CBSE Class 12 Chemistry 2024 — 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 one of the following first row transition elements is expected to have the highest third ionization enthalpy?

(a) Iron (Z = 26)

(b) Manganese (Z = 25) <<

(c) Chromium (Z = 24)

(d) Vanadium (Z = 23)

Explanation:

Third ionization enthalpy removes an electron from M^{2+}.

Mn^{2+} is $3d^5$ (half-filled, extra stable), so removing the third electron from Mn costs the most (IE_3: Mn ≈ 3248, Cr ≈ 2987, Fe ≈ 2957, V ≈ 2833 kJ/mol).

Fe^{2+} ($3d^6$) readily loses an electron to reach stable $3d^5$.

Answer: (B) Manganese.

Q.2

Which of the following compounds will give a ketone on oxidation with chromic anhydride (CrO3)?

(a) (CH3)2CH-CH2OH

(b) CH3CH2CH2OH

(c) (CH3)3C-OH

(d) CH3-CH2-CH(OH)-CH3 <<

Explanation:

CrO3 oxidizes primary alcohols to aldehydes/carboxylic acids and secondary alcohols to ketones.

Tertiary alcohols are not oxidized.

Option (D) CH3CH2CH(OH)CH3 is a secondary alcohol (butan-2-ol) and will give butan-2-one (a ketone) on oxidation with CrO3.

Options (A) and (B) are primary alcohols (give aldehydes/acids);

option (C) is a tertiary alcohol (not oxidized).

Q.3

Two among the three components of DNA are beta-D-2-deoxyribose and a heterocyclic base. The third component is:

(a) Adenine
(b) Phosphoric acid <<
(c) Sulphuric acid
(d) Uracil

Explanation:

DNA is composed of three components: (1) a pentose sugar — beta-D-2-deoxyribose, (2) a nitrogenous (heterocyclic) base (Adenine, Guanine, Cytosine, or Thymine), and (3) phosphoric acid (H_3PO_4).

Adenine is itself a heterocyclic base (already one of the two given), sulphuric acid is not a component of DNA, and uracil is found in RNA not DNA.

Therefore the third component is phosphoric acid.

Q.4

For an electrolyte undergoing association in a solvent, the van't Hoff factor:

(a) is always greater than one
(b) has negative value
(c) has zero value
(d) is always less than one <<

Explanation:

The van't Hoff factor i = (observed colligative property)/(calculated colligative property for non-electrolyte).

When association occurs, multiple molecules combine to form fewer particles, so the number of solute particles decreases.

This means $i < 1$ (always less than one).

For dissociation, $i > 1$.

For no change, $i = 1$.

Q.5

For the reaction $X + 2Y \rightarrow P$, the differential form equation of the rate law is:

(a) $2d[P]/dt = -d[Y]/dt$ <<

(b) $-d[P]/dt = -d[X]/dt$

(c) $+d[X]/dt = -d[P]/dt$

(d) $-2d[Y]/dt = +d[P]/dt$

Explanation:

For $X + 2Y \rightarrow P$: rate $= -d[X]/dt = -\frac{1}{2}\, d[Y]/dt = +d[P]/dt$.

Option (A): $2d[P]/dt = -d[Y]/dt$ is correct.

(B) has wrong sign on $d[P]/dt$; (D) should be $-d[Y]/dt = 2d[P]/dt$.

Option (C): $d[X]/dt = -d[P]/dt$ is also algebraically correct, so two options are valid; (A) is kept as the key.

Note: this key is unconfirmed.

Q.6

The compound which undergoes SN1 reaction most rapidly is:

(a) Bromocyclohexene with Br on the carbon adjacent to the C=C (allylic): 3-bromocyclohex-1-ene <<

(b) (Bromomethyl)cyclohexane: $C_6H_{11}–CH_2–Br$

(c) Bromocyclohexane: $C_6H_{11}–Br$

(d) Bromobenzene: $C_6H_5–Br$

Explanation:

SN1 rate depends on carbocation stability.

(A) ionises to a resonance-stabilised allyl carbocation, so it reacts fastest.

(B) is primary (very slow SN1), (C) is a secondary alkyl bromide (moderate), (D) is an aryl halide and does not undergo SN1 (partial double-bond character of C–Br, no stable aryl cation).

Answer: (A).

Q.7

Acetic acid reacts with PCl5 to give:

(a) Cl-CH2-COCl

(b) Cl-CH2-COOH

(c) CH3-COCl <<

(d) CCl3-COOH

Explanation:

PCl5 replaces the -OH group of carboxylic acids with -Cl to form acyl chlorides.

Acetic acid (CH3COOH) reacts with PCl5 to give acetyl chloride (CH3COCl) + POCl3 + HCl.

The reaction is: CH3COOH + PCl5 --> CH3COCl + POCl3 + HCl.

Only the -OH is replaced, not the alpha-H atoms.

Q.8

The formation of cyanohydrin from an aldehyde is an example of:

(a) nucleophilic addition <<

(b) electrophilic addition

(c) nucleophilic substitution

(d) electrophilic substitution

Explanation:

In cyanohydrin formation, HCN adds across the C=O bond of an aldehyde.

The CN^- ion (from HCN) acts as a nucleophile and attacks the electrophilic carbonyl carbon.

This is a nucleophilic addition reaction.

The carbonyl carbon is electron-deficient (delta+), making it susceptible to nucleophilic attack.

Q.9

In the Arrhenius equation, when log k is plotted against 1/T, a straight line is obtained whose:

(a) slope is A/R and intercept is Ea

(b) slope is A and intercept is −Ea/R

(c) slope is −Ea/RT and intercept is log A

(d) slope is −Ea/(2.303 R) and intercept is log A <<

Explanation:

The Arrhenius equation is k = A·e^(-Ea/RT).

Taking log on both sides: log k = log A - Ea/(2.303·R·T).

This can be written as: log k = -(Ea/(2.303·R))·(1/T) + log A.

Comparing with y = mx + c: slope = -Ea/(2.303·R) (negative slope) and y-intercept = log A.

Option (D) states slope is -Ea/(2.303R) and intercept is log A, which is correct.

Q.10

The reaction of an alkyl halide with sodium alkoxide forming ether is known as:

(a) Wurtz reaction

(b) Reimer-Tiemann reaction

(c) Williamson synthesis <<

(d) Kolbe reaction

Explanation:

Williamson synthesis is the method of preparing ethers by reacting an alkyl halide with sodium alkoxide: R-X + NaOR' --> R-O-R' + NaX.

Wurtz reaction involves coupling of alkyl halides with Na metal to form higher alkanes.

Reimer-Tiemann reaction introduces a -CHO group on phenol.

Kolbe reaction involves synthesis of salicylic acid.

