CBSE Class 12 Chemistry Question Paper 2022 with Solution PDF-Set 56-3-3

Question Paper with Solutions

Conducted by the Central Board of Secondary Education (CBSE)

Time Allowed: 2 hours **Maximum Marks: 35**

General Instructions

(i) This question paper contains **12** questions. **All** questions are compulsory.

(ii) This question paper is divided into **three** Sections – Section **A, B** and **C**.

(iii) **Section - A** Q. Nos. **1** to **3** are very short answer type questions carrying **2** marks each.

(iv) **Section - B** Q. Nos. **4** to **11** are short answer type questions carrying **3** marks each.

(v) **Section - C** Q. No. **12** is case based question carrying **5** marks.

(vi) Use of log tables and calculators is NOT allowed.

Section A (6 marks)

1. An Organic compound (A) with molecular formula C_3H_7NO on heating with Br_2 and KOH forms a compound (B). Compound (B) on heating with $CHCl_3$ and alcoholic KOH produces a foul smelling compound (C) and on reacting with $C_6H_5SO_2Cl$ forms a compound (D) which is soluble in alkali. Write the structures of (A), (B), (C) and (D). [2 marks]

Solution:

Concept:

- Hofmann bromamide degradation converts a primary amide $RCONH_2$ into a primary amine RNH_2, with one fewer carbon atom.
- The carbylamine reaction of a primary amine with chloroform and alcoholic KOH gives a foul-smelling isocyanide, RNC.
- A primary amine forms a sulphonamide with benzenesulphonyl chloride; its remaining N–H proton makes it soluble in alkali.

Step 1: Identify the amide and amine The reaction with Br_2/KOH identifies (A) as a primary amide. Its formula C_3H_7NO therefore gives propanamide, $CH_3CH_2CONH_2$. Removal of the carbonyl carbon produces ethanamine (B):

$$CH_3CH_2CONH_2 + Br_2 + 4KOH \longrightarrow CH_3CH_2NH_2 + 2KBr + K_2CO_3 + 2H_2O.$$

Step 2: Identify the carbylamine product Ethanamine is a primary amine, so it gives ethyl isocyanide (C) in the carbylamine test:

$$CH_3CH_2NH_2 + CHCl_3 + 3KOH \longrightarrow CH_3CH_2N{\equiv}C + 3KCl + 3H_2O.$$

The ethyl group is bonded to nitrogen in the product; writing CH_3CH_2CN would incorrectly give a nitrile.

Step 3: Identify the Hinsberg product With $C_6H_5SO_2Cl$, ethanamine gives the sulphonamide (D):

$$C_6H_5SO_2Cl + H_2NCH_2CH_3 \longrightarrow C_6H_5SO_2NHCH_2CH_3 + HCl.$$

The product retains an acidic N–H bond. Alkali removes this proton to form a soluble sulphonamide salt, agreeing with the observation.

Step 4: Conclusion The structures are (A) $CH_3CH_2CONH_2$, (B) $CH_3CH_2NH_2$, (C) $CH_3CH_2N{\equiv}C$, and (D) $C_6H_5SO_2NHCH_2CH_3$.

Quick Tip to Solve: Count one fewer carbon after Hofmann degradation, and attach the ethyl group to N, not C, in the isocyanide.

2. Write the products formed when benzaldehyde reacts with the following reagents (Any two):

(i) CH_3CHO in presence of dilute NaOH

(ii) H_2N-OH in presence of weak acid

(iii) Tollen's reagent [2 marks]

Solution:

Concept:

- Benzaldehyde has no α-hydrogen. In crossed aldol condensation, ethanal supplies the enolate and benzaldehyde supplies the carbonyl group that it attacks.
- Hydroxylamine converts an aldehyde into an oxime, $\mathrm{RCH=NOH}$, by condensation with loss of water.
- Tollens' reagent oxidises an aldehyde to a carboxylate ion in alkaline solution while silver(I) is reduced to metallic silver.

Step 1: Reaction with ethanal and dilute NaOH Ethanal, $\mathrm{CH_3CHO}$, has α-hydrogens and forms the enolate. It adds to benzaldehyde to give the crossed aldol addition product $\mathrm{C_6H_5CH(OH)CH_2CHO}$. Dehydration produces cinnamaldehyde, the crossed aldol condensation product:

$$\begin{aligned}&\mathrm{C_6H_5CHO + CH_3CHO}\\&\xrightarrow{\text{dil. NaOH}} \mathrm{C_6H_5CH(OH)CH_2CHO}\\&\xrightarrow{-\mathrm{H_2O}} \mathrm{C_6H_5CH=CHCHO.}\end{aligned}$$

The final product is 3-phenylprop-2-enal (cinnamaldehyde).

Step 2: Reaction with hydroxylamine In the presence of a weak acid, hydroxylamine reacts with the carbonyl group to form benzaldoxime:

$$\mathrm{C_6H_5CHO + H_2NOH \longrightarrow C_6H_5CH=NOH + H_2O.}$$

Thus the aldehyde's $\mathrm{C=O}$ group is converted into $\mathrm{C=N-OH}$.

Step 3: Reaction with Tollens' reagent The aldehyde group is oxidised, giving benzoate in the alkaline reaction mixture and depositing a silver mirror:

$$\begin{aligned}&\mathrm{C_6H_5CHO + 2[Ag(NH_3)_2]^+ + 3OH^-}\\&\longrightarrow \mathrm{C_6H_5COO^- + 2Ag + 4NH_3 + 2H_2O.}\end{aligned}$$

Acidification of the benzoate gives benzoic acid, $\mathrm{C_6H_5COOH}$.

