CBSE Class 12 Chemistry 2024 — Set 2 — 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

When MnO_2 is fused with KOH in air, it gives :

(a) $KMnO_4$

(b) K_2MnO_4 <<

(c) Mn_2O_7

(d) Mn_2O_3

Explanation:

When MnO_2 is fused with KOH in the presence of air (O_2), the reaction is: $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$.

Manganese is oxidised from +4 (in MnO_2) to +6 (in K_2MnO_4, potassium manganate).

$KMnO_4$ (+7) is formed when K_2MnO_4 is further oxidised or disproportionated in acidic conditions, not directly from this fusion.

Answer: K_2MnO_4.

Q.2

Ligand $EDTA^{4-}$ is an example of a :

(a) Monodentate ligand

(b) Didentate ligand

(c) Tridentate ligand

(d) Polydentate ligand <<

Explanation:

$EDTA^{4-}$ (ethylenediaminetetraacetate) has six donor atoms — two nitrogen atoms and four carboxylate oxygen atoms.

A ligand with more than two donor sites is called a polydentate (hexadentate in EDTA's case) ligand.

Answer: Polydentate ligand.

Q.3

Which of the following ligand forms chelate complex ?

(a) $C_2O_4^{(2-)}$ <<

(b) $Cl(-)$

(c) $NO2(-)$

(d) $NH3$

Explanation:

A chelate complex is formed when a polydentate ligand uses two or more donor atoms to bind to the same central metal ion, forming a ring.

Oxalate ($C2O4(2-)$) is a bidentate ligand that coordinates through both oxygen atoms, forming a stable 5-membered chelate ring.

$Cl-$, $NO2-$, and $NH3$ are monodentate ligands and do not form chelates.

Answer: $C2O4(2-)$.

Q.4

Which of the following contains sp2 hybridised carbon bonded to X ?

(a) $CH2=CH-CH2-X$

(b) $C6H5-CH2-X$ (benzyl halide)

(c) $CH2=CH-X$ <<

(d) $CH3-CH2-X$

Explanation:

In $CH2=CH-X$ (vinyl halide), X is attached directly to a C=C carbon, which is sp^2 hybridised.

(A) allyl halide and (B) benzyl halide: X is on a $CH2$ carbon, which is sp^3.

(D) $CH3-CH2-X$: the C–X carbon is sp^3.

So only (C) has an sp^2 carbon bonded to X.

Q.5

Which of the following is most acidic?

(a) Benzyl alcohol: $C_6H_5–CH_2–OH$

(b) Phenol: $C_6H_5–OH$

(c) Cyclohexanol: $C_6H_{11}–OH$

(d) 4-Chlorophenol: $p\text{-}Cl–C_6H_4–OH$ <<

Explanation:

Phenols are more acidic than alcohols because the phenoxide ion is resonance stabilised.

The –I effect of Cl at the para position further stabilises the phenoxide, so 4-chlorophenol > phenol > benzyl alcohol > cyclohexanol.

Answer: (D).

Q.6

Anisole reacts with HI to give:

(a) $C_6H_5–OH + CH_3–I$ <<

(b) $C_6H_5–I + CH_3–OH$

(c) $C_6H_5–CH_2–OH + CH_3–I$

(d) $C_6H_5–CH_2–I + CH_3–OH$

Explanation:

The aryl C–O bond is stronger (resonance with the ring) so only the $CH_3–O$ bond is cleaved: the ether is protonated and I^- attacks the methyl carbon by SN2, giving phenol and CH_3I.

Answer: (A).

Q.7

Ethanol on heating with conc. H2SO4 at 413 K gives :

(a) C2H5OSO3H

(b) C2H5−O−CH3

(c) C2H5−O−C2H5 <<

(d) CH2=CH2

Explanation:

At 413 K (140°C), ethanol reacts with conc.

H2SO4 by an intermolecular dehydration to form diethyl ether: 2C2H5OH → C2H5−O−C2H5 + H2O.

At higher temperature (443 K / 170°C), intramolecular dehydration gives ethylene (CH2=CH2).

At 413 K, ether formation is favoured.

Answer: $C_2H_5-O-C_2H_5$ (diethyl ether).

Q.8

An azeotropic solution of two liquids has boiling point lower than either of them when it :

(a) is saturated

(b) shows positive deviation from Raoult's law <<

(c) shows negative deviation from Raoult's law

(d) shows no deviation from Raoult's law

Explanation:

A minimum boiling azeotrope has a boiling point lower than either pure component.

It is formed when the mixture shows a positive deviation from Raoult's law — the total vapour pressure is higher than predicted, meaning the mixture boils at a lower temperature than either pure liquid.

Example: ethanol-water azeotrope (95.6% ethanol, bp 78.1°C, lower than water's 100°C or ethanol's 78.4°C).

Answer: shows positive deviation from Raoult's law.

Q.9

The relative lowering of vapour pressure of an aqueous solution containing non-volatile solute is 0·0225. The mole fraction of the non-volatile solute is :

(a) 0·80

(b) 0·725

(c) 0·15

(d) 0·0225 <<

Explanation:

By Raoult's law, relative lowering of vapour pressure = $(P^\circ - P)/P^\circ = x(\text{solute})$, where $x(\text{solute})$ is the mole fraction of the solute.

Given: $(P^\circ - P)/P^\circ = 0.0225$.

Therefore mole fraction of non-volatile solute = 0.0225.

Answer: 0·0225.

Q.10

During electrolysis of aqueous solution of NaCl :

(a) H_2 (g) is liberated at cathode <<

(b) Na is formed at cathode

(c) O_2 (g) is liberated at anode

(d) Cl_2 (g) is liberated at cathode

Explanation:

In the electrolysis of aqueous NaCl: At cathode (reduction): $2H_2O + 2e^- \rightarrow H_2 (g) + 2OH^-$.

Water is preferentially reduced over Na^+ because $E°(H_2O/H_2)$ is less negative than $E°(Na^+/Na)$.

At anode (oxidation): $2Cl^- \rightarrow Cl_2 (g) + 2e^-$.