Q.11

The correct order of the ease of dehydration of the following alcohols by the action of conc. H2SO4 is:

(a) (CH3)3C-OH > (CH3)2CH-OH > CH3CH2-OH <<

(b) (CH3)2CH-OH > CH3CH2-OH > (CH3)3C-OH

(c) CH3CH2-OH > (CH3)2CH-OH > (CH3)3C-OH

(d) (CH3)2CH-OH > (CH3)3C-OH > CH3CH2-OH

Explanation:

Dehydration of alcohols with conc.

H2SO4 proceeds via carbocation intermediates (E1 mechanism for 2° and 3°).

Ease of dehydration follows the order of carbocation stability: tertiary > secondary > primary.
(CH3)3C-OH forms a 3° carbocation (most stable), (CH3)2CH-OH forms a 2° carbocation, and CH3CH2-OH forms a 1° carbocation (least stable).
Therefore the correct order is (CH3)3C-OH > (CH3)2CH-OH > CH3CH2-OH.

Q.12

Which functional groups of glucose interact to form cyclic hemiacetal leading to pyranose structure?

(a) Aldehyde group and hydroxyl group at C-4
(b) Aldehyde group and hydroxyl group at C-5 <<
(c) Ketone group and hydroxyl group at C-4
(d) Ketone group and hydroxyl group at C-5

Explanation:

Glucose is an aldohexose with an aldehyde group at C-1.
When the -OH group at C-5 attacks the aldehyde group at C-1 intramolecularly, a cyclic hemiacetal is formed.
This forms a six-membered ring (pyranose structure) resembling pyran.
The reaction involves the aldehyde group (at C-1) and the hydroxyl group at C-5.

Q.13

Assertion (A): When NaCl is added to water a depression in freezing point is observed. Reason (R): NaCl undergoes dissociation in water.

(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 statements are true.

NaCl added to water does cause depression in freezing point (A is true).
NaCl dissociates in water: NaCl --> Na^+ + Cl^-, increasing the number of solute particles, which is the reason for greater depression in freezing point (R is true and correctly explains A).
Delta Tf = i·Kf·m, where i = 2 for NaCl, making depression twice that of a non-electrolyte.

Q.14

Assertion (A): Separation of Zr and Hf is difficult. Reason (R): Zr and Hf have similar radii due to lanthanoid contraction.

(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 and R correctly explains A.
Zr (4d series) and Hf (5d series) are in the same group.
Due to lanthanoid contraction, the 4f electrons poorly shield the outer electrons, causing Hf to have almost the same atomic radius as Zr (Zr: 160 pm, Hf: 159 pm).
Because of this near-identical size, they have very similar chemical properties, making their separation extremely difficult.

Q.15

Assertion (A): The pKa of ethanoic acid is lower than that of Cl-CH2-COOH. Reason (R): Chlorine shows electron withdrawing (-I) effect which increases the acidic character of Cl-CH2-COOH.

(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: Cl-CH2-COOH (chloroacetic acid, pKa = 2.86) is MORE acidic than ethanoic acid (acetic acid, pKa = 4.74).

Therefore pKa of ethanoic acid is HIGHER (not lower) than pKa of Cl-CH2-COOH.

Reason R is true: Chlorine does show -I (electron-withdrawing inductive) effect which stabilises the carboxylate anion and increases the acidic character of chloroacetic acid.

So A is false but R is true.

Q.16

Assertion (A): Aniline is a stronger base than ammonia. Reason (R): The unshared electron pair on nitrogen atom in aniline becomes less available for protonation due to 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 false: Aniline (pKb = 9.4, Kb = 4×10^-10) is a WEAKER base than ammonia (pKb = 4.7, Kb = 1.8×10^-5).

Reason R is true: In aniline, the lone pair on N is in conjugation with the benzene ring via resonance, making it less available for accepting a proton — this is why aniline is a weaker base than ammonia.

So A is false but R is true.

Q.17

Calculate the potential of Iron electrode in which the concentration of Fe^2+ ion is 0.01 M. (E°(Fe^2+/Fe) = -0.45 V at 298 K) [Given: log 10 = 1]

Answer: −0.509 V (≈ −0.51 V)

Explanation:

$Fe^{2+} + 2e^- \rightarrow Fe$, n = 2.

Nernst: $E = E^\circ - (0.059/2) \log(1/[Fe^{2+}]) = -0.45 - 0.0295 \times \log(100) = -0.45 - 0.0295 \times 2 = -0.45 - 0.059 = -0.509$ V.

Q.18

Define molecularity of the reaction. State any one condition in which a bimolecular reaction may be kinetically of first order.

Answer: Molecularity is the number of reacting species (atoms, ions, or molecules) that collide simultaneously in an elementary reaction to bring about a chemical reaction. A bimolecular reaction is kinetically of first order (pseudo-first order) when one of the reactants is present in very large excess (e.g., water as solvent), so its concentration remains essentially constant throughout the reaction.

Explanation:

Molecularity = total number of molecules/atoms/ions of reactants involved in a single elementary step.

For A + B --> products (bimolecular), if [B] >> [A] (B is in large excess), then [B] ≈ constant = k', so Rate = k[A][B] = k'[A] = k_obs[A], making it pseudo-first order.

Example: hydrolysis of an ester in aqueous solution.

Q.19

What happens when D-glucose is treated with the following reagents? (a) HI (b) Conc. HNO3

Answer: (a) HI reduces D-glucose to n-hexane ($CH_3CH_2CH_2CH_2CH_2CH_3$) by replacing all -OH groups with -H. (b) Conc. HNO_3 oxidizes D-glucose to glucaric acid (saccharic acid) — both the aldehyde group (C-1) and the terminal primary hydroxyl group (C-6) are oxidized to -COOH groups.

Explanation:

(a) HI (hydroiodic acid) is a strong reducing agent.

It reduces all the hydroxyl groups of glucose by replacing each -OH with -H, ultimately converting glucose (C6H12O6) into n-hexane (C6H14).

(b) Conc.

HNO_3 is a strong oxidizing agent.

It oxidizes the terminal -CHO group at C-1 and the primary -CH_2OH group at C-6 to -COOH, producing glucaric acid (also called saccharic acid, a dicarboxylic acid).