Step 4: Conclusion The products are (i) cinnamaldehyde, $\mathrm{C_6H_5CH=CHCHO}$, through the aldol addition intermediate; (ii) benzaldoxime, $\mathrm{C_6H_5CH=NOH}$; and (iii) benzoate, giving benzoic acid on acidification, with metallic silver. Any two reactions may be written.

Quick Tip to Solve: Remember that ethanal supplies the alpha-hydrogens; benzaldehyde forms an oxime with hydroxylamine and is oxidised by Tollens' reagent.

3. The conductivity of 0.001 M acetic acid is 7.8×10^{-5} S cm^{-1}. Calculate its degree of dissociation if Λ°_m for acetic acid is 390 S cm^2 mol^{-1}. [2 marks]

Solution:

Concept:

- Molar conductivity is $\Lambda_m = \kappa \times 1000/c$ when conductivity κ is in $\mathrm{S\,cm^{-1}}$ and concentration c is in $\mathrm{mol\,L^{-1}}$.
- For a weak electrolyte, the degree of dissociation is $\alpha = \Lambda_m/\Lambda^\circ_m$, where Λ°_m is the molar conductivity at infinite dilution and represents complete dissociation.

Step 1: Calculate the molar conductivity The given concentration is $c = 0.001\,\mathrm{mol\,L^{-1}}$ and the conductivity is $\kappa = 7.8 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$. Convert concentration from a litre basis to a cubic-centimetre basis through the factor 1000:

$$\begin{aligned}\Lambda_m &= \frac{\kappa \times 1000}{c} \\ &= \frac{7.8 \times 10^{-5} \times 1000}{0.001} \\ &= 78\,\mathrm{S\,cm^2\,mol^{-1}}.\end{aligned}$$

Step 2: Find the fraction dissociated At infinite dilution the acid is fully dissociated, and the given limiting molar conductivity is $390\,\mathrm{S\,cm^2\,mol^{-1}}$. Therefore,

$$\alpha = \frac{\Lambda_m}{\Lambda^\circ_m} = \frac{78}{390} = 0.20.$$

The conductivity units cancel, so α is dimensionless. Multiplying this fraction by 100 gives the percentage dissociation.

Step 3: Conclusion The degree of dissociation of acetic acid is $\boxed{\alpha = 0.20}$, corresponding to $\boxed{20\%}$ dissociation.

Quick Tip to Solve: Include the factor 1000 when concentration is in mol per litre and conductivity is in S per centimetre; then take the ratio to 390.

Section B (24 marks)

4. (i) Why are melting points of transition metals high?

(ii) Why the transition metals generally form coloured compounds?

(iii) Why E° value for Mn^{3+}/Mn^{2+} couple is highly positive? [3 marks]

Solution:

Concept:

- Metallic bonding depends on the number of electrons available for bonding. In transition metals, both outer ns and $(n-1)d$ electrons can contribute to strong metal-metal bonding.
- In a ligand field, the five d-orbitals split into groups of different energies. Absorption of visible light can promote an electron between these groups; the complementary colour is observed.

Quick Tip to Solve: For manganese reduction potentials, write the two ionic d-electron counts first: reduction from d4 to the stable half-filled d5 configuration explains the positive potential.

- A positive standard reduction potential E° indicates a favourable reduction relative to the standard hydrogen electrode. A half-filled d^5 configuration has extra stability.

Step 1: (i) Explain the high melting points Transition metals generally have several unpaired d-electrons in addition to their outer s-electrons available for metallic bonding. Participation of these electrons produces strong interatomic metallic bonds and high enthalpies of atomisation. A large amount of thermal energy is therefore required to overcome these bonds, so their melting points are generally high. The strength varies across the series with the number of electrons participating in bonding.

Step 2: (ii) Explain the colour of their compounds Most transition-metal ions have incompletely filled d-orbitals. The surrounding ligands split these orbitals into lower- and higher-energy sets. An electron absorbs a suitable wavelength of visible light and undergoes a d-d transition from a lower level to a higher level. The remaining transmitted or reflected light gives the compound its characteristic complementary colour. Ions with d^0 or d^{10} configurations cannot undergo such transitions and are usually colourless when no other colour-producing mechanism operates.

Step 3: (iii) Compare the manganese ion configurations Manganese has the configurations

$$\mathrm{Mn^{3+}} : [\mathrm{Ar}]\, 3d^4, \qquad \mathrm{Mn^{2+}} : [\mathrm{Ar}]\, 3d^5.$$

The reduction is

$$\mathrm{Mn^{3+}} + \mathrm{e^-} \longrightarrow \mathrm{Mn^{2+}}.$$

It converts the d^4 ion into the particularly stable half-filled d^5 ion. Thus $\mathrm{Mn^{3+}}$ readily accepts an electron to form $\mathrm{Mn^{2+}}$, accounting for the highly positive standard reduction potential of this couple.

Step 4: Conclusion (i) Strong metallic bonding gives high melting points. (ii) Absorption of visible light for d-d transitions generally gives coloured compounds. (iii) Reduction of $\mathrm{Mn^{3+}}$ produces the stable half-filled d^5 configuration of $\mathrm{Mn^{2+}}$, making E° highly positive.

Quick Tip to Solve: For manganese reduction potentials, write the two ionic d-electron counts first: reduction from d4 to the stable half-filled d5 configuration explains the positive potential.

