which of the following curve represents the first order reaction ?

(a) Graph (A)

(b) Graph (B) <<

(c) Graph (C)

(d) Graph (D)

Explanation:

For a first order reaction $t_{1/2} = 0{\cdot}693/k$, which is independent of the initial concentration $[R]_0$.

Graph (B) shows $t_{1/2}$ constant (horizontal line) against $[R]_0$ → first order.

Graph (A) ($t_{1/2} \propto [R]_0$) and graph (C) (rate independent of concentration) describe a zero order reaction.

Answer: Graph (B).

Q.2

Which of the following solutions will have the lowest freezing point in water ?

(a) 0.1 M Glucose

(b) 0.1 M CaCl2 <<

(c) 0.1 M KCl

(d) 0.1 M Urea

Explanation:

Freezing point depression depends on the number of solute particles (van't Hoff factor i).

Glucose and Urea: i = 1 (non-electrolytes).

KCl: i = 2 ($K^+ + Cl^-$).

$CaCl_2$: i = 3 ($Ca^{2+} + 2Cl^-$).

Higher i → greater depression → lowest freezing point.

0.1 M $CaCl_2$ gives the most particles (0.3 mol/L effective), so it has the lowest freezing point.

Q.3

Which of the following is not a transition metal ?

(a) Sc

(b) Ag

(c) Hg <<

(d) Cu

Explanation:

Zn, Cd and Hg have completely filled d^{10} subshells in the atoms and in their common (+2) ions, so they are not regarded as transition metals.

Sc (Sc^{2+}, d^1), Cu (Cu^{2+}, d^9) and Ag (Ag^{2+}, d^9) have an incompletely filled d-subshell in at least one ion.

Hence Hg is not a transition metal: (C).

Q.4

Which of the following represents the fraction of molecules with energies equal to or greater than Ea ?

(a) Ea/RT

(b) e^(–Ea/RT) <<

(c) –Ea/RT

(d) e^(+Ea/RT)

Explanation:

According to the Maxwell-Boltzmann distribution, the fraction of molecules having energy equal to or greater than the activation energy Ea is given by e^(–Ea/RT).

This is the Boltzmann factor.

A higher Ea or lower T gives a smaller fraction.

Q.5

What will happen during the electrolysis of aqueous solution of CuCl2 by using platinum electrodes ?

(a) Cu will deposit at Anode

(b) H2 gas will be released at cathode

(c) O2 gas will be released at anode

(d) Cl2 gas will be released at anode <<

Explanation:

In electrolysis of aqueous CuCl2: At cathode — Cu2+ ions are preferentially discharged (Cu deposits).

At anode — Cl– ions are preferentially discharged over OH– (from water) because Cl– concentration is high and its discharge potential is lower.

So Cl2 gas is released at the anode.

Q.6

Aspirin is obtained by acetylation of

(a) Phenol

(b) Salicylaldehyde

(c) 2-Hydroxybenzoic acid <<

(d) Benzoic acid

Explanation:

Aspirin (acetylsalicylic acid) is prepared by acetylation of 2-hydroxybenzoic acid (salicylic acid) with acetic anhydride.

The –OH group of salicylic acid reacts with acetic anhydride to form the acetyl ester (aspirin).

Q.7

The secondary valency of Co in the complex [Co(NH3)5(NO2)]^2+ is

(a) 5

(b) 1

(c) 4

(d) 6 <<

Explanation:

Secondary valency (coordination number) equals the total number of ligands coordinated to the central metal.

In [Co(NH3)5(NO2)]^2+: 5 NH3 ligands + 1 NO2 ligand = 6.

Coordination number = 6.

Q.8

At low temperature, phenol reacts with dil. HNO_3 to yield

(a) 2, 4, 6-Trinitrophenol

(b) o-Nitrophenol only

(c) p-Nitrophenol only

(d) ortho-and para-nitrophenol <<

Explanation:

The –OH group in phenol is an ortho/para director.

With dilute HNO_3 at low temperature, phenol undergoes electrophilic substitution to give a mixture of ortho-nitrophenol and para-nitrophenol.

2,4,6-trinitrophenol (picric acid) requires concentrated HNO_3.

Q.9

Which of the following is 'not' true about enantiomers ?

(a) They have the same chemical reactivity.

(b) They have the same specific rotation. <<

(c) They have the same melting or boiling point.

(d) They have the same refractive index.

Explanation:

Enantiomers are non-superimposable mirror images.

They have the same physical properties (melting point, boiling point, refractive index, etc.) EXCEPT they rotate plane polarised light by equal magnitude but in opposite directions.

Hence they do NOT have the same specific rotation (one is +, the other is –).

Statement (B) is NOT true.

Q.10

Aniline on direct nitration yields

(a) 51%-ortho, 47%-para, 2%-meta derivatives

(b) 51%-meta, 47%-ortho, 2%-para derivatives

(c) 51%-para, 47%-meta, 2%-ortho derivatives <<

(d) 51%-ortho, 47%-meta, 2%-para derivatives

Explanation:

In the strongly acidic nitrating mixture, aniline is protonated to the anilinium ion (–NH3+), which is meta-directing.

So besides the ortho/para products a large amount of meta product forms.

NCERT: direct nitration gives 51% p-nitroaniline, 47% m-nitroaniline and 2% o-nitroaniline.

Option (C) is correct.

Q.11

Which of the following amines has lowest pKb value ?

(a) $C_6H_5–N(CH_3)_2$ <<

(b) $C_6H_5–NH(CH_3)$

(c) $C_6H_5–NH_2$

(d) p-Nitroaniline ($O_2N–C_6H_4–NH_2$)

Explanation:

Lower pKb means a stronger base.

Among these aromatic amines, alkyl groups on N raise the electron density on N (+I effect), so N,N-dimethylaniline is the most basic (pKb ≈ 8.9, against aniline ≈ 9.4).

p-Nitroaniline is the weakest base: the $–NO_2$ group withdraws electrons (–R, –I effect).