Cl^- is preferentially oxidised over water due to higher concentration and overpotential considerations.

Answer: H_2 (g) is liberated at cathode.

Q.11

The addition of catalyst during a chemical reaction alters which of the following quantities of the reaction ?

(a) Enthalpy

(b) Activation energy <<

(c) Entropy

(d) Internal energy

Explanation:

A catalyst provides an alternative reaction pathway with lower activation energy (Ea).

It does not change the thermodynamic quantities of the overall reaction — enthalpy (ΔH), entropy (ΔS), and internal energy (ΔU) of reactants and products remain unchanged.

Only the activation energy (kinetic quantity) is altered.

Answer: Activation energy.

Q.12

For the elementary reaction P → Q, the rate of disappearance of P, when concentration of P is doubled, becomes 8 times. The order of the reaction is :

(a) 3 <<
(b) 4
(c) 2
(d) 1

Explanation:

Rate = k[P]^n.

When [P] is doubled: new rate = k(2[P])^n = 2^n × k[P]^n = 8 × original rate.

So 2^n = 8 = 2^3, therefore n = 3.

The order of the reaction is 3 (third order).

Answer: 3.

Q.13

Assertion (A) : Aliphatic primary amines can be prepared by Gabriel phthalimide synthesis.

Reason (R) : Alkyl halides undergo nucleophilic substitution with anion formed by phthalimide.

(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:

Gabriel phthalimide synthesis is indeed used to prepare aliphatic primary amines.

The mechanism: phthalimide (pKa ~8.3) is deprotonated by KOH to form potassium phthalimide (the phthalimide anion).

This anion undergoes SN2 nucleophilic substitution with an alkyl halide (R−X), placing

the alkyl group on nitrogen.
Subsequent hydrolysis (or hydrazinolysis) releases the primary amine RNH2.
Both A and R are true and R correctly explains A.
Answer: (A).

Q.14

Assertion (A) : Uracil base is present in DNA.

Reason (R) : DNA undergoes self-replication.

(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: Uracil is present in RNA, not DNA.
DNA contains the bases adenine, guanine, cytosine, and thymine;
uracil replaces thymine only in RNA.
Reason (R) is TRUE: DNA does undergo self-replication (semi-conservative replication).
Since A is false and R is true, the answer is (D).
Answer: (D).

Q.15

Assertion (A) : Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

Reason (R) : Diazonium salts of aliphatic amines show resonance.

(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: Aromatic diazonium salts (Ar−N2+) are more stable than aliphatic diazonium salts.

Aromatic diazonium salts are stabilised by resonance delocalization of the positive charge into the benzene ring.

Aliphatic diazonium salts (R−N2+) are very unstable and decompose rapidly, releasing N2.

Reason (R) is FALSE: It is the AROMATIC diazonium salts that show resonance (with the benzene ring), not the aliphatic ones.

Aliphatic diazonium salts have no resonance stabilization.

A is true, R is false.

Answer: (C).

Q.16

Assertion (A) : p-nitroaniline is a weaker base than p-toluidine.

Reason (R) : The electron withdrawing effect of −NO2 group in p-nitroaniline makes it a weaker base.

(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: p-Nitroaniline (pKb ≈ 13) is a much weaker base than p-toluidine (pKb ≈ 8.9).

Reason (R) is TRUE and CORRECTLY explains A: The −NO2 group at para position withdraws electrons from the nitrogen lone pair through resonance (−M effect) and induction, reducing the electron density on N, thereby decreasing its tendency to donate electrons to a proton (weaker base).

p-Toluidine has an electron-donating −CH3 group that increases electron density on

N, making it a stronger base.

Both A and R are true, R correctly explains A.

Answer: (A).

Q.17

A 6% solution of glucose (molar mass = 180 g mol−1) is isotonic with 2·5% solution of an unknown organic substance. Calculate the molecular weight of the unknown organic substance.

Answer: 75 g mol−1

Explanation:

Isotonic solutions have equal osmotic pressure, which at the same temperature means equal molar concentrations (molarity).

For isotonic solutions: C1 = C2 (where C = w/(M×V) = % / M, using same volume basis).

% by mass / Molar mass = constant for isotonic solutions at same temperature.

w1/M1 = w2/M2 (for same volume of solution, % mass is proportional to mass dissolved)

6/180 = 2.5/M2

M2 = (2.5 × 180)/6 = 450/6 = 75 g mol−1

The molecular weight of the unknown organic substance is 75 g mol−1.

Q.18

A first order reaction has a rate constant 1·25 × 10−3 s−1. How long will 5 g of this reactant take to reduce to 2·5 g ?

[log 2 = 0·301, log 3 = 0·4771, log 4 = 0·6021]

Answer: ≈ 554.6 s (about 555 s)

Explanation:

First order: $t = (2.303/k) \log([A]_0/[A]) = (2.303/1.25\times10^{-3}) \times \log(5/2.5) = 1842.4 \times \log 2 = 1842.4 \times 0.301 \approx 554.6$ s.

This is the half-life (0.693/k ≈ 554.4 s).

Q.19

(a) What is lanthanoid contraction ? Actinoid contraction is greater from element to element than lanthanoid contraction. Why ?

Answer: Lanthanoid contraction: successive decrease in atomic/ionic radii of lanthanoids (La to Lu) due to poor shielding by 4f electrons. Actinoid contraction is greater because 5f orbitals have poorer shielding than 4f orbitals.

Explanation:

Lanthanoid contraction: the atomic and ionic radii of lanthanoid elements decrease steadily from La to Lu.

This occurs because as atomic number increases, the additional electrons fill the 4f orbitals, which have poor shielding ability.

The increasing nuclear charge thus attracts all electrons more strongly, reducing the size.

Actinoid contraction is greater element to element: The 5f electrons in actinoids provide even poorer shielding than the 4f electrons in lanthanoids (because 5f orbitals penetrate the core less effectively), and the spin-orbit coupling is larger.