5(a). (i) Which acid of the following pair would you expect to be stronger?

F-CH_2-COOH or CH_3-COOH

(ii) Arrange the following compounds in increasing order of their boiling points:

CH_3CH_2OH, CH_3-CHO, CH_3-COOH

(iii) Give simple chemical test to distinguish between Benzaldehyde and Acetophenone. [3 marks]

Solution:

Concept:

- A carboxylic acid is stronger when its conjugate carboxylate ion is more stable. Electron-withdrawing groups exert a negative inductive effect ($-I$) and stabilise negative charge.
- Boiling point increases with the strength of intermolecular attractions. Alcohols form hydrogen bonds, while carboxylic acids form strongly hydrogen-bonded dimers.

Quick Tip to Solve: Compare acid strength through conjugate-base stability; for this boiling-point trio, rank dipole attractions, alcohol hydrogen bonds, and acid dimer formation in that order.

- Tollens' reagent is ammoniacal silver nitrate, containing $[Ag(NH_3)_2]^+$. Aldehydes reduce it to metallic silver; ordinary ketones do not.

Step 1: (i) Compare the strengths of the two acids Fluoroacetic acid, FCH_2COOH, is stronger than ethanoic acid, CH_3COOH. The highly electronegative fluorine atom withdraws electron density through the sigma bonds by its $-I$ effect. It stabilises the negative charge on the conjugate base FCH_2COO^-, favouring dissociation of the acid. The methyl group in ethanoic acid instead has an electron-releasing $+I$ effect, which makes its carboxylate ion relatively less stable. Hence fluorine substitution increases acid strength.

Step 2: (ii) Arrange the boiling points using intermolecular forces The increasing order is

$$CH_3CHO < CH_3CH_2OH < CH_3COOH.$$

Ethanal has dipole-dipole attractions but lacks an $O-H$ bond and therefore cannot form hydrogen bonds between its own molecules. Ethanol contains an $O-H$ group and forms intermolecular hydrogen bonds, so it boils at a higher temperature. Ethanoic acid forms dimers held by two hydrogen bonds, giving stronger intermolecular association and the highest boiling point among the three compounds.

Step 3: (iii) Distinguish benzaldehyde from acetophenone Add freshly prepared Tollens' reagent to separate samples and warm gently in a water bath. Benzaldehyde, C_6H_5CHO, gives a silver mirror on the inner wall of the test tube because its aldehyde group reduces silver(I) to metallic silver. Acetophenone, $C_6H_5COCH_3$, gives no silver mirror because it is a ketone. The benzaldehyde reaction in alkaline medium is

$$C_6H_5CHO + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow C_6H_5COO^- + 2Ag + 4NH_3 + 2H_2O.$$

Thus the positive silver-mirror test identifies benzaldehyde.

Step 4: Conclusion (i) FCH_2COOH is the stronger acid. (ii) Boiling points increase as $CH_3CHO < CH_3CH_2OH < CH_3COOH$. (iii) Tollens' reagent gives a silver mirror with benzaldehyde and no silver mirror with acetophenone.

Quick Tip to Solve: Compare acid strength through conjugate-base stability; for this boiling-point trio, rank dipole attractions, alcohol hydrogen bonds, and acid dimer formation in that order.

OR

5(b). (i) Which will undergo faster nucleophilic addition reaction? Acetaldehyde or Propanone
(ii) What is the composition of Fehling's reagent?
(iii) Draw structure of the semicarbazone of Ethanal. [3 marks]

Solution:

Concept:

- Nucleophiles attack the electron-deficient carbonyl carbon. Electron-donating alkyl groups reduce its positive character, while bulky groups hinder the approaching nucleophile.
- Fehling's reagent is prepared by mixing equal volumes of Fehling's solutions A and B freshly before use; the alkaline tartrate complex keeps copper(II) in solution.
- Semicarbazide, $H_2N{-}NH{-}CO{-}NH_2$, condenses with an aldehyde or ketone through its terminal amino group, replacing $C{=}O$ by $C{=}N{-}NH{-}CO{-}NH_2$.

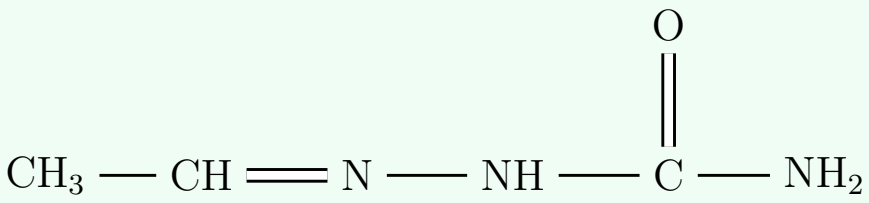
Step 1: (i) Compare the carbonyl groups Acetaldehyde is CH_3CHO, whereas propanone is CH_3COCH_3. Acetaldehyde has only one electron-donating methyl group attached to the carbonyl carbon, while propanone has two. Thus the positive charge on the carbonyl carbon is reduced more in propanone by the $+I$ effect. In addition, acetaldehyde has a small hydrogen atom in place of propanone's second methyl group, so the nucleophile experiences less steric hindrance. Both electronic and steric factors therefore favour faster nucleophilic addition to acetaldehyde.

Step 2: (ii) State the two components of Fehling's reagent Fehling's solution A is aqueous copper(II) sulphate, $CuSO_4$. Fehling's solution B is an alkaline solution of sodium potassium tartrate (Rochelle salt) containing sodium hydroxide. Fresh mixing of A and B produces the deep-blue copper(II)-tartrate reagent. The tartrate complexes copper(II), preventing its precipitation as copper(II) hydroxide in the alkaline medium.