So (A) has the lowest pKb.

Q.12

The deficiency of which of the following vitamins causes increased fragility of red blood cells and muscular weakness :

(a) Vitamin A

(b) Vitamin K

(c) Vitamin E <<

(d) Vitamin D

Explanation:

Vitamin E (tocopherol) deficiency causes increased fragility of red blood cells

(haemolytic anaemia) and muscular weakness.

It acts as an antioxidant protecting cell membranes.

Q.13

Assertion (A) : It is not possible to separate the components of an azeotrope by fractional distillation.

Reason (R) : Components of an azeotrope have the same composition in liquid and vapour phase and boil at a constant temperature.

(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A). <<

(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

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

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

Explanation:

Both A and R are true.

An azeotrope boils at a constant temperature and distills over with the same composition in both liquid and vapour phase.

Because the composition doesn't change during distillation, fractional distillation cannot separate the components.

R correctly explains A.

Q.14

Assertion (A) : The presence of –OH group in phenols directs the incoming group to meta position in the ring.

Reason (R) : –OH group in phenols activates the aromatic ring towards electrophilic substitution reaction.

(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

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

(d) Assertion (A) is false, but Reason (R) is true. <<

Explanation:

Assertion (A) is FALSE: the –OH group directs incoming groups to ortho and para positions (not meta).

Reason (R) is TRUE: the –OH group activates the ring toward electrophilic substitution through resonance (+M effect).

Hence option (D).

Q.15

Assertion (A) : Actinoids show wide range of oxidation states.

Reason (R) : Actinoids are radioactive in nature.

(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A). <<

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

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

Explanation:

Assertion (A) is TRUE: actinoids show a wide range of oxidation states (+2 to +7) because the energies of 5f, 6d and 7s orbitals are close together.

Reason (R) is also TRUE: most actinoids are radioactive.

However, the wide range of oxidation states is due to the comparable energies of 5f, 6d, 7s orbitals — not due to radioactivity.

So R is not the correct explanation of A.

Answer: (B).

Q.16

Assertion (A) : The pentaacetate of glucose does not react with H2N – OH.

Reason (R) : It indicates the presence of free – CHO group in glucose.

(a) Both Assertion (A) and Reason (R) are true and Reason (R) is the

correct explanation of the Assertion (A).

(b) Both Assertion (A) and Reason (R) are true, but Reason (R) is not the correct explanation of the Assertion (A).

(c) Assertion (A) is true, but Reason (R) is false. <<

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

Explanation:

Assertion (A) is TRUE: the pentaacetate of glucose (all –OH groups acetylated) does not react with H2N–OH (hydroxylamine) because the –CHO group is absent (it has been acetylated or because all active groups are blocked).

Reason (R) is FALSE: the fact that pentaacetate does NOT react with H2N–OH indicates the ABSENCE of a free –CHO group in the pentaacetate form.

Hence A is true, R is false → option (C).

Q.17

What type of deviation from Raoult's law is shown by a mixture of phenol and aniline ? Give reason.

What will happen to the boiling point of the solution on mixing phenol and aniline ?

Answer: Phenol and aniline show negative deviation from Raoult's law. Reason: phenol and aniline form intermolecular hydrogen bonds (–OH of phenol with $–NH_2$ of aniline) that are stronger than the phenol–phenol and aniline–aniline interactions, so the vapour pressure is lower than the ideal value.

Because the vapour pressure is lowered, the boiling point of the solution is higher than expected for an ideal solution (the mixture can form a maximum-boiling azeotrope).

Explanation:

Negative deviation: vapour pressure of mixture < sum of ideal partial pressures.

Stronger A–B (phenol–aniline H-bond) than A–A/B–B interactions cause this.

Lower vapour pressure → higher boiling point compared to an ideal solution.

Q.18

Why are haloarenes less reactive towards nucleophilic substitution reaction ? Give two reasons.

Answer: Haloarenes are less reactive towards nucleophilic substitution because: (1) Resonance — the lone pairs of the halogen atom are delocalized into the aromatic ring by resonance, giving the C–X bond partial double bond character. This makes the carbon less electrophilic and harder for a nucleophile to attack. (2) Strong C–X bond — the C–X bond in haloarenes is shorter and stronger (sp2 C–X) compared to haloalkanes (sp3 C–X) due to the partial double bond character from resonance, making it difficult to break.

Explanation:

Two reasons: (i) Resonance stabilization gives partial double bond character to C–X bond, making the carbon less susceptible to nucleophilic attack.

(ii) The sp2 hybridised carbon in haloarenes holds the halogen more tightly (shorter, stronger bond) than sp3 in haloalkanes.

Q.19

(a) Write IUPAC names of the following coordination compounds :

(i) [Ag(NH3)2] [Ag(CN)2]

(ii) K3[Fe(C2O4)3]

Answer: (i) $[Ag(NH_3)_2][Ag(CN)_2]$: diamminesilver(I) dicyanidoargentate(I).

(ii) $K_3[Fe(C_2O_4)_3]$: potassium tris(oxalato)ferrate(III) (potassium trioxalatoferrate(III)); Fe is +3 since $3(+1) + x + 3(-2) = 0$.

Explanation:

(i) The cation has Ag(+1) with two NH_3 ligands;

the anion has Ag(+1) with two CN^- ligands, so the metal in the anion is named argentate.

(ii) The anion $[Fe(C_2O_4)_3]^{3-}$ has Fe in the +3 state, so the name is potassium tris(oxalato)ferrate(III).

OR

Q.19

(b) OR

(i) Give a chemical test to show that [Co(NH3)5SO4]Cl and [Co(NH3)5Cl]SO4 are ionisation isomers.

(ii) What is meant by the 'Chelate effect' ? Give an example.