Q.20

(a) Draw the structures of major monohalo products in each of the following reactions: (i) C_6H_5–CH=CH_2 (styrene) + HBr → (ii) cyclohexene + Br_2 (UV light) →

Answer: (i) Reactant = STYRENE (C6H5-CH=CH2, benzene ring + vinyl), not vinylcyclohexane. Styrene + HBr by Markovnikov's rule: H adds to terminal =CH2, carbocation forms on the benzylic carbon (resonance-stabilized by the ring), Br adds there. Major monohalo product = (1-bromoethyl)benzene, C6H5-CHBr-CH3 (alpha-bromoethylbenzene / 1-phenyl-1-bromoethane). (ii) Reactant = CYCLOHEXENE (six-membered ring with one C=C), not cyclohexane; conditions = Br2 + UV light (free-radical). Under UV light the major MONOHALO product is from ALLYLIC substitution, not addition (addition would give the 1,2-dibromo compound). Major monohalo product = 3-bromocyclohexene (3-bromocyclohex-1-ene).

Explanation:

(i) Styrene + HBr (Markovnikov): H adds to the terminal CH_2, giving the resonance-stabilised benzylic carbocation;

Br^- adds there, giving C_6H_5–CHBr–CH_3, (1-bromoethyl)benzene.

(ii) Cyclohexene + Br_2/UV light: free-radical allylic substitution (monohalo product), giving 3-bromocyclohexene;

addition would give the dibromo compound.

OR

Q.20

OR (b) Give reasons for the following: (i) Grignard reagent should be

prepared under anhydrous conditions. (ii) Alkyl halides give alcohol with aqueous KOH whereas in the presence of alcoholic KOH, alkenes are formed.

Answer: (i) Grignard reagent (RMgX) is very reactive and reacts readily with moisture (water, alcohol, CO2). Water protonates the C-MgX bond: RMgX + H2O --> RH + Mg(OH)X, destroying the Grignard reagent. Therefore, anhydrous (dry) conditions (using dry ether as solvent) are essential. (ii) Aqueous KOH provides OH^- ions in polar aqueous medium, which acts as a nucleophile and attacks the carbon bearing the halide by SN2 mechanism, giving alcohol (substitution). Alcoholic KOH in non-polar medium provides free OH^- which acts as a strong base, abstracting a beta-hydrogen and promoting E2 elimination to form an alkene.

Explanation:

(i) RMgX is an organometallic compound where C-Mg bond is highly polar (C^delta- - Mg^delta+).

Water's O-H bond protonates the carbanionic carbon, decomposing the reagent.

(ii) In aqueous medium, OH^- is solvated and acts as a nucleophile (substitution favored).

In alcoholic medium, OH^- is unsolvated and acts as a stronger base (elimination favored, giving alkene via E2 mechanism).

Q.21

Write the chemical equation when: (a) Butan-2-one is treated with Zn(Hg) and conc. HCl. (b) Two molecules of benzaldehyde are treated with conc. NaOH.

Answer: (a) Clemmensen reduction: CH3COCH2CH3 + Zn(Hg)/conc.HCl --> CH3CH2CH2CH3 (butane). The C=O group is reduced to -CH2-. (b) Cannizzaro reaction: 2C6H5CHO + conc. NaOH --> C6H5CH2OH (benzyl alcohol) + C6H5COONa (sodium benzoate). One molecule is oxidized to carboxylate and the other is reduced to alcohol.

Explanation:

(a) Zn(Hg)/conc.

HCl is the Clemmensen reduction reagent, which reduces the carbonyl group (C=O) of ketones to a methylene group (-CH2-).

Butan-2-one (CH3COCH2CH3) is reduced to butane (CH3CH2CH2CH3).

(b) Benzaldehyde has no alpha-hydrogen, so it undergoes Cannizzaro reaction (disproportionation) with conc.

NaOH: one molecule of benzaldehyde acts as the reducing agent (gets oxidized to benzoate) and another acts as the oxidizing agent (gets reduced to benzyl alcohol).

2C6H5CHO + NaOH --> C6H5COO^-Na^+ + C6H5CH2OH.

Q.22

When a certain conductivity cell was filled with 0.05 M KCl solution, it has a resistance of 100 ohm at 25°C. When the same cell was filled with 0.02 M AgNO3 solution, the resistance was 90 ohm. Calculate the conductivity and molar conductivity of AgNO3 solution. (Given: Conductivity of 0.05 M KCl solution = 1.35 × 10^-2 ohm^-1 cm^-1)

Answer: Conductivity of AgNO3 = 1.50 × 10^-2 ohm^-1 cm^-1; Molar conductivity = 750 S cm^2 mol^-1

Explanation:

Step 1: Find cell constant using KCl solution.

Cell constant = conductivity × resistance = 1.35 × 10^-2 ohm^-1 cm^-1 × 100 ohm = 1.35 cm^-1.

Step 2: Calculate conductivity of AgNO3.

Conductivity = cell constant / resistance = 1.35 / 90 = 0.015 ohm^-1 cm^-1 = 1.5 × 10^-2 S cm^-1.

Step 3: Calculate molar conductivity.

Molar conductivity (Lambda_m) = (conductivity × 1000) / molarity = (1.5 × 10^-2 × 1000) / 0.02 = 15 / 0.02 = 750 S cm^2 mol^-1.

Q.23

The following initial rate data were obtained for the reaction: 2NO(g) + Br2(g)

--> 2NOBr(g). Expt. 1: [NO]=0.05 mol/L, [Br2]=0.05 mol/L, Rate=1.0×10^-3 mol/L/s. Expt. 2: [NO]=0.05 mol/L, [Br2]=0.15 mol/L, Rate=3.0×10^-3 mol/L/s. Expt. 3: [NO]=0.15 mol/L, [Br2]=0.05 mol/L, Rate=9.0×10^-3 mol/L/s. (a) What is the order with respect to NO and Br2 in the reaction? (b) Calculate the rate constant (k). (c) Determine the rate of reaction when concentration of NO and Br2 are 0.4 M and 0.2 M, respectively.

Answer: (a) Order w.r.t. NO = 2; Order w.r.t. Br2 = 1. (b) k = 8 L^2 mol^-2 s^-1. (c) Rate = 0.256 mol L^-1 s^-1.

Explanation:

(a) Comparing Expt 1 and 2: [NO] constant, [Br2] triples (0.05 to 0.15), rate triples (1.0 to 3.0) x 10^-3.

So rate is proportional to [Br2]^1 → order w.r.t.

Br2 = 1.

Comparing Expt 1 and 3: [Br2] constant, [NO] triples (0.05 to 0.15), rate increases 9-fold (1.0 to 9.0) x 10^-3.

3^x = 9 → x = 2.

Order w.r.t.

NO = 2.

Rate = k[NO]^2[Br2].

(b) Using Expt 1: 1.0×10^-3 = k×(0.05)^2×(0.05) = k×0.0025×0.05 = k×1.25×10^-4.

k = 1.0×10^-3 / 1.25×10^-4 = 8 L^2 mol^-2 s^-1.

(c) Rate = 8×(0.4)^2×(0.2) = 8×0.16×0.2 = 8×0.032 = 0.256 mol L^-1 s^-1.