Step 3: (iii) Form the semicarbazone of ethanal The terminal $-NH_2$ group of semicarbazide reacts with ethanal's carbonyl group, followed by elimination of water:

$$CH_3CHO + H_2N{-}NH{-}CO{-}NH_2 \longrightarrow CH_3CH{=}N{-}NH{-}CO{-}NH_2 + H_2O.$$

The carbonyl-derived carbon retains its methyl group and hydrogen. The original $-CO{-}NH_2$ group of semicarbazide remains intact, as shown in the structure below.



Structural formula of ethanal semicarbazone

Step 4: Conclusion (i) Acetaldehyde undergoes faster nucleophilic addition. (ii) Fehling's reagent contains aqueous copper(II) sulphate mixed freshly with alkaline sodium potassium tartrate solution. (iii) Ethanal semicarbazone is $CH_3CH{=}N{-}NH{-}C(=O){-}NH_2$.

Quick Tip to Solve: For semicarbazones, replace only the aldehyde C=O by C=N-NH-CO-NH2; retain the semicarbazide carbonyl group.

6. Give reasons:

(i) Ammonolysis of alkyl halides is not a good method to prepare pure primary amines.

(ii) Aniline does not give Friedel-Crafts reaction.

(iii) Although –NH_2 group is o/p directing in electrophilic substitution reactions, yet aniline on nitration gives good yield of m-nitroaniline. [3 marks]

Solution:

Concept:

- In ammonolysis, ammonia acts as a nucleophile towards an alkyl halide. The amine produced also has a nitrogen lone pair and can undergo further alkylation.
- The nitrogen lone pair in aniline normally activates its ring and directs electrophilic substitution to the ortho and para positions.
- A Lewis acid such as $AlCl_3$ binds the nitrogen lone pair; a strong acid protonates it to form $C_6H_5NH_3^+$. These interactions remove the lone pair's activating effect on the benzene ring.

Step 1: (i) Further alkylation prevents a pure primary amine Ammonolysis first produces a primary amine: $RX + 2NH_3 \longrightarrow RNH_2 + NH_4X$. The primary amine still contains a nitrogen lone pair and can attack another molecule of alkyl halide. Successive alkylation gives secondary and tertiary amines and finally a quaternary ammonium salt:

$$RNH_2 \longrightarrow R_2NH \longrightarrow R_3N \longrightarrow R_4N^+X^-.$$

Hence a difficult-to-separate mixture results. Excess ammonia favours the primary amine, but does not make ammonolysis a good general method for obtaining it pure.

Step 2: (ii) The Friedel–Crafts catalyst binds aniline Friedel–Crafts alkylation or acylation requires a Lewis acid catalyst such as anhydrous $AlCl_3$. Aniline's basic amino group coordinates strongly to this catalyst through its nitrogen lone pair: $C_6H_5NH_2 + AlCl_3 \longrightarrow C_6H_5NH_2 \rightarrow AlCl_3$. The complex has positive character on nitrogen and deactivates the ring. Its nitrogen lone pair cannot activate the ring by resonance, and the amino group ties up the catalyst. Thus the usual Friedel–Crafts reaction fails.

Step 3: (iii) Nitrating acid converts aniline into a meta-directing ion In the strongly acidic nitrating mixture of concentrated nitric and sulphuric acids, aniline is protonated:

$$C_6H_5NH_2 + H^+ \rightleftharpoons C_6H_5NH_3^+.$$

The electron-withdrawing $-NH_3^+$ group has no free nitrogen lone pair to donate into the ring and is deactivating and meta directing. Ortho/para attack creates especially unstable resonance contributors with positive charge close to the positively charged nitrogen; meta attack avoids this. Consequently, direct nitration gives a good yield of meta-nitroaniline although free aniline is ortho/para directing.

Step 4: Conclusion (i) Repeated alkylation gives a mixture of primary, secondary and tertiary amines and quaternary ammonium salts. (ii) Aniline binds $AlCl_3$, deactivating its ring towards Friedel–Crafts reaction. (iii) Nitration protonates aniline to the meta-directing anilinium ion, giving a good yield of meta-nitroaniline.

Quick Tip to Solve: Before predicting aniline's directing effect, check the medium: free -NH2 directs ortho/para, while protonated -NH3+ directs meta.

7(a). What happens when

(i) Propanone is treated with CH_3MgBr and then hydrolysed?

(ii) Ethanal is treated with excess ethanol and acid?

(iii) Methanal undergoes Cannizzaro reaction? [3 marks]

Solution:

Concept:

- A Grignard reagent adds its alkyl group to the electrophilic carbonyl carbon. Hydrolysis of the magnesium alkoxide gives an alcohol; addition to a ketone gives a tertiary alcohol.
- An aldehyde reacts with excess alcohol in the presence of acid to form an acetal. Two alkoxy groups replace the carbonyl oxygen, with elimination of water.
- An aldehyde without an alpha hydrogen undergoes the Cannizzaro reaction in concentrated alkali: one molecule is oxidised to a carboxylate and another is reduced to an alcohol.