Answer: (i) Add $AgNO_3$ solution to each. $[Co(NH_3)_5SO_4]Cl$ has free Cl^- outside the coordination sphere and gives a white precipitate of AgCl. $[Co(NH_3)_5Cl]SO_4$ has free SO_4^{2-} instead, so it gives no AgCl; with $BaCl_2$ solution it gives a white precipitate of $BaSO_4$, while $[Co(NH_3)_5SO_4]Cl$ gives none. This shows they are ionisation isomers.

(ii) Chelate effect: a complex containing a ring formed by a polydentate (chelating) ligand is more stable than a similar complex with monodentate ligands. Example: $[Ni(en)_3]^{2+}$ (or $[Cu(en)_2]^{2+}$) is more stable than $[Ni(NH_3)_6]^{2+}$ (or $[Cu(NH_3)_4]^{2+}$).

Explanation:

Ionisation isomers give different ions in solution.

Free Cl^- is detected by $AgNO_3$ (AgCl); free SO_4^{2-} by $BaCl_2$ ($BaSO_4$).

Chelating ligands such as en form rings, which gives extra stability.

Q.20

Differentiate between the following :

(i) Peptide linkage and Glycosidic linkage

(ii) Essential amino acids and Non-essential amino acids

Answer: (i) Peptide linkage vs Glycosidic linkage:

- Peptide linkage: –CO–NH– bond formed between the carboxyl group (–COOH) of one amino acid and the amino group (–NH2) of another amino acid with elimination of water. Found in proteins and polypeptides.

- Glycosidic linkage: –C–O–C– (acetal/hemiacetal) bond formed between the anomeric –OH of one monosaccharide and an –OH of another monosaccharide with elimination of water. Found in disaccharides and polysaccharides.

(ii) Essential amino acids vs Non-essential amino acids:

- Essential amino acids: Those that cannot be synthesised by the human body and must be supplied through the diet. Example: Valine, Leucine, Lysine.
- Non-essential amino acids: Those that can be synthesised by the human body and need not be supplied through diet. Example: Glycine, Alanine.

Explanation:

Peptide bond = amide linkage between amino acids;
glycosidic bond = ether/acetal linkage between sugars.
Essential amino acids must come from food; non-essential are biosynthesised by the body.

Q.21

Following reaction takes place in one step :

$2A + B \rightarrow 2C$

How will the rate of above reaction change if the volume of the reaction vessel is decreased to one third of its original volume ? Will there be any change in the order of reaction with the reduced volume ?

Answer: Rate law: Rate = k[A]^2[B] (since the reaction takes place in one step, molecularity = order; $2A + B \rightarrow 2C$ is termolecular, so Rate = k[A]^2[B]).

If volume is decreased to 1/3: concentrations become 3 times ([A] → 3[A], [B] → 3[B]).

New rate = k(3[A])^2(3[B]) = k × 9[A]^2 × 3[B] = 27 k[A]^2[B] = 27 × original rate.

The rate increases by a factor of 27.

No, there will be no change in the order of reaction. The order depends on the mechanism/stoichiometry of the elementary step, not on concentrations or volume. Order remains 3 (second order in A, first order in B).

Explanation:

For a one-step reaction 2A + B → 2C: Rate = k[A]^2[B].

Reducing volume to 1/3 triples all concentrations: new rate = k(3[A])^2(3[B]) = 27k[A]^2[B].

Rate increases 27 times.

Order is unchanged (still 3rd order overall).

Q.22

For the first order thermal decomposition reaction, following data was obtained :

$C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$

S. No.	Time(s)	Total Pressure (atm)
1	0	0.30
2	30	0.50

Calculate rate constant. [Given : log 3 = 0.48]

Answer: Let initial pressure of C_2H_5Cl = P0 = 0.30 atm. At time t, let pressure decreased by x.

$C_2H_5Cl \rightarrow C_2H_4 + HCl$

At t=0: P0, 0, 0

At t=30: (P0 – x), x, x

Total pressure at t=30: Pt = (P0 – x) + x + x = P0 + x

0.50 = 0.30 + x → x = 0.20 atm

Pressure of C_2H_5Cl at t=30: P(C_2H_5Cl) = 0.30 – 0.20 = 0.10 atm

For first order: $k = (2.303/t) \times \log(P0/P)$

$k = (2.303/30) \times \log(0.30/0.10)$

$k = (2.303/30) \times \log 3$

$k = (2.303/30) \times 0.48$

$k = (2.303 \times 0.48) / 30$

k = 1.10544 / 30

k ≈ 0.0368 s^–1

k ≈ 3.68 × 10^–2 s^–1

Explanation:

First order reaction.

P0 = 0.30 atm, Pt = 0.50 atm (at t=30 s).

P(reactant) at t = P0 – (Pt – P0) = 2P0 – Pt = 0.60 – 0.50 = 0.10 atm.

k = (2.303/30) × log(0.30/0.10) = (2.303/30) × 0.48 = 0.0368 s^–1.

Q.23

(a) Answer the following :

(i) Why is the Equilibrium Constant (Kc) related to Ecell° and not to Ecell ?

(ii) Two metals 'A' and 'B' have standard electrode potential values of –0.24 V and +0.80 V respectively. Which of these will liberate hydrogen gas from dil. H2SO4 ?

(iii) Write the cell reaction which occurs in lead storage battery when it is in charging.

Answer: (i) The relationship is ΔG° = –nFEcell° and also ΔG° = –RT ln Kc. Both ΔG° and Kc refer to standard conditions (unit activities). Ecell° is measured under standard conditions (all concentrations = 1 M, all gases at 1 atm). Only under standard conditions does Ecell = Ecell°, and only then is ΔG° = –nFEcell° equivalent to –RT ln Kc. Hence Kc is related to Ecell° (standard cell potential), not to Ecell (which varies with concentration according to the Nernst equation).

(ii) Metal A (E° = –0.24 V) has a more negative electrode potential than the standard hydrogen electrode (E° = 0.00 V). Metal A can reduce H+ ions from the acid, so Metal A will liberate hydrogen gas from dil. H2SO4. Metal B (E° = +0.80 V) is less reactive and cannot displace hydrogen.