Q.24

(a) Write the formula for the following coordination compound: Potassium tetrahydroxidozincate (II). (b) Arrange the following complexes in the increasing order of conductivity of their solution: [Cr(NH3)5Cl]Cl2, [Cr(NH3)3Cl3], [Cr(NH3)6]Cl3. (c) Identify the type of isomerism exhibited by the following complexes: (i) [Co(NH3)5NO2]^2+ (ii) [Co(en)3]Cl3

Answer: (a) K2[Zn(OH)4]. (b) [Cr(NH3)3Cl3] < [Cr(NH3)5Cl]Cl2 < [Cr(NH3)6]Cl3 (increasing order of conductivity). (c) (i) Linkage isomerism (NO2^- can bind

through N as nitro or through O as nitrito); (ii) Optical isomerism (the complex with en ligands is chiral — exists as d and l forms).

Explanation:

(a) Potassium tetrahydroxidozincate(II): Zn^2+ with 4 OH^- ligands gives [Zn(OH)4]^2- as the complex ion;
with 2 K^+ counterions: K2[Zn(OH)4].
(b) Conductivity depends on the number of ions dissociated: [Cr(NH3)3Cl3] gives 0 ions (non-electrolyte, lowest conductivity);
[Cr(NH3)5Cl]Cl2 gives 3 ions (1:2 electrolyte);
[Cr(NH3)6]Cl3 gives 4 ions (1:3 electrolyte, highest conductivity).
(c) (i) NO2^- is an ambidentate ligand — can coordinate through N (nitro, -NO2) or O (nitrito, -ONO) →
linkage isomerism.
(ii) [Co(en)3]^3+ with three bidentate en ligands has no plane of symmetry →
optical isomerism (d and l enantiomers).

Q.25

(a) Which of the following is an allylic halide? (i) CH3-CH=CH-Br (ii) CH2=CH-CH(Br)-CH3. (b) Out of chlorobenzene and 2,4,6-trinitrochlorobenzene, which is more reactive towards nucleophilic substitution and why? (c) Which isomer of C4H9Cl has the lowest boiling point?

Answer: (a) (ii) $CH_2=CH–CH(Br)–CH_3$ is the allylic halide. (b) 2,4,6-Trinitrochlorobenzene is more reactive towards nucleophilic substitution: the three $–NO_2$ groups at ortho/para positions withdraw electrons and stabilise the intermediate carbanion. (c) 2-Chloro-2-methylpropane, $(CH_3)_3C–Cl$ (tert-butyl chloride), has the lowest boiling point: most branched, smallest surface area, weakest van der Waals forces.

Explanation:

(a) Allylic halide: halogen on an sp^3 carbon next to C=C.
In (i) Br is on the double-bond carbon (vinylic).

(b) Nitro groups at o/p positions activate SNAr.

(c) Among C_4H_9Cl isomers boiling point falls with branching: n-butyl 78 °C, sec-butyl 68 °C, isobutyl 69 °C, tert-butyl 51 °C.

Q.26

(a) Write the mechanism of the following reaction: $CH_3CH_2OH \rightarrow CH_2=CH_2$ (H^+, 443 K). (b) Write the main product in each of the following reactions: (i) $CH_3–CH_2–CH=CH_2$ → (a) B_2H_6, (b) $3H_2O_2/OH^-$ (ii) phenol (C_6H_5OH) → (a) aq. NaOH, (b) CO_2, H^+

Answer: (a) Dehydration of ethanol (E1, acid-catalysed): Step 1 - H+ protonates the -OH oxygen of CH3CH2OH to form the ethyloxonium ion CH3CH2-OH2+. Step 2 - Loss of water gives a carbocation CH3CH2+ (the rate-determining step). Step 3 - Loss of a beta-proton forms the C=C double bond, giving ethene CH2=CH2 (+ H+ regenerated). (b)(i) But-1-ene (CH3CH2CH=CH2) with a) B2H6 then b) 3H2O2/OH- : hydroboration-oxidation = anti-Markovnikov, syn addition; boron adds to the terminal CH2, then is replaced by -OH -> major product = butan-1-ol (CH3CH2CH2CH2OH). (b)(ii) PHENOL (C6H5OH) with a) aq. NaOH then b) CO2, H+ : this is KOLBE'S (Kolbe-Schmitt) REACTION. Phenol + NaOH -> sodium phenoxide; sodium phenoxide + CO2 (under pressure) then acidification -> SALICYLIC ACID (2-hydroxybenzoic acid, o-HO-C6H4-COOH).

Explanation:

(a) Acid-catalysed dehydration (E1): protonation of OH, loss of water to give $CH_3CH_2^+$, loss of β-H^+ gives ethene.

(b)(i) Hydroboration–oxidation gives anti-Markovnikov alcohol, butan-1-ol.

(b)(ii) Kolbe's reaction: phenol →
sodium phenoxide →
carboxylation with CO_2 →
acidification gives salicylic acid (2-hydroxybenzoic acid).

Q.27

Answer the following (any three): (a) What is peptide linkage? (b) What type

of bonds hold a DNA double helix together? (c) Which one of the following is a polysaccharide? Sucrose, Glucose, Starch, Fructose. (d) Give one example each for water-soluble vitamins and fat-soluble vitamins.

Answer: (a) Peptide linkage (peptide bond) is the amide bond (-CO-NH-) formed between the carboxyl group (-COOH) of one amino acid and the amino group (-NH2) of another amino acid with the loss of a water molecule. (b) Hydrogen bonds (between complementary base pairs: A-T and G-C) hold the two strands of DNA double helix together. (c) Starch is a polysaccharide. (d) Water-soluble vitamin example: Vitamin C (ascorbic acid) or Vitamin B complex. Fat-soluble vitamin example: Vitamin A (retinol) or Vitamin D or E or K.

Explanation:

(a) When two amino acids combine, the -COOH of one reacts with -NH2 of another: R1CH(NH2)COOH + H2N-CHR2-COOH --> R1CH(NH2)CO-NH-CHR2-COOH + H2O. The -CO-NH- linkage is the peptide bond.

(b) The two complementary strands in DNA are held together by hydrogen bonds between base pairs (A=T has 2 H-bonds;
G≡C has 3 H-bonds).

(c) Sucrose is a disaccharide;
glucose and fructose are monosaccharides;
starch is a polysaccharide (polymer of glucose).

(d) Vitamins C and B-group are water-soluble; Vitamins A, D, E, K are fat-soluble.