Step 1: Add methylmagnesium bromide to propanone In part (i), the methyl group from CH_3MgBr forms a new carbon-carbon bond with the carbonyl carbon of propanone. The resulting alkoxide has three methyl groups attached to that carbon. Hydrolysis then protonates its oxygen:

$$CH_3COCH_3 + CH_3MgBr \longrightarrow (CH_3)_3COMgBr$$

$$(CH_3)_3COMgBr + H_2O \longrightarrow (CH_3)_3COH + Mg(OH)Br.$$

This is a nucleophilic addition followed by hydrolysis; the original three-carbon ketone gains one carbon from the reagent.

Step 2: Form the acetal of ethanal In part (ii), acid catalyses the addition of ethanol to ethanal. A hemiacetal is formed first; with excess ethanol, the hydroxyl group on that carbon is replaced by a second ethoxy group, forming the acetal:

$$CH_3CHO + 2\,C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3CH(OC_2H_5)_2 + H_2O.$$

Excess ethanol favours the acetal, rather than stopping at the hemiacetal. The aldehydic hydrogen remains attached to the same carbon.

Step 3: Disproportionate methanal in concentrated alkali In part (iii), methanal has no alpha hydrogen and therefore undergoes Cannizzaro disproportionation. Of two methanal molecules, one is reduced to methanol and the other is oxidised to methanoate. Using concentrated sodium hydroxide, the balanced equation is

$$2\,HCHO + NaOH \longrightarrow HCOONa + CH_3OH.$$

Under the alkaline reaction conditions the oxidised product is a salt, sodium methanoate, rather than free methanoic acid.

Step 4: Conclusion (i) Propanone gives 2-methylpropan-2-ol, $(CH_3)_3COH$. (ii) Ethanal gives its diethyl acetal, 1,1-diethoxyethane, $CH_3CH(OC_2H_5)_2$. (iii) Methanal gives methanol and a methanoate salt, for example CH_3OH and $HCOONa$ with concentrated $NaOH$.

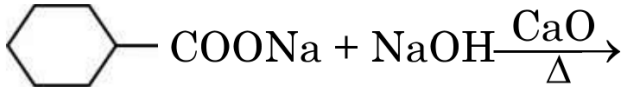
Quick Tip to Solve: Track the carbonyl carbon: Grignard addition adds a methyl group, excess ethanol installs two ethoxy groups, and Cannizzaro converts two methanal molecules into one alcohol and one carboxylate.

OR

7(b). Write the main product in the following reactions:

(i) $2\,CH_3COCl + (CH_3)_2Cd \longrightarrow$

(ii) $CH_3CH_2CHO \xrightarrow{Zn(Hg)/Conc\cdot HCl}$ [3 marks]

(iii) 

Solution:

Concept:

- Dialkylcadmium reacts with acyl chlorides to form ketones. Each alkyl group replaces the chlorine of an acyl chloride, without further addition to the ketone product.
- Clemmensen reduction uses amalgamated zinc and concentrated hydrochloric acid to reduce an aldehyde or ketone carbonyl group to a methylene group.
- Heating a sodium carboxylate with soda lime, $NaOH$ mixed with CaO, removes the carboxyl group. The resulting hydrocarbon has one carbon fewer than the carboxylate.

Step 1: Replace the acyl chloride chlorine with methyl In part (i), each methyl group of dimethylcadmium reacts with one molecule of ethanoyl chloride. The carbonyl group remains intact, and the incoming methyl group attaches to its carbon:

$$2\,CH_3COCl + (CH_3)_2Cd \longrightarrow 2\,CH_3COCH_3 + CdCl_2.$$

Both methyl groups therefore produce the same ketone. The mild reagent does not add further to this ketone.

Step 2: Reduce the aldehyde group of propanal In part (ii), $Zn(Hg)$ with concentrated HCl is the reagent combination for Clemmensen reduction. The terminal $-CHO$ group becomes $-CH_3$; the carbon skeleton is retained:

$$CH_3CH_2CHO + 4\,[H] \xrightarrow{Zn(Hg)/conc\cdot HCl} CH_3CH_2CH_3 + H_2O.$$

Here $[H]$ denotes reducing hydrogen equivalents; reduction gives the hydrocarbon.

Step 3: Decarboxylate the cyclohexanecarboxylate salt In part (iii), the saturated ring carries a $-COONa$ substituent: sodium cyclohexanecarboxylate, $C_6H_{11}COONa$. Soda lime removes its carboxyl carbon as carbonate and replaces the substituent by hydrogen:

$$C_6H_{11}COONa + NaOH \xrightarrow[\Delta]{CaO} C_6H_{12} + Na_2CO_3.$$

The saturated ring is retained; only the external carboxyl carbon is lost.

Step 4: Conclusion The main products are (i) propanone, CH_3COCH_3; (ii) propane, $CH_3CH_2CH_3$; and (iii) cyclohexane, C_6H_{12}.

Quick Tip to Solve: Keep the carbonyl for dialkylcadmium, remove its oxygen for Clemmensen reduction, and remove the entire external carboxyl carbon for soda-lime decarboxylation while preserving the ring.

8(a). Differentiate between the following:

(i) Adsorption and Absorption

(ii) Lyophobic Sol and Lyophilic Sol

(iii) Multimolecular Colloid and Macromolecular colloid. [3 marks]

Solution:

Concept:

- Adsorption is the accumulation of a substance at a surface, whereas absorption involves its entry into the bulk of another substance.
- The affinity of the dispersed phase for the dispersion medium determines whether a sol is lyophilic or lyophobic.
- A colloidal particle may be an aggregate of many small species or a single large molecule whose size lies in the colloidal range.