(iii) During charging of lead storage battery, the cell reaction is the reverse of the

discharge reaction:

$2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4(aq)$

(Electrical energy is converted to chemical energy during charging.)

Explanation:

(i) $K_c \leftrightarrow \Delta G^\circ \leftrightarrow E_{cell}^\circ$; standard conditions required.

(ii) $E^\circ < 0$ (vs SHE) means metal can reduce H^+; Metal A qualifies.

(iii) Charging reverses discharge: $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$.

OR

Q.23

(b) OR — What type of battery is Mercury cell ? Why it is more advantageous than dry cell ? Write overall reaction taking place in Mercury cell.

Answer: Mercury cell is a primary battery (galvanic cell — converts chemical energy directly to electrical energy; non-rechargeable).

Advantages over dry cell: (i) Mercury cell provides a constant voltage (about 1.35 V) throughout its life because neither the electrolyte nor the electrode materials are consumed in the cell reaction (the concentration of electrolyte does not change). In a dry cell, the voltage drops as the cell is used. (ii) Mercury cells have a longer shelf life.

Overall reaction in Mercury cell:

$Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

(Zinc amalgam anode: $Zn(Hg) \rightarrow Zn^{2+} + 2e^-$; Cathode: $HgO + H_2O + 2e^- \rightarrow Hg + 2OH^-$; Net in alkaline KOH/ZnO medium: $Zn(Hg) + HgO \rightarrow ZnO + Hg$)

Explanation:

Primary cell.

Constant voltage because the electrolyte (KOH/ZnO paste) concentration stays constant — no change in ion concentrations.

Overall: Zn(Hg) + HgO → ZnO + Hg.

Q.24

Calculate the boiling point of a solution containing 0.61 g of benzoic acid (Molar mass = 122 g mol^–1) in 5 g of CS2 in which it dimerises to the extent of 88%. The boiling point and Kb of CS2 are 46.2 °C and 2.3 K kg mol^–1 respectively.

Answer: Moles of benzoic acid = 0.61 / 122 = 0.005 mol

Benzoic acid dimerises: 2C6H5COOH ⇌ (C6H5COOH)2
Degree of association α = 0.88 (88%)

For dimerisation (association), van't Hoff factor:
i = 1 – α/2 = 1 – 0.88/2 = 1 – 0.44 = 0.56

Molality (m) = moles of solute / mass of solvent (kg)
m = 0.005 / (5/1000) = 0.005 / 0.005 = 1 mol kg^–1

ΔTb = i × Kb × m = 0.56 × 2.3 × 1 = 1.288 K ≈ 1.29 K

Boiling point of solution = 46.2 + 1.288 = 47.488 °C ≈ 47.49 °C

Explanation:
n(benzoic acid) = 0.005 mol.
Dimerisation: i = 1 – α/2 = 1 – 0.44 = 0.56.
Molality = 0.005 mol / 0.005 kg = 1 mol/kg.
ΔTb = 0.56 × 2.3 × 1 = 1.288 K.
Tb(solution) = 46.2 + 1.288 = 47.49 °C.

Q.25

Write the reactions of D-Glucose with the following :
(a) HI

(b) Br2 water

(c) Conc. HNO3

Answer: (a) D-Glucose + HI (prolonged heating) → n-hexane: $C_6H_{12}O_6 + 14HI \rightarrow CH_3(CH_2)_4CH_3 + 6H_2O + 7I_2$.

(b) D-Glucose + Br_2 water → D-gluconic acid: CHO → COOH (the aldehyde group is oxidised): $CH_2OH(CHOH)_4CHO + [O] \rightarrow CH_2OH(CHOH)_4COOH$.

(c) D-Glucose + conc. HNO_3 → D-saccharic (glucaric) acid: both –CHO and $–CH_2OH$ are oxidised to –COOH: $HOOC(CHOH)_4COOH$.

Explanation:

(a) Excess HI + P reduces glucose to n-hexane via sequential iodination and reduction.

(b) Br2/H2O (mild oxidant) oxidises only –CHO → –COOH, giving gluconic acid.

(c) Conc.

HNO3 (strong oxidant) oxidises both ends: –CHO and –CH2OH both to –COOH, giving glucaric (saccharic) acid.

Q.26

Give reasons for the following :

(a) Carboxylic acids have higher boiling point than alcohols of comparable molecular masses.

(b) Alpha (α) hydrogens of aldehydes and ketones are acidic in nature.

(c) Nucleophilic addition of ammonia and its derivatives does not occur with carbonyl group in strongly acidic medium.

Answer: (a) Carboxylic acids have higher boiling points than alcohols of comparable molecular masses because carboxylic acids exist as dimers in the liquid and gaseous state due to intermolecular hydrogen bonding between two –COOH groups (cyclic dimer formation). This results in an effectively higher molecular mass and stronger association, requiring more energy to break, hence higher boiling points.

(b) The α-hydrogens (on the carbon adjacent to C=O) are acidic because the

carbanion formed after removal of an α-H is stabilised by resonance with the carbonyl group (enolate ion formation). The negative charge is delocalised over the α-carbon and oxygen atom:

–CH2–C=O ⇌ –CH=C–O– (enolate resonance). The stability of the enolate makes the α-H relatively acidic.

(c) In strongly acidic medium, the nucleophile (NH3 or its derivative H2N–R) gets protonated:

H2N–R + H+ → H3N+–R

The protonated species (ammonium ion) is no longer a nucleophile (the lone pair on N is now involved in the N–H bond). Hence nucleophilic addition to the carbonyl group does not occur.

Explanation:

(a) Carboxylic acids form dimers via two O–H---O=C hydrogen bonds; effective MW is doubled →

higher bp.

(b) Enolate stabilisation makes α-H acidic.

(c) In strong acid, –NH2 is protonated to –NH3+, losing nucleophilicity.