Therefore the effective nuclear charge increases more rapidly across the actinoid series, leading to a greater decrease in size per element.

OR

Q.19

(b) [OR] Why do transition metals have high enthalpy of atomization ? Which element of 3d-series has lowest enthalpy of atomization ?

Answer: High enthalpy of atomization due to strong metallic bonding from unpaired d electrons. Zinc (Zn) has the lowest enthalpy of atomization in the 3d series.

Explanation:

Transition metals have high enthalpy of atomization because of strong metallic bonds.

The metallic bond involves sharing of both 4s and 3d electrons;

the large number of unpaired d electrons available for bonding results in stronger and more extensive metallic bonding, requiring more energy to convert solid metal to

gaseous atoms.

Zinc (Zn) has the lowest enthalpy of atomization in the 3d series: Zn has the electronic configuration [Ar]3d10 4s2, with completely filled d orbitals.

The d electrons are not available for metallic bonding (no unpaired d electrons), so the metallic bond is weaker.

Hence Zn has the lowest enthalpy of atomization (~130 kJ mol−1) among 3d transition metals.

Q.20

(a) In the following pair of compounds, which compound undergoes SN2 reaction faster and why? $CH_3CH_2CH_2CH_2$–I or $CH_3CH_2CH_2CH_2$–Br

Answer: (a) 1-Iodobutane reacts faster in SN2: I^- is a better leaving group than Br^- (larger, more polarisable, weaker C–I bond).

Explanation:

(a) The two substrates are identical primary alkyl halides apart from the halogen, so the SN2 rate depends on leaving-group ability: $I^- > Br^-$.

Q.20(b)

(b) Write the major product in the following: C_6H_5–CH_2CH_3 + Cl_2, UV light →

Answer: Major product: C6H5−CHCl−CH3 (1-chloro-1-phenylethane / α-chloroethylbenzene)

Explanation:

Cl_2 with UV light causes free-radical side-chain chlorination.

The benzylic C–H is replaced because the benzylic radical is resonance stabilised, so the major product is C_6H_5–CHCl–CH_3 (1-chloro-1-phenylethane).

Q.21

Define the following terms :

(a) Denaturation of protein

(b) Invert sugar

Answer: (a) Denaturation of protein: disruption of secondary, tertiary and

quaternary structure of a protein without breaking peptide bonds, causing loss of biological activity. (b) Invert sugar: equimolar mixture of glucose and fructose obtained by hydrolysis of sucrose; it rotates plane-polarised light to the left (levorotatory).

Explanation:

(a) Denaturation of protein: when a protein is subjected to physical (heat, UV radiation) or chemical (acids, bases, salts) changes, the secondary and tertiary structures are disrupted.

The hydrogen bonds, disulfide bridges and other non-covalent interactions holding the structure are broken, though the primary structure (peptide bonds) remains intact.

The protein loses its specific biological activity and becomes non-functional.

(b) Invert sugar: Sucrose (+66.5°) is hydrolysed by dilute acid or enzyme invertase/sucrase to give an equimolar mixture of glucose (+52.5°) and fructose (−92.4°).

The optical rotation of the mixture is −39.9° (net levorotatory).

Since the sign of rotation is inverted from positive (sucrose) to negative (mixture), the product is called 'invert sugar'.

Q.22

Write the structures of A, B and C in the following reactions: (a) $CH_3–CH_2–Br$ →(KCN) A →(OH^-, partial hydrolysis) B →(NaOH + Br_2) C (b) nitrobenzene ($C_6H_5–NO_2$) →(Fe + HCl) A →($NaNO_2$ + HCl, 273–278 K) B →(C_2H_5OH) C

Answer: (a) A = CH_3CH_2CN (propanenitrile); B = $CH_3CH_2CONH_2$ (propanamide); C = $CH_3CH_2NH_2$ (ethanamine). (b) A = $C_6H_5NH_2$ (aniline); B = $C_6H_5N_2^+Cl^-$ (benzenediazonium chloride); C = C_6H_6 (benzene).

Explanation:

(a) KCN substitutes Br to give the nitrile;

partial hydrolysis gives the amide;

Hofmann bromamide degradation removes one carbon to give ethanamine.

(b) Fe/HCl reduces $–NO_2$ to $–NH_2$;

$NaNO_2$/HCl at 273–278 K gives the diazonium salt;

ethanol reduces the diazonium group (replaced by H), giving benzene (with CH_3CHO, N_2 and HCl).

Q.23

Write the reaction involved in the following :

(a) Wolff-Kishner reduction

(b) Decarboxylation reaction

(c) Cannizzaro reaction

Answer: (a) RCOR' + H2NNH2 → RC(=NNH2)R' (hydrazone) →(KOH/ethylene glycol, heat)→ RCH2R' + N2. (b) RCOONa →(CaO/NaOH, heat)→ RH + Na2CO3. (c) 2HCHO →(conc. NaOH)→ CH3OH + HCOONa.

Explanation:

(a) Wolff-Kishner reduction: An aldehyde or ketone is reacted with hydrazine (H2NNH2) to form a hydrazone, which is then heated with KOH in ethylene glycol (high-boiling solvent).
The C=N bond is reduced and N2 is eliminated, converting C=O to CH2.
Reaction: RCOR' + H2NNH2 → RC(=NNH2)R' → RCH2R' + N2.

(b) Decarboxylation: Sodium salt of a carboxylic acid (or the acid itself) when heated with soda lime (NaOH/CaO) loses CO2.
Reaction: RCOONa + NaOH →(CaO, heat)→ R−H + Na2CO3.
Example: CH3COONa + NaOH →(CaO)→ CH4 + Na2CO3.

(c) Cannizzaro reaction: Aldehydes without alpha-hydrogen (e.g., HCHO, C6H5CHO) undergo disproportionation in conc.
NaOH.
One molecule is oxidised to the carboxylate and another is reduced to the alcohol.
Reaction: 2HCHO + NaOH → CH3OH + HCOONa.
Or: 2C6H5CHO + NaOH → C6H5CH2OH + C6H5COONa.