Q.28

Compound (A) (C6H12O2) on reduction with LiAlH4 gives two compounds (B) and (C). The compound (B) on oxidation with PCC gives compound (D) which upon treatment with dilute NaOH and subsequent heating gives compound (E). Compound (E) on catalytic hydrogenation gives compound (C). The compound (D) is oxidized further to give compound (F) which is found to be a monobasic acid (Molecular weight = 60). Identify the compounds (A), (B), (C), (D), (E) and (F).

Answer: A = $CH_3COOCH_2CH_2CH_2CH_3$ (butyl acetate); B = CH_3CH_2OH (ethanol); C

= $CH_3CH_2CH_2CH_2OH$ (butan-1-ol); D = CH_3CHO (ethanal); E = $CH_3CH=CHCHO$ (but-2-enal); F = CH_3COOH (ethanoic acid)

Explanation:

F is a monobasic acid of M = 60, so F = CH_3COOH and D = CH_3CHO, hence B = CH_3CH_2OH.

$LiAlH_4$ reduces the ester A ($C_6H_{12}O_2$) to ethanol and C; D with dil.

NaOH/heat undergoes aldol condensation to E = $CH_3CH=CHCHO$, whose hydrogenation gives butan-1-ol = C.

So A = $CH_3COOC_4H_9$ (n-butyl acetate).

Q.29(a)

(Case study — Batteries and Fuel Cells) Batteries and fuel cells are very useful forms of galvanic cell. Any battery or cell that we use as a source of electrical energy is basically a galvanic cell. However, for a battery to be of practical use it should be reasonably light, compact and its voltage should not vary appreciably during its use. There are mainly two types of batteries — primary batteries and secondary batteries.

In the primary batteries, the reaction occurs only once and after use over a period of time the battery becomes dead and cannot be reused again, whereas the secondary batteries are rechargeable.

Production of electricity by thermal plants is not a very efficient method and is a major source of pollution. To solve this problem, galvanic cells are designed in such a way that energy of combustion of fuels is directly converted into electrical energy, and these are known as fuel cells. One such fuel cell was used in the Apollo space programme.

(a) How do primary batteries differ from secondary batteries?

Answer: In primary batteries, the electrochemical reaction occurs only once and the battery cannot be recharged — once discharged, it becomes dead and must be discarded. Examples: dry cell (Leclanche cell), mercury cell. In secondary batteries (rechargeable batteries), the electrode reactions are reversible — the

battery can be recharged by passing an electric current through it in the reverse direction. Examples: lead storage battery, nickel-cadmium cell.

Explanation:

Primary batteries: energy stored during manufacture is released during use;
reaction is irreversible;
non-rechargeable.
Secondary batteries: the discharge reaction is reversed during charging (electrical energy converts back to chemical energy);
rechargeable;
can be used multiple times.

Q.29(b)

(Case study — Batteries and Fuel Cells) (b) The cell potential of Mercury cell is 1.35 V, and remains constant during its life. Give reason.

Answer: The cell potential of the mercury cell remains constant throughout its life because the overall cell reaction does not involve any ion in solution whose concentration changes during the operation of the cell. The cell reaction is: Zn(Hg) + HgO(s) --> ZnO(s) + Hg(l). Since the reactants and products are all in solid or amalgam form (no dissolved ions that change concentration), the Nernst equation gives a constant cell potential.

Explanation:

Mercury cell: anode = Zn-Hg amalgam (Zn loses electrons), cathode = paste of HgO and KOH (HgO gains electrons).
Overall: Zn + HgO --> ZnO + Hg.
All species are solids/liquids — their activities are 1 and do not change.
Since Q (reaction quotient) = 1 throughout, E = E° - (RT/nF)lnQ = E° = constant = 1.35 V.

Q.29(c)

(Case study — Batteries and Fuel Cells) (c) Write the reactions involved in the recharging of the lead storage battery.

Answer: Recharging reverses the discharge reactions. Anode (oxidation): $PbSO_4(s) + 2H_2O(l) \rightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$. Cathode (reduction): $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$. Overall: $2PbSO_4(s) + 2H_2O(l) \rightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$, i.e. H_2SO_4 is regenerated.

Explanation:

On recharging an external potential greater than the cell's own is applied, so the cell works as an electrolytic cell: $PbSO_4$ is converted back to Pb at one electrode and to PbO_2 at the other, and H_2SO_4 is regenerated.

OR

Q.29(c)

OR (Case study — Batteries and Fuel Cells) (c) Write two advantages of fuel cells over other galvanic cells.

Answer: Two advantages of fuel cells over other galvanic cells: (1) High efficiency — fuel cells convert the energy of combustion of fuels directly into electrical energy without going through heat engines (no Carnot cycle limitation), so they have higher efficiency (up to 70%) compared to thermal power plants (~40%). (2) Pollution-free — fuel cells (especially H2-O2 fuel cells) produce only water as the by-product, causing no environmental pollution, unlike thermal plants which emit CO2, SO2, etc.

Explanation:

Fuel cells operate as long as fuel is supplied.

The H2-O2 fuel cell used in Apollo space programme produced water as the only product.

Advantages include: continuous operation (unlike batteries that need recharging), no moving parts, high energy density, environment-friendly operation.

Q.30(a)

(Case study — Crystal Field Theory) The Valence Bond Theory (VBT) explains the formation, magnetic behaviour and geometrical shapes of coordination compounds whereas ‘The Crystal Field Theory’ for coordination

compounds is based on the effect of different crystal fields (provided by 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. The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron. Coordination compounds find extensive applications in metallurgical processes, analytical and medicinal chemistry.

(a) What is crystal field splitting energy?

Answer: Crystal field splitting energy (Delta or 10Dq) is the difference in energy between the two sets of d-orbitals (eg and t2g) that arise from the splitting of the degenerate d-orbitals of the central metal ion in the presence of ligands (crystal field). In an octahedral field, the d-orbitals split into higher energy eg (dx^2-y^2 and dz^2) and lower energy t2g (dxy, dyz, dxz) sets, and the energy difference between them is the crystal field splitting energy.

Explanation:

In a free metal ion, all five d-orbitals are degenerate (equal energy).

When ligands approach as point charges, this degeneracy is lifted (splitting).

In an octahedral complex: eg orbitals (pointing towards ligands) are raised by 0.6 Delta, and t2g orbitals (pointing between ligands) are lowered by 0.4 Delta.

The gap Delta_o (octahedral crystal field splitting energy) determines colour and magnetic properties.

Q.30(b)

(Case study — Crystal Field Theory) (b) Give reason for the violet colour of the complex [Ti(H2O)6]^3+ on the basis of crystal field theory.

Answer: [Ti(H2O)6]^3+ is violet because Ti^3+ has d^1 configuration. In the octahedral crystal field, the single d-electron occupies the lower-energy t2g orbital. When white light falls on the complex, the electron absorbs energy corresponding to yellow-green light (around 500 nm) and is excited from t2g to eg orbital (d-d transition). The complementary colour of yellow-green is violet, which is

transmitted/reflected, making the complex appear violet.