Q.27

Write the reaction involved in the following :

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Friedal-Crafts acylation of anisole

Answer: (a) Reimer–Tiemann reaction: $C_6H_5OH + CHCl_3 + 3NaOH \rightarrow$ o-HOC_6H_4CHO (salicylaldehyde, major) + 3NaCl + $2H_2O$ (the p-isomer is minor); the electrophile is dichlorocarbene $:CCl_2$.

(b) Kolbe's reaction: $C_6H_5ONa + CO_2$ (≈ 400 K, 4–7 atm) → o-HOC_6H_4COONa, then H^+ → o-HOC_6H_4COOH (salicylic acid).

(c) Friedel–Crafts acylation of anisole: $C_6H_5OCH_3 + CH_3COCl$ (or $(CH_3CO)_2O$), anhyd. $AlCl_3$ → p-$CH_3OC_6H_4COCH_3$ (major, 4-methoxyacetophenone) + o-isomer

(minor) + HCl.

Explanation:

(a) Phenol + CHCl3/NaOH → salicylaldehyde (via dichlorocarbene).

(b) Sodium phenoxide + CO2 (high T, P) → salicylate → acidify → salicylic acid.

(c) Anisole + (CH3CO)2O/AlCl3 → para-methoxyacetophenone (major) + ortho isomer.

Q.28

Compound 'X' with molecular formula C4H9Br reacts with aqueous KOH to give an alcohol. The rate of this reaction depends only on the concentration of the compound 'X'. When an optically active isomer 'Y' of the compound 'X' was treated with aqueous KOH solution, the rate of reaction was found to be dependent on concentration of compound 'Y' and aqueous KOH both.

(a) Write down the structural formula of both 'X' and 'Y'.

(b) Out of 'X' and 'Y', which one will undergo racemisation and why ?

(c) Out of 'X' and 'Y', which one will form product with inversion of configuration and why ?

Answer: (a) X: Rate depends only on concentration of X → SN1 mechanism (unimolecular). C4H9Br with SN1 = tertiary haloalkane = (CH3)3CBr (2-bromo-2-methylpropane / tert-butyl bromide). X = (CH3)3C–Br.

Y: Rate depends on both [Y] and [KOH] → SN2 mechanism (bimolecular). Y is optically active (has a chiral centre). C4H9Br with SN2 = secondary haloalkane with chiral centre = CH3CH2CHBrCH3 (2-bromobutane). Y = CH3CH2CH(Br)CH3.

(b) X [(CH3)3CBr] will undergo racemisation. In SN1 mechanism, the leaving group departs first to form a planar carbocation intermediate. The nucleophile (OH–) can attack from either face (top or bottom) of the planar carbocation, giving a racemic mixture (50% R + 50% S configuration). Hence X undergoes racemisation.

(c) Y [CH3CH2CH(Br)CH3] will form product with inversion of configuration. In SN2 mechanism, the nucleophile attacks from the back side (opposite to the leaving group) in a single concerted step. This results in Walden inversion — the stereochemistry of the product is inverted (if R → gives S, and vice versa).

Explanation:
X = (CH3)3CBr (tertiary, SN1, unimolecular rate).
Y = CH3CH2CHBrCH3 (secondary, chiral, SN2, bimolecular rate).
SN1 → carbocation → racemisation.
SN2 → backside attack → inversion (Walden inversion).

Q.29

[Case-based] Read the passage:
The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Aliphatic amines are stronger bases than ammonia whereas aromatic amines are weaker bases than ammonia. Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters by nucleophilic substitution reaction. The main problem encountered during electrophilic substitution reactions of aromatic amines is that of their high reactivity. Substitution tends to occur at ortho-and para-positions. Hinsberg reagent is used for the identification and distinction between primary, secondary and tertiary amines. Aryldiazonium salts, usually obtained from arylamines, undergo replacement of the diazonium group with a variety of nucleophiles to provide advantageous methods for producing aryl halides, cyanides, phenols and arenes.

(a)(i) Why CH3 – NH2 is a stronger base than (CH3)3N in aqueous solution ?
(a)(ii) Write structural formulae of the compound A and B :
CH3CONH2 →[NaOBr]→ A →[C6H5COCl / Base]→ B

Answer: (a)(i) CH3–NH2 is a stronger base than (CH3)3N in aqueous solution due to the steric effect and solvation. Although three methyl groups in (CH3)3N donate more electrons to N (increasing intrinsic basicity), the bulky methyl groups also hinder the solvation of the resulting (CH3)3NH+ ion by water molecules. The protonated ion CH3NH3+ is better solvated (smaller, less hindered) and its formation is thermodynamically more favourable. Hence CH3–NH2 is a stronger base in aqueous solution.

(a)(ii) CH3CONH2 + NaOBr → A:
This is the Hoffmann bromamide degradation (Hoffmann rearrangement). CH3CONH2 (acetamide) with NaOBr gives CH3NH2 (methylamine). A = CH3NH2.

A + C6H5COCl + Base → B:
Methylamine reacts with benzoyl chloride (C6H5COCl) in the presence of a base by nucleophilic acyl substitution to give N-methylbenzamide. B = C6H5CONHCH3 (N-methylbenzamide).

Explanation:
(a)(i) Aqueous basicity: steric hindrance to solvation of (CH3)3NH+ makes trimethylamine weaker than methylamine in water.
(a)(ii) Hoffmann rearrangement: CH3CONH2 + NaOBr → CH3NH2 (A).
CH3NH2 + C6H5COCl/base → C6H5CONHCH3 (B, N-methylbenzamide).

Q.29(b)

[Case-based Q29] (b) A compound 'X' with molecular formula C3H9N reacts with Hinsberg reagent to give a product insoluble in alkali. Identify 'X'.

Answer: The Hinsberg reagent is benzenesulphonyl chloride. A product insoluble in alkali indicates a secondary amine. Among the C_3H_9N isomers, the secondary amine is $CH_3–NH–CH_2CH_3$ (N-methylethanamine), so X = $CH_3NHC_2H_5$.