Q.24

Give the equations of reactions for the preparation of (any three) :

(a) Phenol from chlorobenzene

(b) Salicylaldehyde from phenol

(c) 2-Methoxyacetophenone from anisole

(d) Picric acid from phenol

Answer: (a) C6H5Cl →(NaOH, 623 K, 300 atm)→ C6H5ONa →(HCl)→ C6H5OH. (b) C6H5OH + CHCl3 + NaOH → 2-HO-C6H4-CHO (Reimer-Tiemann). (c) C6H5OCH3 + CH3COCl →(AlCl3, Friedel-Crafts)→ 2-CH3CO-C6H4-OCH3. (d) C6H5OH + 3HNO3 (dil. then conc.) →(H2SO4)→ 2,4,6-(NO2)3-C6H2-OH.

Explanation:

(a) Phenol from chlorobenzene (Dow process): C6H5Cl + 2NaOH →(623 K, 300 atm)→ C6H5ONa + NaCl + H2O; then C6H5ONa + HCl → C6H5OH + NaCl.

The drastic conditions are needed to break the strong C−Cl bond with resonance stabilization.

(b) Salicylaldehyde from phenol (Reimer-Tiemann reaction): C6H5OH + CHCl3 + 3KOH → 2-hydroxybenzaldehyde (salicylaldehyde) + 3KCl + 2H2O.

Mechanism involves dichlorocarbene (:CCl2) as the electrophile.

(c) 2-Methoxyacetophenone from anisole (Friedel-Crafts acylation): C6H5OCH3 + CH3COCl →(AlCl3)→ CH3CO-C6H4-OCH3 + HCl.

The −OCH3 group is ortho/para directing; the major product is the ortho isomer (2-methoxyacetophenone) or para (4-methoxyacetophenone) due to steric effects.

(d) Picric acid from phenol (nitration): C6H5OH →(dil. HNO3)→ o- and p-nitrophenol mixture →(conc. HNO3/H2SO4)→ 2,4,6-trinitrophenol (picric acid).

Direct treatment with conc. HNO3 would oxidise phenol; dilute acid is used first.

Q.25

Give reasons for the following :

(a) Chlorine is ortho/para directing in electrophilic aromatic substitution reactions, though chlorine is an electron withdrawing group.

(b) Racemic mixture is optically inactive.

(c) Allyl chloride is hydrolysed more readily than n-propyl chloride.

Answer: (a) Cl is −I but +M effect dominant for directing; lone pairs donate into ring at o/p positions. (b) Equal amounts of enantiomers cancel plane-polarised light rotation. (c) Allyl cation (CH2=CH−CH2+) is resonance-stabilised; n-propyl gives a primary carbocation without resonance.

Explanation:

(a) Chlorine has two effects: inductive (−I, electron withdrawing through sigma bond) and mesomeric (+M, electron donating through lone pair donation into the ring).
The mesomeric effect dominates in directing: lone pairs on Cl are donated to ortho and para positions of the ring via resonance, increasing electron density there, so electrophiles attack preferentially at ortho/para positions.
Although Cl deactivates the ring overall (−I > +M for reactivity), it still directs to o/p.

(b) A racemic mixture contains equal amounts of the two enantiomers (mirror images).
Each enantiomer rotates plane-polarised light by an equal amount but in opposite directions (+α and −α).
Since the amounts are equal, the rotations cancel out, giving zero net optical rotation.
The mixture is therefore optically inactive.

(c) Allyl chloride (CH2=CH−CH2Cl) undergoes hydrolysis more readily because the intermediate allyl carbocation (CH2=CH−CH2+) is resonance-stabilised (the positive charge is delocalised over C1 and C3 via the pi bond).
n-Propyl chloride gives a primary carbocation (CH3CH2CH2+) with no resonance stabilisation, which is much less stable.
Lower activation energy for allyl → faster hydrolysis.

Q.26

The vapour pressure of a solvent at 283 K is 100 mm Hg. Calculate the vapour pressure of a dilute solution containing 1 mole of a strong electrolyte AB in 50 moles of the solvent at 283 K (assuming complete dissociation of solute AB).

Answer: 96.15 mm Hg

Explanation:

AB is a strong electrolyte that completely dissociates: AB → A+ + B−.

So 1 mol AB gives 2 mol ions (i = 2).

Effective moles of solute = 1 × 2 = 2 mol.

Moles of solvent = 50 mol.

Mole fraction of solvent: x(solvent) = 50/(50 + 2) = 50/52 = 25/26

By Raoult's law: P = P° × x(solvent) = 100 × (50/52) = 5000/52 = 96.15 mm Hg

Vapour pressure of the solution = 96.15 mm Hg (≈ 96.2 mm Hg).

Q.27

Calculate emf of the following cell :

Zn (s) | Zn2+ (0·1 M) || Sn2+ (0·001 M) | Sn (s)

[Given : E°(Zn2+/Zn) = −0·76 V, E°(Sn2+/Sn) = −0·14 V; log 10 = 1]

Answer: 0.56 V (0.5609 V)

Explanation:

E°cell = E°cathode − E°anode = −0.14 − (−0.76) = +0.62 V.

$Zn + Sn^{2+} \rightarrow Zn^{2+} + Sn$, n = 2, $Q = [Zn^{2+}]/[Sn^{2+}] = 0.1/0.001 = 100$.

Ecell = 0.62 − (0.0591/2) × log 100 = 0.62 − 0.02955 × 2 = 0.62 − 0.0591 = 0.5609 V ≈ 0.56 V.

Q.28

The rate of a gaseous reaction triples when temperature is increased from 17°C to 27°C. Calculate the energy of activation for this reaction.

[Given : 2·303 R = 19·15 J K−1 mol−1, log 3 = 0·48]

Answer: Ea ≈ 79.97 kJ mol^{-1} (≈ 80 kJ mol^{-1})

Explanation:

$\log(k_2/k_1) = [Ea / 2.303R] \times (T_2 - T_1)/(T_1T_2)$

$T_1 = 17 + 273 = 290$ K; $T_2 = 27 + 273 = 300$ K; $k_2/k_1 = 3$.