Step 1: (i) Compare adsorption and absorption In adsorption, the adsorbate is concentrated on the surface of the adsorbent; its concentration at the surface is greater than in the bulk. For example, charcoal adsorbs gases on its surface. In absorption, the substance penetrates throughout the bulk of the absorbing material, for example, water taken up by a sponge. Thus adsorption is a surface phenomenon, while absorption is a bulk phenomenon.

Step 2: (ii) Compare lyophobic and lyophilic sols A lyophobic sol has little affinity between its dispersed phase and dispersion medium. It is relatively unstable and is readily coagulated by a small amount of electrolyte; it is generally irreversible. Gold sol is an example. A lyophilic sol has strong affinity between the dispersed phase and medium, with the particles strongly solvated. It is relatively stable, needs a much larger amount of electrolyte for coagulation, and is reversible. Starch sol in water is an example. Reversibility means that the sol can be formed again by adding the dispersion medium to the separated dispersed phase.

Step 3: (iii) Compare multimolecular and macromolecular colloids In a multimolecular colloid, many atoms or small molecules aggregate to form a colloidal particle. The individual atoms or molecules are smaller than colloidal dimensions, but their aggregate is colloidal in size; gold sol and sulphur sol are examples. In a macromolecular colloid, each particle is a single giant molecule with colloidal dimensions, rather than an aggregate of small molecules. Starch and proteins are examples of macromolecular substances that form colloidal solutions in a suitable medium.

Step 4: Conclusion Adsorption occurs at a surface and absorption in the bulk; lyophobic sols have little affinity for the medium and lyophilic sols have strong affinity; multimolecular particles are aggregates, whereas macromolecular particles are individual giant molecules.

Quick Tip to Solve: Compare the location of uptake, affinity for the medium and composition of one colloidal particle, respectively, and give an example for each side.

OR

8(b). (I) Define the following terms:

(i) Zeta Potential

(ii) Coagulation

(II) Why a negatively charged sol is obtained when $AgNO_3$ solution is added to KI solution? [3 marks]

Solution:

Concept:

- Preferential adsorption of ions gives colloidal particles an electric charge. The charged surface attracts oppositely charged ions, producing an electrical double layer.
- Like-charged colloidal particles repel one another. Removing their charge allows aggregation and coagulation.
- Silver iodide particles preferentially adsorb an ion common to their composition; the ion present in excess determines the sign of the sol.

Step 1: (I)(i) Define zeta potential Zeta potential, or electrokinetic potential, is the potential difference between the fixed ionic layer attached to a colloidal particle and the diffuse layer of counter-ions in the dispersion medium. The fixed layer moves with the particle, whereas ions farther away belong to the surrounding liquid. This potential is associated with the electrical double layer and helps account for the repulsion between similarly charged colloidal particles and hence their stability.

Step 2: (I)(ii) Define coagulation Coagulation is the aggregation and precipitation of colloidal particles, usually following neutralisation of their electric charge. For example, an added electrolyte supplies counter-ions that reduce or neutralise the particle charge. Once electrostatic repulsion is sufficiently reduced, the particles come together into larger aggregates, which separate from the dispersion medium. Coagulation is also called flocculation.

Step 3: (II) Explain the negative charge on silver iodide sol When silver nitrate solution is added to potassium iodide solution, silver iodide is formed:

$$\mathrm{AgNO_3(aq) + KI(aq) \longrightarrow AgI + KNO_3(aq).}$$

Since silver nitrate is added to the potassium iodide solution, iodide ions are available in excess in the medium during formation of the sol. The freshly formed AgI particles preferentially adsorb $\mathrm{I^-}$, an ion common to silver iodide, on their surfaces. Consequently the particles acquire a negative charge, conventionally represented as $\mathrm{AgI : I^-}$. Potassium ions act as counter-ions in the surrounding medium; they do not determine the negative sign of the particle charge.

Step 4: Conclusion Zeta potential is the potential difference between the fixed and diffuse ionic layers; coagulation is aggregation and precipitation of colloidal particles. The silver iodide sol is negatively charged because its particles adsorb excess $\mathrm{I^-}$ ions from the potassium iodide solution.

Quick Tip to Solve: For a silver halide sol, identify which common ion is in excess: adsorption of excess iodide gives a negative sol, while excess silver ions give a positive sol.

9. Define transition metals. Why Zn, Cd and Hg are not called transition metals? How is the variability in oxidation states of transition metals different from that of p-block elements? [3 marks]

Solution:

Concept:

- A transition element has a partially filled d subshell in its atom or in at least one of its usual oxidation states.
- In transition metals, the energies of the $(n-1)d$ and ns orbitals are close, so electrons from both subshells can participate in bonding.
- Variable oxidation states of typical transition metals often differ by one; those of typical p-block elements commonly differ by two.

Step 1: State the definition of a transition metal A transition metal is an element whose atom has an incompletely filled d subshell, or which forms cations having an incompletely filled d subshell. Thus, membership of the d-block alone does not establish that an element is a transition metal; the electronic configurations must also satisfy this condition.

Step 2: Examine the configurations of zinc, cadmium and mercury The relevant outer configurations of the atoms are

$$\begin{aligned} \text{Zn}: &\quad 3d^{10}4s^2, \\ \text{Cd}: &\quad 4d^{10}5s^2, \\ \text{Hg}: &\quad 5d^{10}6s^2. \end{aligned}$$

On forming their usual $+2$ ions, the two ns electrons are removed, leaving $3d^{10}$, $4d^{10}$ and $5d^{10}$, respectively. Both their atoms and usual ions therefore have completely filled d subshells, rather than partially filled ones. Consequently, Zn, Cd and Hg are not classified as transition metals.