Explanation:

Hinsberg test: insoluble in alkali → secondary amine.

C3H9N secondary amine = N-methylethylamine (CH3NHCH2CH3).

OR

Q.29(b)

[Case-based Q29] (b) OR — How can you convert aniline to benzonitrile ?

Answer: Aniline → benzonitrile via the diazonium salt route (Sandmeyer reaction with CuCN):

Step 1: C6H5NH2 + NaNO2 + HCl (0–5 °C) → C6H5N2+Cl– (benzene diazonium chloride)

Step 2: C6H5N2+Cl– + CuCN → C6H5CN (benzonitrile) + N2 + CuCl

(Sandmeyer reaction using CuCN replaces the diazonium group with –CN)

Explanation:

Aniline → diazonium salt (NaNO2/HCl, 0–5°C) → benzonitrile (CuCN, Sandmeyer reaction).

Q.29(c)

[Case-based Q29] (c) Why is –NH2 group of aniline acetylated before carrying out nitration ?

Answer: The –NH2 group of aniline is acetylated before nitration for two reasons: (1) The –NH2 group is a very powerful activating group and ortho/para director. Without protection, aniline would react vigorously with the nitrating mixture (conc. H2SO4 + conc. HNO3) — the amine gets oxidised and gives mainly meta-nitration products (as the anilinium ion, formed by protonation in strong acid, is a meta director). (2) Acetylation converts –NH2 to –NHCOCH3 (acetamide group), which is a weaker activating group. This moderates the reactivity, prevents oxidation, and still directs predominantly to the para position, giving p-nitroacetanilide as the main product. After nitration, the acetyl group can be removed by hydrolysis to get the desired nitraniline.

Explanation:

Acetylation protects –NH2: prevents oxidation by the strong nitrating mixture, moderates reactivity, changes the directing effect from over-reactive to controlled ortho/para (mainly para) direction.

Q.30

[Case-based] Read the passage:

The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometry of coordination compounds. The Crystal Field Theory (CFT) of coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of d-orbital energies of the central metal atom/ion. The splitting of the d-orbitals provides different electronic arrangements in strong and weak crystal fields.

(a) In octahedral crystal field, energies of which d-orbitals will be raised when ligands approach the central metal atom/ion ? Give reason in support of your answer.

Answer: In an octahedral crystal field, the energies of the dz2 and dx2–y2 orbitals (the eg set) are raised. Reason: In an octahedral complex, the six ligands approach along the ±x, ±y, and ±z axes. The dz2 and dx2–y2 orbitals point directly along these axes (lobes directed towards the approaching ligands). The electron density of these orbitals interacts (repels) directly with the negative charge/electron pairs of the approaching ligands, causing an increase in their energy. The dxy, dyz, and dxz orbitals (t2g set) point between the axes and therefore experience less repulsion, so their energy is lowered relative to the barycentre.

Explanation:

eg set (dz2 and dx2–y2) — lobes point along axes (directly toward ligands) → repulsion → raised energy.

t2g set (dxy, dxz, dyz) — lobes between axes → less repulsion → lowered energy.

Q.30(b)

[Case-based Q30] (b) Using crystal field theory, write the electronic configuration of central metal atom/ion of the following :

(i) [CoF6]^3–

(ii) [Co(NH3)6]^3+

[At. No. : Co = 27]

Answer: Co has atomic number 27: electronic configuration [Ar] 3d7 4s2. Co3+ (loses 3 electrons): [Ar] 3d6. t2g and eg split:

(i) [CoF6]^3–: F– is a weak field ligand. Weak field → small Δo → electrons fill t2g and eg following Hund's rule (high spin).

Co3+ = 3d6 (high spin in weak field): t2g^4 eg^2

Configuration: t2g^4 eg^2 (4 unpaired electrons, paramagnetic)

(ii) [Co(NH3)6]^3+: NH3 is a strong field ligand. Strong field → large Δo → electrons are forced to pair in t2g before occupying eg (low spin).

Co3+ = 3d6 (low spin in strong field): t2g^6 eg^0

Configuration: t2g^6 eg^0 (0 unpaired electrons, diamagnetic)

Explanation:

Co3+ = 3d6.

F– = weak field (high spin): t2g^4 eg^2, 4 unpaired.

NH3 = strong field (low spin): t2g^6 eg^0, 0 unpaired, diamagnetic.

Q.30(c)

[Case-based Q30] (c) [NiCl4]^2– is paramagnetic while [Ni(CO)4] is diamagnetic though both are tetrahedral. Why ? [Atomic No. : Ni = 28]

Answer: In $[NiCl_4]^{2-}$, Ni is Ni^{2+} ($3d^8$) and Cl^- is a weak-field ligand, so the two unpaired electrons stay unpaired (sp^3, tetrahedral): paramagnetic.

In $[Ni(CO)_4]$, Ni is in the 0 state and CO is a strong-field ligand that pushes the 4s electrons into 3d ($3d^{10}$), so all electrons are paired (sp^3, tetrahedral): diamagnetic.

Explanation:

^2–: Ni2+, 3d8, weak field Cl–, sp3, 2 unpaired → paramagnetic.

[Ni(CO)4]: Ni0, CO strong field causes electron pairing →

3d10, sp3, 0 unpaired →

diamagnetic.

OR

Q.30(c)

[Case-based Q30] (c) OR — Write hybridization and magnetic behaviour of the complex [Fe(CN)6]^3–. [Atomic No. : Fe = 26]

Answer: $[Fe(CN)_6]^{3-}$: Fe^{3+} is $3d^5$. CN^- is a strong-field ligand, so the electrons pair up in the t_2g orbitals (t_2g^5 e_g^0) leaving two 3d orbitals empty.

Hybridisation: d^2sp^3 (inner-orbital, octahedral).

Magnetic behaviour: one unpaired electron, so paramagnetic.