$0.48 = [Ea / 19.15] \times 10/(290 \times 300)$

$Ea = 0.48 \times 19.15 \times 87000/10 = 0.48 \times 19.15 \times 8700$

$Ea = 79{,}970$ J mol^{-1} $\approx$ 79.97 kJ mol^{-1}

Q.29(a)

(Case Study — Carbohydrates) Carbohydrates are essential for life in both plants and animals. Carbohydrates are used as storage molecules as starch in plants and glycogen in animals. Chemically they are polyhydroxy aldehydes or ketones. On the basis of their behaviour on hydrolysis, carbohydrates are classified as monosaccharides, oligosaccharides and polysaccharides. All monosaccharides are reducing sugars, i.e., they are oxidized by Tollens' reagent and Fehling's solution. A monosaccharide like glucose is aldohexose and its molecular formula was found to be $C_6H_{12}O_6$. After reacting with different reagents like HI, $H_2N - OH$, Bromine water, $(CH_3CO)_2O$, etc. its structure was found to contain one aldehyde group, one primary alcoholic group, ($- CH_2OH$) and four secondary alcoholic groups (>CHOH). Despite having the aldehyde group, glucose does not give some of the reactions of aldehyde group like Schiff's test, $NaHSO_3$ addition. This explains the existence of glucose in two cyclic hemiacetal forms which differ only in the configuration of the hydroxyl group at C – 1.

What are reducing sugars ?

Answer: Reducing sugars are carbohydrates that reduce Tollens' reagent and Fehling's solution because they have a free aldehyde or ketone group (free anomeric –OH). All monosaccharides, and disaccharides such as maltose and lactose, are reducing sugars; sucrose is non-reducing.

Explanation:

A reducing sugar has a free aldehyde group or a hemiacetal/hemiketal carbon that can open to the free carbonyl form, so it reduces Tollens' reagent (silver mirror) and Fehling's solution (red Cu_2O precipitate).

Q.29(b)

(Case Study — Carbohydrates) Classify the following into monosaccharide and disaccharide : Fructose, Sucrose, Lactose, Galactose

Answer: Monosaccharides: fructose, galactose. Disaccharides: sucrose, lactose.

Explanation:

Monosaccharides cannot be hydrolysed into simpler sugars.

Sucrose hydrolyses to glucose + fructose and lactose to glucose + galactose, so both are disaccharides.

Q.29(c)

(Case Study — Carbohydrates) Name the polysaccharide which is called animal starch. Why is it called animal starch ?

Answer: Glycogen is called animal starch. It is called animal starch because it is the storage form of carbohydrate (glucose) in animals, just as starch is the storage form in plants.

Explanation:

Glycogen is a polysaccharide stored in the liver and muscles of animals.

It is called animal starch because: (1) Like starch, it is a polymer of glucose stored as an energy reserve.

(2) Starch is the storage carbohydrate in plants;

glycogen serves the same role in animals.

(3) Both are made of glucose units.

Glycogen is more branched than starch (amylopectin): it has α-1,4 glycosidic linkages in chains and α-1,6 glycosidic linkages at branch points, with branches every 8–12 glucose units (more frequent than amylopectin's branching every 24–30 units).

OR

Q.29(c)

(Case Study — Carbohydrates) [OR]

(i) Name the isomers of glucose which in the cyclic form differ only in the configuration of the −OH group at C-1.

(ii) Presence of which functional group was detected when glucose reacted with Br2 water ?

Answer: (i) α-D-Glucose and β-D-Glucose (anomers). (ii) Aldehyde group (−CHO); Br2 water oxidises the aldehyde to gluconic acid, confirming the presence of −CHO.

Explanation:

(i) The isomers that differ only in the configuration of −OH at C-1 (the anomeric carbon) are called anomers.

For glucose: α-D-Glucose has −OH at C-1 in axial position (below the ring in Haworth projection), β-D-Glucose has −OH at C-1 in equatorial position (above the ring).

These two cyclic hemiacetal forms interconvert via the open-chain form (mutarotation).

(ii) Glucose reacts with bromine water (a mild oxidising agent): the −CHO group is oxidised to −COOH (gluconic acid).

Since bromine water decolorises (Br2 is reduced), this confirms the presence of an aldehyde (−CHO) group in glucose.

Ketones (like fructose) do NOT decolorise bromine water under mild conditions, confirming glucose is an aldehyde (aldohexose) not a ketone.

Q.30(a)

(Case Study — Transition Metals) Transition metals have incomplete d-subshell either in neutral atom or in their ions. The presence of partly filled d-orbitals in their atoms makes transition elements different from that of the non-transition elements. With partly filled d-orbitals, these elements exhibit certain characteristic properties such as display of a variety of oxidation states, formation of coloured ions and entering into complex formation with a

variety of ligands. The transition metals and their compounds also exhibit catalytic properties and paramagnetic behaviour. The transition metals are very hard and have low volatility. An examination of the $E°(M^{2+}/M)$ values shows the varying trends :

Metal	$E°(M^{2+}/M)$
V	–1·18
Cr	–0·91
Mn	–1·18
Fe	–0·44
Co	–0·28
Ni	–0·25
Cu	+0·34
Zn	–0·76

On what basis can we say that Cu is a transition element but Zn is not ? (Atomic number : Cu = 29, Zn = 30)

Answer: A transition element has an incompletely filled d subshell in its ground state or in any of its common oxidation states. Cu ($3d^{10}4s^1$) forms Cu^{2+} with $3d^9$ (incomplete), so it is a transition element. Zn ($3d^{10}4s^2$) has a completely filled 3d subshell in the atom and in Zn^{2+}, so it is not.

Explanation:

Definition (NCERT): transition elements have partly filled d orbitals in the atom or in a stable ion.

Cu^{2+} is d^9; Zn^{2+} is d^{10}.

Q.30(b)

(Case Study — Transition Metals) Why do transition elements show variety of oxidation states ?