Step 3: Compare the patterns of variable oxidation states Transition metals commonly show successive oxidation states differing by one unit, since different numbers of ns and $(n-1)d$ electrons can participate in bonding. For example, manganese shows $+2, +3, +4, +5, +6$ and $+7$ oxidation states.

Typical variable oxidation states of p-block elements differ by two units. Examples are $+3$ and $+5$ for phosphorus and $+2$ and $+4$ for tin. The two-unit difference corresponds to participation or non-participation of the outer ns^2 electron pair, whereas transition-metal variability involves different numbers of closely spaced s and d electrons.

Step 4: Conclusion Transition metals have a partially filled d subshell in their atoms or usual ions. Zn, Cd and Hg do not satisfy this condition because their d subshells remain full. Transition-metal oxidation states commonly differ by one unit, while typical variable p-block oxidation states differ by two.

Quick Tip to Solve: Test both the atom and its usual ions for a partially filled d subshell; a d-block position alone is insufficient. Use manganese and tin to remember the one-unit and two-unit patterns.

10. (a) Using valence bond theory, predict the hybridization and magnetic character of the complex: $[Ni(CO)_4]$ (Atomic number: Ni = 28)

(b) Write IUPAC name of $[Pt(NH_3)_2Cl(NO_2)]$.

(c) Why $[Co(en)_3]^{3+}$ is a more stable complex than $[Co(NH_3)_6]^{3+}$? [3 marks]

Solution:

Concept:

- Valence bond theory predicts hybridisation from the vacant metal orbitals used for ligand donation; unpaired electrons determine magnetic character.
- In naming a coordination entity, list ligands alphabetically and write the metal oxidation state in Roman numerals.
- Chelating ligands bind through two or more donor atoms and form rings; this produces the chelate effect and increases complex stability.

Step 1: Determine the hybridisation and magnetism of the nickel complex (a) In $[Ni(CO)_4]$, each CO ligand is neutral, so nickel has oxidation state zero. Nickel $(Z = 28)$ has the free-atom configuration $[Ar]3d^8 4s^2$. In the valence-bond description of the complex, the strong-field CO ligands cause rearrangement and pairing to give a filled $3d^{10}$ subshell, leaving the $4s$ and $4p$ orbitals vacant.

One $4s$ and three $4p$ orbitals hybridise to form four equivalent sp^3 hybrid orbitals. Each accepts a lone pair from a carbonyl ligand, giving a tetrahedral complex. The ten $3d$ electrons are all paired; hence there are no unpaired electrons and the complex is diamagnetic.

Step 2: Name the platinum coordination entity (b) For $[Pt(NH_3)_2Cl(NO_2)]$, ammonia is neutral, while chlorido and nitrito ligands each have charge -1. Since the complex is neutral, the oxidation state x of platinum satisfies

$$x + 2(0) - 1 - 1 = 0, \qquad x = +2.$$

The ligand names are ammine, chlorido and nitrito-N, listed alphabetically without using the multiplicative prefix di to decide order. The written NO_2 group represents nitrogen coordination, so the linkage is specified as nitrito-N. The metal in this neutral entity is named platinum, followed by (II).

Step 3: Explain the greater stability of the ethylenediamine complex (c) Ethylenediamine, en, is a bidentate ligand: its two nitrogen donor atoms bind to the same cobalt ion, forming a five-membered chelate ring. Three en ligands form three such rings in $[Co(en)_3]^{3+}$. By contrast, each NH_3 ligand in $[Co(NH_3)_6]^{3+}$ is monodentate and forms no chelate ring.

The ring-forming bidentate ligands give extra stability through the chelate effect. Displacement by three en molecules releases six ammonia molecules, giving a favourable increase in the number of free ligand molecules and an entropy contribution to stability. Thus the ethylenediamine complex is more stable even though both complexes have six nitrogen donor atoms around cobalt.

Step 4: Conclusion (a) $[Ni(CO)_4]$ has sp^3 hybridisation, tetrahedral geometry and diamagnetic character. (b) The IUPAC name is diamminechloridonitrito-N-platinum(II). (c) $[Co(en)_3]^{3+}$ is more stable because its bidentate ligands form three chelate rings, producing the chelate effect.

Quick Tip to Solve: For nickel carbonyl, first note that CO is neutral, so nickel is in oxidation state zero. For stability, count chelate rings rather than merely counting donor atoms.

11(a). Calculate $\Delta_r G^\circ$ and log K_c for the following cell:

$Ni(s) + 2\,Ag^+(aq) \rightarrow Ni^{2+}(aq) + 2Ag(s)$

Given that $E^\circ_{cell} = 1.05$ V, 1F = 96,500 C mol^{-1}. [3 marks]

Solution:

Concept:

- The standard Gibbs energy change is related to the standard cell potential by $\Delta_r G^\circ = -nFE^\circ_{\text{cell}}$, where n is the number of electrons transferred and F is the Faraday constant.
- At equilibrium, $\Delta_r G^\circ = -RT\ln K_c$. Combining these relations gives $E^\circ_{\text{cell}} = \dfrac{0.0591}{n}\log K_c$ at 298 K, where the logarithm is to base ten.