Explanation:

Crystal field theory explains colour of transition metal complexes: electrons absorb a specific wavelength of visible light for d-d transition (from lower to higher energy d-orbitals).

The transmitted/reflected colour (complementary colour) is what we see.

For Ti^3+ (d^1): one electron, only one possible d-d transition (t2g --> eg).

The absorbed wavelength corresponds to yellow-green (~498 nm), and the complementary colour is violet.

Q.30(c)

(Case study — Crystal Field Theory) (c) [Cr(NH3)6]^3+ is paramagnetic while [Ni(CN)4]^2- is diamagnetic. Explain why. [Atomic No.: Cr = 24, Ni = 28]

Answer: Cr (Z=24): [Ar]3d^5 4s^1; Cr^3+ = [Ar]3d^3. In [Cr(NH3)6]^3+, NH3 is a moderate-field ligand. The 3d^3 configuration has 3 unpaired electrons (one in each t2g orbital). Since there are unpaired electrons, it is paramagnetic. Ni (Z=28): [Ar]3d^8 4s^2; Ni^2+ = [Ar]3d^8. CN^- is a very strong field ligand causing square planar geometry (for d^8). The 8 d-electrons pair up in 4 orbitals (dsp^2 hybridisation), leaving no unpaired electrons. Therefore [Ni(CN)4]^2- is diamagnetic.

Explanation:

Paramagnetic means unpaired electrons present; diamagnetic means all electrons are paired.

Cr^3+ (d^3): three unpaired electrons → paramagnetic regardless of ligand strength.

Ni^2+ (d^8) + CN^- (strong field): CN^- causes large crystal field splitting, forces all 8 electrons to pair in lower-energy orbitals →

square planar [Ni(CN)4]^2- with zero unpaired electrons →

diamagnetic.

Hybridisation: dsp^2.

OR

Q.30(c)

OR (Case study — Crystal Field Theory) (c) Explain why [Fe(CN)6]^3- is an inner orbital complex, whereas [Fe(H2O)6]^3+ is an outer orbital complex. [Atomic No.: Fe = 26]

Answer: Fe^{3+} is $3d^5$. CN^- is a strong-field ligand: the five d electrons pair up in the t_2g orbitals (one unpaired), leaving two inner 3d orbitals empty for d^2sp^3 hybridisation, so $[Fe(CN)_6]^{3-}$ is an inner orbital (low-spin) complex. H_2O is a weak-field ligand: no pairing, all five 3d orbitals are singly occupied (5 unpaired electrons), so the vacant 4s, 4p and 4d orbitals are used (sp^3d^2 hybridisation), making $[Fe(H_2O)_6]^{3+}$ an outer orbital (high-spin) complex.

Explanation:

Inner orbital complexes use inner d-orbitals (3d) for hybridisation (d^2sp^3 for octahedral) — occurs with strong field ligands (CN^-, CO, NO2^-) that cause electron pairing.

Outer orbital complexes use outer d-orbitals (4d) for hybridisation (sp^3d^2 for octahedral) — occurs with weak field ligands (H2O, F^-, Cl^-) that do not cause pairing.

Strong field: low spin; Weak field: high spin.

Q.31(a)

(a)(i) At the same temperature, CO2 gas is more soluble in water than O2 gas. Which one of them will have higher value of KH and why? (a)(ii) How does the size of blood cells change when placed in an aqueous solution containing more than 0.9% (mass/volume) sodium chloride? (a)(iii) 1 molal aqueous solution of an electrolyte A2B3 is 60% ionized. Calculate the boiling point of the solution. (Given: Kb for H2O = 0.52 K kg mol^-1)

Answer: (i) O2 has higher KH. Henry's law: p = KH × x (mole fraction). Higher KH means lower solubility. Since CO2 is more soluble, its KH is lower; O2 is less soluble, so O2 has higher KH. (ii) Blood cells shrink (crenation). A solution with more than 0.9% NaCl is hypertonic. When blood cells are placed in a hypertonic

solution, water flows out of the cells by osmosis (from low solute concentration inside the cell to high solute concentration outside), causing the cells to shrink. (iii) A2B3 --> 2A^3+ + 3B^2-: 1 mol --> 5 ions total. i = 1 + (n-1)alpha = 1 + (5-1)×0.60 = 1 + 4×0.60 = 1 + 2.4 = 3.4. Delta Tb = i × Kb × m = 3.4 × 0.52 × 1 = 1.768 K. Boiling point = 100 + 1.768 = 101.768°C ≈ 101.77°C.

Explanation:

(i) Henry's law constant KH: p_gas = KH × x_gas.

For a given partial pressure, higher solubility means smaller mole fraction ratio p/x, i.e., smaller KH.

CO2 more soluble → smaller KH; O2 less soluble → larger KH.

(ii) Hypertonic solution (>0.9% NaCl) has higher osmotic pressure than blood plasma; water leaves blood cells by exosmosis →

cells shrink/crenate.

(iii) A2B3 fully dissociates to 5 ions; at 60% ionisation: i = 1 + (5-1)×0.6 = 3.4.

Elevation in boiling point = i×Kb×m = 3.4×0.52×1 = 1.768 K.

Boiling point of solution = 373.15 + 1.768 = 374.918 K (or 100 + 1.768 = 101.768°C).

OR

Q.31(b)

OR (b)(i) The vapour pressures of A and B at 25°C are 75 mm Hg and 25 mm Hg, respectively. If A and B are mixed such that the mole fraction of A in the mixture is 0.4, then calculate the mole fraction of B in vapour phase. (b)(ii) Define colligative property. Which colligative property is preferred for the molar mass determination of macromolecules? (b)(iii) Why are equimolar solutions of sodium chloride and glucose not isotonic?

Answer: (i) Mole fraction of A in mixture xA = 0.4; xB = 1 - 0.4 = 0.6. PA = PA° × xA = 75 × 0.4 = 30 mm Hg. PB = PB° × xB = 25 × 0.6 = 15 mm Hg. Total pressure Ptotal = 30 + 15 = 45 mm Hg. Mole fraction of B in vapour = PB/Ptotal = 15/45 = 1/3 = 0.333. (ii) Colligative properties are those properties of dilute solutions that depend only on the number of solute particles (molecules/ions) and not on the nature of the solute. Examples: relative lowering of vapour pressure, elevation of

boiling point, depression of freezing point, osmotic pressure. For macromolecules (polymers, proteins), osmotic pressure measurement is preferred because even at small concentrations it gives a measurable osmotic pressure, whereas other colligative effects are too small to measure accurately. (iii) Equimolar solutions of NaCl and glucose are not isotonic because NaCl dissociates in water (NaCl --> Na^+ + Cl^-), giving approximately twice the number of particles as glucose (which does not dissociate). Therefore, the NaCl solution has a higher osmotic pressure than the glucose solution of the same molarity, making them not isotonic.