Answer: The (n−1)d and ns electrons have nearly the same energy, so both can take part in bonding. Different numbers of d electrons can be lost, giving a variety

of oxidation states differing by one unit (e.g. Mn: +2 to +7).

Explanation:

Because the ns and (n−1)d orbitals are close in energy, electrons from both can be used for bond formation, so transition elements show several oxidation states.

Q.30(c)

(Case Study — Transition Metals)

(i) Why do E°(M2+/M) values show irregular trend from Vanadium to Zinc ?

(ii) How is the variability in oxidation states of transition metals different from that of the non-transition elements ?

Answer: (i) Irregular trend because factors like ionisation enthalpy, sublimation enthalpy, and hydration enthalpy vary irregularly across the series due to varying electronic configurations (particularly half-filled and fully filled d-subshells). (ii) Transition metals show a continuous range of adjacent oxidation states (differ by 1), while non-transition elements show oxidation states that differ by 2 (group valence and group valence minus 2).

Explanation:

(i) E°(M2+/M) depends on three energy terms: ionisation enthalpy (IE1+IE2), sublimation enthalpy (ΔsubH°), and hydration enthalpy.

All three vary irregularly across the 3d series — particularly because of the extra stability of half-filled (d5, e.g.

Mn) and fully-filled (d10, e.g.

Cu, Zn) configurations.

For example, Mn has unusually low E° (−1.18 V) because Mn2+ has a stable half-filled d5 configuration, making it harder to reduce.

Cu has positive E° (+0.34 V) due to its higher second ionisation enthalpy and anomalous electronic configuration.

(ii) Transition metals show oxidation states that differ by 1 unit (e.g., Fe: +2 and +3; Mn: +2, +3, +4, +5, +6, +7 — a continuous range), made possible by the availability of both ns and (n−1)d electrons.

Non-transition elements (p-block) show oxidation states differing by 2 — the group valence and (group valence − 2), e.g., S: +6 and +4;
Cl: +7, +5, +3, +1 — because electrons are lost in pairs from s and p subshells.
d electrons give finer gradation.

OR

Q.30(c)

(Case Study — Transition Metals) [OR]

(i) Of the d4 species, Cr2+ is strongly reducing while Mn3+ is strongly oxidising. Why ? (Atomic number : Cr = 24, Mn = 25)

(ii) Complete the following ionic equation : 2MnO4− + H2O + I− → ?

Answer: (i) Cr2+ (d4) readily loses one more electron to reach Cr3+ (d3, half-filled t2g — stable), so it is a strong reductant. Mn3+ (d4) readily gains one electron to reach Mn2+ (d5, half-filled — stable), so it is a strong oxidant. (ii) 2MnO4− + H2O + I− → 2MnO2 + IO3− + 2OH− (in neutral/slightly basic).

Explanation:

(i) Cr^{2+} (d^4) →
Cr^{3+} (d^3, stable half-filled t_2g) so it is a strong reductant; Mn^{3+} (d^4) →
Mn^{2+} (d^5, half-filled, extra stable) so it is a strong oxidant.
(ii) Mn: +7 → +4 (gains $3e^-$ each, 2 Mn gain $6e^-$); I: −1 → +5 (loses $6e^-$).
$2MnO_4^- + H_2O + I^- \rightarrow 2MnO_2 + IO_3^- + 2OH^-$.
Check: Mn 2=2; I 1=1; O 9=9; H 2=2; charge −3 = −3.

Q.31(a)

(Section E — any five) (a) How is the crystal field splitting energy for octahedral complex (Δo) related to that of tetrahedral complex (Δt) ?

Answer: Δt = (4/9) × Δo, i.e., the tetrahedral splitting is approximately 4/9 of the octahedral splitting for the same metal and ligands.

Explanation:

In an octahedral complex, all six ligands directly approach along the axes, causing a larger splitting.

In a tetrahedral complex, only four ligands are present and none approach directly along the d-orbital axes, causing smaller splitting.
The mathematical relationship is Δt = (4/9) × Δo (approximately, for the same metal ion and ligands).
This means tetrahedral splitting is about 44% of octahedral splitting, explaining why most tetrahedral complexes are high spin (the small Δt rarely exceeds the pairing energy).

Q.31(b)

(Section E — any five) (b) Write the IUPAC name of the following complex : [PtCl2(en)2](NO3)2

Answer: Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate

Explanation:
Analysis of [PtCl2(en)2](NO3)2:
- Central metal: Pt
- Ligands in complex: 2 Cl− (chlorido) and 2 en (ethane-1,2-diamine)
- Charge on complex cation: NO3− outside means the cation has charge +2 (2 × NO3−).
Cl contributes −2, en is neutral.
So Pt + (−2) = +2, giving Pt oxidation state = +4.
- Naming: ligands alphabetically — chlorido (×2) before ethane-1,2-diamine (×2, using bis prefix for the chelating ligand 'en').

IUPAC name: Dichloridobis(ethane-1,2-diamine)platinum(IV) nitrate.
(Counter ion NO3− is named last as 'nitrate';
complex cation is named with metal last with oxidation state in Roman numerals.)

Q.31(c)

(Section E — any five) (c) Write the geometry and magnetic behaviour of the complex [Ni(CO)4] on the basis of Valency Bond Theory (VBT).

Answer: Geometry: Tetrahedral. Magnetic behaviour: Diamagnetic.

Explanation:

Ni in [Ni(CO)4]: CO is a strong field ligand; Ni is Ni(0) with configuration [Ar]3d8 4s2.

In the complex Ni(0): [Ar] 3d10 (the 3d8 4s2 electrons rearrange to 3d10 with the 4s electrons pairing into 3d).

With 3d10 (all d electrons paired), no d electrons are available for sp3 hybridisation using the 4s, 4p orbitals (sp3 hybridisation): 4 sp3 hybrid orbitals are formed from one 4s and three 4p orbitals, giving a tetrahedral geometry.

Since all electrons are paired (3d10, no unpaired electrons), the complex is DIAMAGNETIC.