Explanation:

Fe3+ = 3d5.

CN– = strong field.

Low spin: t2g^5 eg^0 → 1 unpaired electron.

Hybridisation = d2sp3 (inner orbital complex).

Magnetic behaviour = paramagnetic (1 unpaired electron).

Q.31(a)

(a)(i) An organic compound (X) has the molecular formula C5H10O. Draw structures for (X) if it :

(I) does not give Tollen's test but gives a positive iodoform test.

(II) does not give Tollen's test and iodoform test but undergoes Aldol condensation.

(III) undergoes Cannizzaro's reaction.

Answer: (I) Does not give Tollen's test → not an aldehyde (no –CHO). Gives positive iodoform test → has CH3CO– group (methyl ketone) or CH3CH(OH)– group. C5H10O, ketone with iodoform: methyl ketone. Structure:

CH3–CO–CH2–CH2–CH3 (pentan-2-one) or CH3CO–CH(CH3)2 (3-methylbutan-2-one) or CH3–CH2–CO–CH2–CH3 (pentan-3-one would not give iodoform). The iodoform-positive ketone from C5H10O is pentan-2-one (CH3COCH2CH2CH3) or 3-methylbutan-2-one (CH3COCH(CH3)2).
Representative structure: CH3–CO–CH2–CH2–CH3 (pentan-2-one)

(II) Does not give Tollen's test (not an aldehyde) and does not give iodoform test (no CH3CO– or CH3CHOH– group), but undergoes Aldol condensation → must be a ketone with α-hydrogens. Structure: pentan-3-one (CH3CH2COCH2CH3) — it has no CH3CO– group (iodoform negative) but has α-H → Aldol condensation.
Structure: CH3CH2–CO–CH2CH3 (pentan-3-one)

(III) Cannizzaro's reaction is shown by aldehydes with no α-hydrogen. C5H10O aldehyde with no α-H: (CH3)3C–CHO (2,2-dimethylpropanal / pivaldehyde) — the carbon adjacent to –CHO has no H (it's a quaternary carbon).
Structure: (CH3)3C–CHO (2,2-dimethylpropanal)

Explanation:
(I) No Tollen's → ketone; iodoform positive → CH3CO– group: pentan-2-one (CH3COCH2CH2CH3).
(II) No Tollen's, no iodoform, Aldol: pentan-3-one (CH3CH2COCH2CH3).
(III) Cannizzaro: aldehyde without α-H: 2,2-dimethylpropanal [(CH3)3CCHO].

Q.0

(a)(ii) Show how each of the following compounds can be converted to benzoic acid :
(I) Acetophenone
(II) Ethyl benzene

Answer: (I) Acetophenone → Benzoic acid:
Acetophenone (C6H5COCH3) can be converted to benzoic acid by oxidation with alkaline KMnO4 or acidic K2Cr2O7/H2SO4:

C6H5COCH3 + [O] (KMnO4/OH–, heat) → C6H5COOH (benzoic acid) + CO2 + H2O

(The methyl group attached to the carbonyl is oxidised and removed; the ring remains intact with the –COOH group)

(II) Ethyl benzene → Benzoic acid:

Ethyl benzene (C6H5CH2CH3) can be oxidised by alkaline KMnO4 followed by acidification:

C6H5CH2CH3 + [O] (KMnO4, H+, heat) → C6H5COOH (benzoic acid)

(Both the –CH2CH3 side chain is oxidised to –COOH regardless of chain length, as long as there is a benzylic hydrogen)

Explanation:

(I) Acetophenone + KMnO4 (acidic/alkaline) → benzoic acid + CO2.

(II) Ethylbenzene + KMnO4/H+ → benzoic acid (side chain oxidised to –COOH).

OR

Q.31(b)

(b) OR — Answer the following questions :

(i) Draw structure of the 2, 4-dinitrophenyl hydrazone derivative of benzaldehyde.

(ii) Arrange the following in increasing order of their reactivity towards HCN : Di-tert. butyl ketone, Acetaldehyde, Acetone

(iii) Give a simple chemical test to distinguish between benzoic acid and ethyl benzoate.

(iv) Write the name of the reagent to convert Ethanenitrile to Ethanal.

(v) Draw the structure of 'X' in the following reaction :

cyclohexanol (cyclohexane ring bearing –OH) —CrO_3→ 'X'

Answer: (i) C_6H_5–CH=N–NH–$C_6H_3(NO_2)_2$ (2,4-dinitrophenyl on the hydrazine N; NO_2 at positions 2 and 4).

(ii) Di-tert-butyl ketone < Acetone < Acetaldehyde (steric hindrance and +I effect

decrease along the series).

(iii) Add $NaHCO_3$ solution: benzoic acid gives brisk effervescence of CO_2; ethyl benzoate does not.

(iv) DIBAL-H (then H_2O) [or $SnCl_2$/HCl followed by H_3O^+, Stephen reduction].

(v) X = cyclohexanone (a six-membered saturated ring with C=O): CrO_3 oxidises the secondary alcohol cyclohexanol to the ketone.

Explanation:

The figure in (v) is cyclohexanol (saturated ring with –OH), not phenol or benzaldehyde.

CrO_3 oxidises a secondary alcohol to a ketone, so X = cyclohexanone.

Parts (i)–(iv): standard DNP derivative, reactivity order towards nucleophilic addition, $NaHCO_3$ test for –COOH, and DIBAL-H partial reduction of the nitrile.

Q.32(a)

(a)(i) From the given data of E° values, answer the following questions :

	V	Cr	Mn	Fe	Co	Ni	Cu
E°(M2+/M):	–1.18	–0.91	–1.18	–0.44	–0.28	–0.25	+0.34

(I) Why do E°(M2+/M) show irregular trend in the above values ?

(II) Why is E°(Cu2+/Cu) value exceptionally positive ?

(III) Why is E°(Mn2+/Mn) value highly negative ?