Explanation:

(i) Dalton's law + Raoult's law.

Mole fraction of B in vapour = YB = PB/Ptotal = 15/45 = 0.333.

(ii) Osmotic pressure is preferred for macromolecules: Pi = MRT, where even small molar mass gives measurable pressure;

other properties (Delta Tb, Delta Tf) are too small for accurate measurement with high-MW solutes.

(iii) Isotonic solutions have the same osmotic pressure.

NaCl gives i=2 (2 ions per formula unit), glucose gives i=1 (no dissociation).

So equimolar NaCl has twice the particle concentration and twice the osmotic pressure of equimolar glucose — they are not isotonic.

Q.32(a)

(Answer any five) (a) N,N-diethyl-benzenesulphonamide is insoluble in alkali. Give reason.

Answer: N,N-diethyl-benzenesulphonamide has no N-H bond (both H atoms on nitrogen are replaced by ethyl groups). Sulphonamides dissolve in alkali by forming water-soluble sodium salts via deprotonation of the N-H group. Since N,N-diethyl derivative has no acidic N-H proton to be removed, it cannot form such a salt and is therefore insoluble in alkali.

Explanation:

Benzenesulphonamide (C6H5SO2NH2) dissolves in NaOH because its N-H is acidic: C6H5SO2NH2 + NaOH --> C6H5SO2NHNa + H2O.

N-monosubstituted sulphonamide (one N-H left) also dissolves.
But N,N-diethyl-benzenesulphonamide (C6H5SO2N(C2H5)2) has no N-H bond — it cannot be deprotonated →
insoluble in alkali.
This is the basis of Hinsberg's test to distinguish 1°, 2°, and 3° amines.

Q.32(b)

(Answer any five) (b) Aniline does not undergo Friedel-Crafts reaction. Why?

Answer: Aniline does not undergo Friedel-Crafts reaction because it reacts with the Lewis acid catalyst (AlCl3) used in Friedel-Crafts reactions. The lone pair on the nitrogen of aniline coordinates with AlCl3 to form an acid-base complex (C6H5NH2·AlCl3), which deactivates both the catalyst and renders the nitrogen strongly electron-withdrawing (rather than electron-donating). This deactivates the benzene ring towards electrophilic substitution, making Friedel-Crafts reaction impossible.

Explanation:

Friedel-Crafts reaction requires AlCl3 or other Lewis acid catalysts.
Aniline (C6H5NH2) is a Lewis base and forms a stable salt/complex: C6H5NH2 + AlCl3 --> C6H5NH2^+·AlCl4^-.
In this complex, the N becomes positively charged (ammonium-like), making it a strong -I (electron-withdrawing) group that strongly deactivates the ring towards electrophilic attack.
So Friedel-Crafts alkylation/acylation fails.

Q.32(c)

(Answer any five) (c) Write a simple chemical test to distinguish between methylamine and aniline.

Answer: Azo dye test: treat each with $NaNO_2$ + HCl at 273–278 K, then add alkaline β-naphthol. Aniline gives a stable diazonium salt that couples to give an orange-red azo dye; methylamine gives an unstable diazonium salt that decomposes with evolution of N_2 and no dye.

Explanation:

Azo dye test: primary aromatic amines (aniline) form stable diazonium salts at 0-5°C that couple with phenols/naphthols to give coloured azo dyes.

Primary aliphatic amines (methylamine) form unstable diazonium salts that immediately decompose (N2 evolved as bubbles, no dye).

Therefore: add NaNO2/HCl at 0-5°C, then add alkaline beta-naphthol solution — aniline gives orange-red colour, methylamine gives no colour (gas evolution instead).

Q.32(d)

(Answer any five) (d) Write the chemical reaction involved in Gabriel phthalimide synthesis.

Answer: Gabriel phthalimide synthesis: Step 1 — Phthalimide reacts with KOH to form potassium phthalimide: C6H4(CO)2NH + KOH --> C6H4(CO)2NK + H2O. Step 2 — Potassium phthalimide reacts with an alkyl halide (R-X) by SN2: C6H4(CO)2NK + R-X --> C6H4(CO)2NR + KX. Step 3 — Acid hydrolysis of the N-alkyl phthalimide: C6H4(CO)2NR + H2O/H+ (or NH2NH2) --> C6H4(COOH)2 + R-NH2. The product is a primary amine (R-NH2). This method gives pure primary amines without contamination by secondary or tertiary amines.

Explanation:

Gabriel synthesis is used to synthesize primary amines from alkyl halides.

The phthalimide anion (potassium phthalimide) is a good nucleophile that reacts with primary/secondary alkyl halides.

The N-alkyl phthalimide intermediate is then hydrolyzed (acid or base or using hydrazine — hydrazinolysis) to free the primary amine.

Limitations: cannot use aryl/vinyl halides (no SN2); gives only primary amines.

Q.32(e)

(Answer any five) (e) How will you convert aniline to p-bromoaniline?

Answer: Direct bromination of aniline gives 2,4,6-tribromoaniline (polyhalogenation), not p-bromoaniline. To get p-bromoaniline selectively: Step 1 — Protect the -NH2 group by acetylation: C6H5NH2 + (CH3CO)2O --> C6H5NHCOCH3 (acetanilide) + CH3COOH. Step 2 — Brominate acetanilide with

Br2/CH3COOH (or Br2/AcOH): gives predominantly p-bromoacetanilide (since -NHCOCH3 is less activating than -NH2, mono substitution occurs and para product predominates). Step 3 — Hydrolysis: p-BrC6H4NHCOCH3 + H2O/H+ --> p-BrC6H4NH2 (p-bromoaniline) + CH3COOH.

Explanation:

The -NH2 group is too activating and gives polyhalogenation.

Acetylation reduces the activating effect (acetamido group is less activating, directs to para preferentially due to steric effect).

After bromination at para position, hydrolysis removes the acetyl protecting group to regenerate -NH2 as p-bromoaniline.

Q.32(f)

(Answer any five) (f) Complete the following reaction: $C_6H_5–N_2^+Cl^-$ —(i) HBF_4, (ii) $NaNO_2/Cu$, Δ→ ?

Answer: $C_6H_5NO_2$ (nitrobenzene). (i) HBF_4 gives $C_6H_5N_2^+BF_4^-$; (ii) $NaNO_2/Cu$, Δ replaces the diazonium group by $–NO_2$.