Answer: Tetrahedral geometry, diamagnetic.

Q.31(d)

(Section E — any five) (d) What type of isomerism is shown by the complex [Co(NH3)6][Cr(CN)6] ?

Answer: Coordination isomerism

Explanation:

$[Cr(CN)_6]$ has both a complex cation and a complex anion.

Exchanging ligands between the two metal centres gives $[Cr(NH_3)_6][Co(CN)_6]$, an isomer of the same formula, so the compound shows coordination isomerism.

(Ionisation isomerism involves exchange of a ligand with a counter ion.)

Q.31(e)

(Section E — any five) (e) For the coordination compound on the basis of crystal field theory, write the electronic configuration for d4 ion if $\Delta o < P$. Is the coordination compound a high spin or low spin complex ?

Answer: Electronic configuration: t2g3 eg1 (3 electrons in t2g, 1 in eg). High spin complex.

Explanation:

For a d4 ion in an octahedral field:

- If $\Delta o < P$ (crystal field splitting energy is less than pairing energy), electrons do not pair in the t2g level — they spread to higher energy orbitals before pairing.

This is because it costs less energy to jump to the eg level (cost = Δo) than to pair in t2g (cost = P).
When Δo < P, the electrons fill singly first: t2g3 eg1.
- t2g3 eg1 configuration: 3 electrons in t2g (one each in the three t2g orbitals) and 1 electron in eg.
- With 4 unpaired electrons, this is a HIGH SPIN complex.
High spin complexes result from weak field ligands (small Δo) where Δo < P.

Q.31(f)

(Section E — any five) (f) Out of [Co(NH3)6]3+ and [Co(NH3)4Cl2]+, which complex is heteroleptic and why ?

Answer: [Co(NH3)4Cl2]+ is heteroleptic because it contains two different types of ligands (NH3 and Cl−).

Explanation:
Homoleptic complexes contain only one type of ligand;
heteroleptic complexes contain two or more different types of ligands.
[Co(NH3)6]3+: only NH3 ligands — HOMOLEPTIC.
[Co(NH3)4Cl2]+: contains both NH3 and Cl− ligands (two different types) — HETEROLEPTIC.
Answer: [Co(NH3)4Cl2]+ is heteroleptic because it has two different ligands (NH3 and Cl−).

Q.31(g)

(Section E — any five) (g) Draw the structures of optical isomers of [PtCl2(en)2]2+.

Answer: $[PtCl_2(en)_2]^{2+}$ is octahedral (Pt(IV), coordination number 6). The cis isomer, with the two Cl^- on adjacent positions and each en chelating two adjacent positions, is chiral and exists as a pair of non-superimposable mirror images (d and l, or Δ and Λ). The trans isomer is achiral. The two optical isomers are the mirror-image pair of cis-$[PtCl_2(en)_2]^{2+}$.

Explanation:

Two bidentate en ligands and two Cl^- fill six octahedral sites.

In the cis arrangement there is no plane or centre of symmetry, so the two mirror-image forms are optical isomers;

the trans form has a plane of symmetry.

(The drawn structures are not reproduced here.)

Q.32(a)

(a)(i) Account for the following :

(1) Oxidation of aldehydes is easier as compared to ketones.

(2) The alpha (α) hydrogen atoms of aldehydes are acidic in nature.

Answer: (1) Aldehydes have a hydrogen on the carbonyl carbon (−CHO) that can be oxidised; ketones (−CO−) lack this. Aldehyde is oxidised to carboxylic acid by mild oxidants (Tollens, Fehling, CrO_3/H^+); ketones resist mild oxidation because breaking a C−C bond is needed. (2) α-H atoms are on the carbon adjacent to C=O; the C=O group withdraws electrons by induction and the resulting carbanion (enolate) is stabilised by resonance with the C=O pi bond, making α-H acidic (pKa ≈ 20).

Explanation:

(1) Aldehydes (RCHO) are more easily oxidised because: the C−H bond of the carbonyl group is weak and can be cleaved by mild oxidising agents.

The reaction RCHO → RCOOH involves oxidation of the C1 carbon from +1 to +3 (gain of 2O).

Ketones (RCOR') would require C−C bond cleavage to be oxidised, needing stronger conditions (like concentrated HNO_3).

Hence aldehydes respond to mild oxidants (Tollens: Ag^+, Fehling: Cu^{2+}, even atmospheric O_2) while ketones do not.

(2) α-Hydrogens of carbonyl compounds are acidic because: (a) the carbonyl group is electron-withdrawing by induction (+I effect of carbonyl reduces electron density on α-carbon), weakening the C−H bond;

(b) more importantly, when α-H is removed, the carbanion (enolate) formed is

stabilised by resonance with the adjacent C=O: R−CH(−)−C=O ↔ R−CH=C−O(−). This resonance delocalises the negative charge onto the electronegative oxygen, stabilising the conjugate base and making the α-H relatively easy to remove (acidic, pKa ≈ 20 for aldehydes).

Q.0

(a)(ii) Write the products in the following reactions: (1) C_6H_5–$COCH_3$ + $NaOH/I_2$ → ? + ? (2) C_6H_5–COCl + $(CH_3)_2Cd$ → ? + $CdCl_2$

Answer: (1) Acetophenone (C6H5COCH3) + NaOH/I2 → CHI3 (iodoform, yellow precipitate) + C6H5COONa (sodium benzoate). (2) Benzoyl chloride (C6H5COCl) + (CH3)2Cd → C6H5COCH3 (acetophenone) + CdCl2.

Explanation:

(1) Iodoform reaction of the methyl ketone: $C_6H_5COCH_3 + 3I_2 + 4NaOH$ → CHI_3 (yellow) + C_6H_5COONa + 3NaI + $3H_2O$.

(2) Acid chloride + dialkylcadmium gives a ketone: $2C_6H_5COCl + (CH_3)_2Cd$ → $2C_6H_5COCH_3 + CdCl_2$.

Q.0

(a)(iii) Give a simple chemical test to distinguish between ethanoic acid and ethanal.