Answer: (I) The values of $E°(M^{2+}/M)$ vary irregularly because the sum of the enthalpy of atomisation, the ionisation enthalpies (IE_1 + IE_2) and the hydration enthalpy of M^{2+}, which together fix E°, varies irregularly along the series.

(II) $E°(Cu^{2+}/Cu)$ is positive because the very high enthalpy of atomisation of copper and its high IE_1 + IE_2 are not compensated by the hydration enthalpy of Cu^{2+}.

(III) $E°(Mn^{2+}/Mn)$ is highly negative because Mn^{2+} has the stable half-filled $3d^5$ configuration, so a large amount of energy (the $3d^5$ stability) is lost on forming Mn from Mn^{2+}; Mn is therefore strongly reducing.

Explanation:

E° of M^{2+}/M depends on $\Delta_{atom}H + \Delta_{I}H$ ($IE_1 + IE_2$) + $\Delta_{hyd}H$.

(I) These terms change irregularly across the series.

(II) For Cu the hydration enthalpy cannot make up for the high atomisation and ionisation enthalpies.

(III) Mn^{2+} ($3d^5$) is exceptionally stable, so $E^\circ(Mn^{2+}/Mn)$ is highly negative.

Q.0

(a)(ii) Write the ionic equations for the oxidising action of potassium permanganate for its reaction with I– in both acidic and alkaline solutions.

Answer: Acidic solution: $2MnO_4^- + 16H^+ + 10I^- \rightarrow 2Mn^{2+} + 8H_2O + 5I_2$

Alkaline (neutral/faintly alkaline) solution: $2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + 2OH^- + IO_3^-$

Explanation:

In acid, MnO_4^- is reduced to Mn^{2+} and I^- is oxidised to I_2.

In alkaline/neutral solution, MnO_4^- is reduced to MnO_2 and I^- is oxidised to IO_3^-.

Both equations balance in atoms and charge (second: −3 on each side, 9 O on each side).

OR

Q.32(b)

(b) OR — Answer the following questions :

(i) Name a member of the lanthanoid series

(I) which exhibits +4 oxidation state

(II) which exhibits +2 oxidation state.

(ii) Why transition metals act as good catalyst ?

(iii) Why Cr has higher melting point than Mn ?

(iv) What happens when acidic solution of potassium permanganate is allowed to stand for sometime ? Give the equation involved. What is this type of reaction called ?

Answer: (i)(I) Cerium (Ce^{4+}). (II) Europium (Eu^{2+}) or ytterbium (Yb^{2+}).

(ii) Transition metals have variable oxidation states (they form unstable intermediates) and provide a surface on which reactants are adsorbed, which lowers the activation energy.

(iii) Cr ($3d^5 4s^1$) has six unpaired electrons (five 3d + one 4s) available for metallic bonding, whereas in Mn the $3d^5$ half-filled set is stable and its d electrons contribute much less, so metallic bonding is weaker and Mn melts lower than Cr.

(iv) Acidified $KMnO_4$ on standing decomposes slowly: $4MnO_4^- + 4H^+ \rightarrow 4MnO_2 + 3O_2 + 2H_2O$. This is a redox (decomposition) reaction.

Explanation:

(i) Ce^{4+} has the noble-gas configuration; Eu^{2+} has $4f^7$.

(iii) More electrons in metallic bonding give a higher melting point.

(iv) Mn(VII) is reduced to Mn(IV) while water/oxide is oxidised to O_2.

Note: the name of this reaction type is unconfirmed.

Q.33(a)

Calculate emf and ΔG for the following cell at 298 K :

Mg(s) / Mg^2+(0.01 M) // Ag^+(0.001 M) / Ag(s)

Given : E°(Mg2+/Mg) = –2.37 V, E°(Ag+/Ag) = +0.80 V

[1 F = 96500 C mol^–1, log 10 = 1]

Answer: $E°_{cell} = 0.80 - (-2.37) = 3.17$ V. Cell reaction: $Mg + 2Ag^+ \rightarrow Mg^{2+} + 2Ag$, n = 2. $Q = [Mg^{2+}]/[Ag^+]^2 = 0.01/(0.001)^2 = 10^4$.

$E_{cell} = 3.17 - (0.0591/2) \log 10^4 = 3.17 - 0.1182 = 3.0518$ V ≈ 3.05 V.

$\Delta G = -nFE_{cell} = -2 \times 96500 \times 3.0518 \approx -5.89 \times 10^5$ J $mol^{-1} = -589$ kJ mol^{-1}.

Explanation:

$E°_{cell} = 3.17$ V, $Q = 10^4$, $E_{cell} = 3.17 - 0.02955 \times 4 = 3.0518$ V ≈ 3.05 V.

$\Delta G = -2 \times 96500 \times 3.0518 = -588997$ J ≈ −589 kJ mol^{-1}.

OR

Q.33(b)

OR — For the reaction :

2AgCl(s) + H2(g) (0.4 atm) → 2Ag(s) + 2H+(0.1 M) + 2Cl–(0.2 M)

Calculate emf of the cell at 25 °C.

Given : ΔG° = – 43500 J mol^–1

[log 10 = 1, 1 F = 96500 C mol^–1]

Answer: $2AgCl + H_2 \rightarrow 2Ag + 2H^+ + 2Cl^-$, n = 2.

$E°cell = -\Delta G°/nF = 43500/(2 \times 96500) = 0.2254\ V \approx 0.225\ V$.

$Q = [H^+]^2[Cl^-]^2/p(H_2) = (0.1)^2(0.2)^2/0.4 = 10^{-3}$.

$Ecell = 0.2254 - (0.0591/2) \log 10^{-3} = 0.2254 + 0.0887 = 0.314\ V$.

Explanation:

$E° = 43500/193000 = 0.2254\ V$.

$Q = 0.01 \times 0.04/0.4 = 10^{-3}$.

$E = 0.2254 + (0.0591/2) \times 3 = 0.2254 + 0.0887 \approx 0.314\ V$.