Explanation:

Step (i): HBF_4 converts benzenediazonium chloride into benzenediazonium tetrafluoroborate, $C_6H_5N_2^+BF_4^-$.

Step (ii): heating this salt with $NaNO_2$ in the presence of Cu replaces the diazonium group by $–NO_2$: $C_6H_5N_2^+BF_4^- + NaNO_2$ →

$C_6H_5NO_2 + N_2 + NaBF_4$.

Q.32(g)

(Answer any five) (g) Write the structures of A and B in the following reaction: $C_6H_5–COOH$ → (NH_3, Δ) A → (Br_2 + NaOH) B

Answer: Starting material: benzoic acid (benzene ring with -COOH group). A = benzamide (C6H5CONH2), formed by heating benzoic acid with NH3 (ammonium benzoate → benzamide + H2O on heating). B = aniline (C6H5NH2), formed by Hoffmann bromamide degradation of benzamide with Br2 + NaOH (benzamide loses one carbon as CO2/CO3^2-, giving aniline: C6H5CONH2 + Br2 + 4NaOH →

C6H5NH2 + Na2CO3 + 2NaBr + 2H2O).

Explanation:

Benzoic acid + NH_3 on heating gives ammonium benzoate, which loses water to give benzamide, A = $C_6H_5CONH_2$.

Hoffmann bromamide degradation (Br_2 + NaOH) of benzamide gives aniline, B = $C_6H_5NH_2$ (one carbon fewer).

Q.33(a)

(a)(i) Account for the following: (1) The melting and boiling points of Zn, Cd and Hg are low. (2) Of the d^4 species, Cr^2+ is strongly reducing while Mn^3+ is strongly oxidizing. (3) E° value of Cu^2+/Cu is +0.34 V. (a)(ii) Complete and balance the following chemical equations: (1) KMnO4 --heat--> (2) Cr2O7^2- + 6I^- + 14H^+ -->

Answer: (i)(1) In Zn, Cd and Hg the d subshell is completely filled (d^{10}), so d electrons do not take part in metallic bonding; the metallic bond is weak, hence low melting and boiling points. (2) Cr^{2+} (d^4) → Cr^{3+} (d^3, stable t_2g^3) so it is strongly reducing; Mn^{3+} (d^4) → Mn^{2+} (d^5, half-filled) so it is strongly oxidising. (3) The sum of enthalpy of atomisation and ionisation enthalpies (IE_1 + IE_2) of Cu is not compensated by the hydration enthalpy of Cu^{2+}, so E° is positive (+0.34 V). (ii)(1) $2KMnO_4 \rightarrow K_2MnO_4 + MnO_2 + O_2$ (2) $Cr_2O_7^{2-} + 6I^- + 14H^+ \rightarrow 2Cr^{3+} + 3I_2 + 7H_2O$

Explanation:

(ii)(1) Check: K 2=2, Mn 2=2, O 8 = 4+2+2.

(ii)(2) Check: Cr 2, I 6, H 14, O 7; charge −2−6+14 = +6 = 2×(+3).

(i)(3): high atomisation enthalpy plus high IE_1+IE_2 outweigh the hydration enthalpy of Cu^{2+}, so Cu does not displace H_2 from acids and E° is positive.

OR

Q.33(b)

OR (b)(i) Out of Cu2Cl2 and CuCl2, which is more stable in aqueous solution and why? (b)(ii) Write the general electronic configuration of f-block elements. (b)(iii) Predict which of the following will be coloured in aqueous

solution and why? Sc^3+, Fe^3+, Zn^2+. [Atomic number: Sc=21, Fe=26, Zn=30] (b)(iv) How can you obtain potassium dichromate from sodium chromate? (b)(v) Why do transition metals and their compounds show catalytic activities?

Answer: (i) CuCl2 (Cu^2+) is more stable in aqueous solution than Cu2Cl2 (Cu^+). Cu^+ undergoes disproportionation in water: 2Cu^+(aq) --> Cu(s) + Cu^2+(aq). The greater hydration enthalpy of Cu^2+ (due to higher charge density) more than compensates for the higher ionisation enthalpy, making Cu^2+ thermodynamically more stable in aqueous solution. (ii) General electronic configuration of f-block elements: (n-2)f^1-14 (n-1)d^0-1 ns^2. (iii) Fe^3+ will be coloured (pale yellow/orange in aqueous solution); Sc^3+ and Zn^2+ are colourless. Sc^3+ has d^0 configuration (no d-electrons for d-d transition); Zn^2+ has d^10 configuration (all d-orbitals filled, no vacant d-orbital for electron to be excited to); Fe^3+ has d^5 configuration with unpaired electrons — d-d transitions possible → coloured. (iv) Sodium chromate to potassium dichromate: First, acidify Na2CrO4 with H2SO4: 2Na2CrO4 + H2SO4 --> Na2Cr2O7 + Na2SO4 + H2O. Then treat with KCl: Na2Cr2O7 + 2KCl --> K2Cr2O7 + 2NaCl (K2Cr2O7 is less soluble and crystallises out). (v) Transition metals and compounds show catalytic activity due to: (1) Variable oxidation states — can form intermediate compounds with reactants by changing oxidation state, providing alternative reaction pathways with lower activation energy; (2) Ability to adsorb reactants on their surfaces (for heterogeneous catalysis) — d-orbitals can bond with reactant molecules, weakening their bonds and facilitating reaction.

Explanation:

(i) Disproportionation of Cu^+: E°(Cu^2+/Cu^+) = +0.15V, E°(Cu^+/Cu) = +0.52V; since E°(Cu^+/Cu) > E°(Cu^2+/Cu^+), the disproportionation 2Cu^+ --> Cu + Cu^2+ is spontaneous (E°_cell = 0.52-0.15 = +0.37V > 0).

(ii) f-block: lanthanoids [Xe]4f^1-14 5d^0-1 6s^2; actinoids [Rn]5f^1-14 6d^0-1 7s^2. General: (n-2)f^0-14 (n-1)d^0-1 ns^2.

(iii) Colour requires partially filled d-orbitals AND d-d electronic transitions.

d^0 (Sc^3+) and d^10 (Zn^2+) — no d-d transition possible → colourless.
d^5 (Fe^3+) — d-d transition possible (though spin-forbidden, it still imparts faint colour) →
coloured.
(iv) 2Na2CrO4(yellow) + H2SO4 --> Na2Cr2O7(orange) + Na2SO4 + H2O;
then add KCl: Na2Cr2O7 + 2KCl --> K2Cr2O7↓ + 2NaCl.
(v) Variable oxidation states provide intermediate oxidation state pathways;
d-orbitals and empty orbitals facilitate adsorption of reactant molecules.