Answer: Add Tollens reagent (ammoniacal AgNO3): ethanal gives a silver mirror (positive), ethanoic acid gives no reaction (negative). Alternatively: add Na2CO3 solution — ethanoic acid effervesces (CO2 gas), ethanal does not.

Explanation:

Test 1 (Tollens test): Ethanal (CH3CHO) is an aldehyde and reduces Tollens reagent (Ag(NH3)2+OH−) to give a bright silver mirror on the inner surface of the test tube. Ethanoic acid (CH3COOH) does not reduce Tollens reagent — no silver mirror.

Test 2 (Na2CO3 test): Ethanoic acid is acidic (pKa 4.75); it reacts with Na2CO3 to produce CO2 gas with effervescence: 2CH3COOH + Na2CO3 → 2CH3COONa + H2O + CO2↑.

Ethanal is neutral and does not react with Na2CO3.

Test 3 (Sodium bicarbonate / NaHCO3 test): Ethanoic acid dissolves and produces CO2 (brisk effervescence);
ethanal does not.

Any one of these tests is sufficient to distinguish the two.

Q.32(b)

(b) [OR]

(i) Draw structure of the 2,4-dinitrophenylhydrazone of benzaldehyde.

(ii) Arrange the following in increasing order of their reactivity towards HCN : CH3COCH3, (CH3)3C−COCH3, CH3CHO

(iii) How can you convert phenyl magnesium bromide to benzoic acid ?

(iv) Give a simple chemical test to distinguish between benzaldehyde and ethanal.

(v) Write the main product in the following reaction : $CH_3COCH_2COOC_2H_5$ —(i) $NaBH_4$, (ii) $H^+\rightarrow$?

Answer: (i) C6H5−CH=N−NH−C6H3(NO2)2-2,4 [2,4-dinitrophenylhydrazone of benzaldehyde]. (ii) Increasing reactivity towards HCN: (CH3)3C−COCH3 < CH3COCH3 < CH3CHO. (iii) C6H5MgBr + CO2 (dry) → C6H5COOMgBr; then H3O+ → C6H5COOH (benzoic acid). (iv) Iodoform test: ethanal gives yellow CHI3 precipitate with I2/NaOH; benzaldehyde does not. (v) Main product: CH3−CH(OH)−CH2−COOC2H5 (ethyl 3-hydroxybutanoate).

Explanation:

(i) 2,4-DNP hydrazone: benzaldehyde + 2,4-dinitrophenylhydrazine gives $C_6H_5CH=N–NH–C_6H_3(NO_2)_2$.

(ii) Reactivity towards HCN falls with steric hindrance and +I effect of alkyl groups: $(CH_3)_3C–COCH_3 < CH_3COCH_3 < CH_3CHO$.

(iii) $C_6H_5MgBr + CO_2$ (dry ice) → $C_6H_5COOMgBr$, then H_3O^+ gives C_6H_5COOH.

(iv) Iodoform test: ethanal ($CH_3CO–$ group) gives yellow CHI_3 with $NaOH/I_2$,

benzaldehyde does not.

(v) $NaBH_4$ reduces only the ketone (not the ester): $CH_3CH(OH)CH_2COOC_2H_5$ (ethyl 3-hydroxybutanoate).

Q.33(a)

(a)(i) The resistance of 0·05 M CH3COOH solution is found to be 100 ohm. If the cell constant is 0·0354 cm−1, calculate the molar conductivity of the acetic acid solution.

(ii) State Faraday's first law of electrolysis. How many Faraday is required for the reduction of 1 mol of MnO4− to Mn2+ ?

Answer: (i) Molar conductivity = 7.08 S cm2 mol−1. (ii) Faraday's first law: mass deposited is proportional to quantity of charge passed (m = Z × Q = Z × I × t). Faradays required: 5 F (MnO4− + 8H+ + 5e− → Mn2+ + 4H2O).

Explanation:

(i) Molar conductivity calculation:

Conductivity (κ) = cell constant / resistance = 0.0354 cm−1 / 100 Ω = 3.54 × 10−4 S cm−1

Concentration = 0.05 mol L−1 = 0.05 × 10−3 mol cm−3 = 5 × 10−5 mol cm−3

Molar conductivity (Λm) = κ / c = (3.54 × 10−4 S cm−1) / (5 × 10−5 mol cm−3)

= (3.54 × 10−4) / (5 × 10−5) S cm2 mol−1

= 7.08 S cm2 mol−1

(ii) Faraday's first law: The mass of a substance deposited or liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.

m = Z × Q, where Z is the electrochemical equivalent.

For reduction of MnO4− to Mn2+:

MnO4− → Mn2+: Mn goes from +7 to +2, a change of 5 electrons.

Half-reaction: MnO4− + 8H+ + 5e− → Mn2+ + 4H2O

For 1 mol MnO4−, 5 mol electrons are needed = 5 Faraday.

Q.33(b)

(b) [OR]

(i) The conductivity of 0·0025 mol L−1 acetic acid is 5·25 × 10−5 S cm−1. Calculate its degree of dissociation if Λ°m for acetic acid is 390 S cm2 mol−1.

(ii) Write anode, cathode and overall reaction of lead storage battery.

Answer: (i) Degree of dissociation α = 0.0538 (≈ 5.38%). (ii) Anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$. Cathode: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$. Overall: $Pb + PbO_2 + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$.

Explanation:

(i) Degree of dissociation:

Concentration c = 0.0025 mol L−1 = 0.0025 × 10−3 mol cm−3 = 2.5 × 10−6 mol cm−3

Λm (observed) = κ/c = (5.25 × 10−5 S cm−1) / (2.5 × 10−6 mol cm−3) = 21 S cm2 mol−1

Degree of dissociation α = Λm/Λ°m = 21/390 = 0.0538 ≈ 5.38% (0.054)

(ii) Lead storage battery reactions (discharging):

At anode (oxidation): $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

At cathode (reduction): $PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$

Overall cell reaction: $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

E°cell = +2.04 V (approximately).