Step 1: Determine the electron transfer Nickel is oxidised and silver ions are reduced. The balanced half-reactions are

$$\mathrm{Ni(s)} \longrightarrow \mathrm{Ni^{2+}(aq)} + 2e^-,$$
$$2\mathrm{Ag^+(aq)} + 2e^- \longrightarrow 2\mathrm{Ag(s)}.$$

Thus, two electrons are transferred for the reaction as written, so $n = 2$. The electron number comes from the oxidation-state change of nickel, from zero to $+2$; the stoichiometric coefficient of silver agrees with it.

Step 2: Calculate the standard Gibbs energy change Substitute $n = 2$, $F = 96{,}500\,\mathrm{C\,mol^{-1}}$ and $E^\circ_{\text{cell}} = 1.05\,\mathrm{V}$:

$$\begin{aligned}\Delta_r G^\circ &= -2 \times 96{,}500 \times 1.05 \\ &= -202{,}650\,\mathrm{J\,mol^{-1}}.\end{aligned}$$

The units follow because $1\,\mathrm{C} \times 1\,\mathrm{V} = 1\,\mathrm{J}$. A positive standard cell potential therefore gives a negative standard Gibbs energy change, indicating that the forward reaction is thermodynamically favourable under standard conditions.

Step 3: Calculate the equilibrium logarithm Using the standard room-temperature relation at 298 K,

$$\log K_c = \frac{nE^\circ_{\text{cell}}}{0.0591} = \frac{2 \times 1.05}{0.0591} = 35.53.$$

The large positive logarithm indicates a very large equilibrium constant, consistent with the negative standard Gibbs energy change and the strong tendency to form nickel ions and silver metal.

Step 4: Conclusion $\boxed{\Delta_r G^\circ = -202.65\,\mathrm{kJ\,mol^{-1}}}$ and, at 298 K, $\boxed{\log K_c \approx 35.53}$.

Quick Tip to Solve: First obtain $n = 2$ from nickel's oxidation-state change; use the same n in both the Gibbs energy and equilibrium-constant formulae.

OR

11(b). Calculate the e.m.f. of the following cell at 298 K:

Fe(s) | Fe^{2+} (0.001 M) || H^+ (0.01 M) | H_2(g) (1 bar) | Pt(s)

Given that E°_{cell} = +0.44 V

[log 2 = 0.3010, log 3 = 0.4771, log 10 = 1] [3 marks]

Solution:

Concept:

- In cell notation, the left electrode is the anode and the right electrode is the cathode. Iron loses electrons, while hydrogen ions gain electrons to form hydrogen gas.
- At 298 K, the Nernst equation is $E_{\text{cell}} = E^\circ_{\text{cell}} - \dfrac{0.0591}{n}\log Q$, where n is the electron number and Q is the reaction quotient. Pure solids have unit activity.

Step 1: Write the cell reaction The oxidation and reduction half-reactions are

$$\begin{aligned} \mathrm{Fe(s)} &\longrightarrow \mathrm{Fe^{2+}(aq)} + 2e^-, \\ \mathrm{2H^+(aq)} + 2e^- &\longrightarrow \mathrm{H_2(g)}. \end{aligned}$$

Adding them gives $\mathrm{Fe(s)} + \mathrm{2H^+(aq)} \longrightarrow \mathrm{Fe^{2+}(aq)} + \mathrm{H_2(g)}$. Hence $n = 2$. Platinum provides an inert conducting surface for the hydrogen electrode and does not enter the reaction quotient.

Step 2: Evaluate the reaction quotient Using concentrations relative to 1 M and gas pressure relative to 1 bar, the reaction quotient is

$$Q = \frac{[\mathrm{Fe^{2+}}](p_{\mathrm{H_2}}/p^\circ)}{[\mathrm{H^+}]^2} = \frac{0.001 \times 1}{(0.01)^2} = 10.$$

The concentration of hydrogen ions is squared because their coefficient in the balanced reaction is two. Iron is omitted because it is a pure solid, and hydrogen has unit pressure ratio here. Therefore $\log Q = \log 10 = 1$; the supplied values of $\log 2$ and $\log 3$ are not needed.

Step 3: Substitute in the Nernst equation With $E^\circ_{\text{cell}} = +0.44\,\text{V}$,

$$\begin{aligned} E_{\text{cell}} &= 0.44 - \frac{0.0591}{2} \times 1 \\ &= 0.44 - 0.02955 \\ &= 0.41045\,\text{V}. \end{aligned}$$

Since $Q > 1$, the logarithmic correction is positive and is subtracted from the standard potential. Thus the calculated emf must be smaller than 0.44 V, providing a useful sign check.

Step 4: Conclusion The emf of the cell at 298 K is $\boxed{E_{\text{cell}} = 0.41045\,\text{V} \approx 0.410\,\text{V}}$.

Quick Tip to Solve: Balance the cell reaction before forming Q: the two hydrogen ions give $[\mathrm{H^+}]^2$, so $Q = 10$ and the emf falls below 0.44 V.

Section C (5 marks)

12. Read the following passage and answer the questions that follow:

The rate of reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. It can be expressed as instantaneous rate at a particular instant of time and average rate over a large interval of time. A number of factors such as temperature, concentration of reactants, catalyst affect the rate of reaction. Mathematical representation of rate of a reaction is given by rate law:

$$\textbf{Rate} = k[A]^x[B]^y$$

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of $x + y$ gives the overall order of a reaction.

When a sequence of elementary reactions gives us the products, the reactions are called complex reactions. Molecularity and order of an elementary reaction are same. Zero order reactions are relatively uncommon but they occur under special conditions. All natural and artificial radioactive decay of unstable nuclei take place by first order kinetics. [5 marks]

12(a). What is the effect of temperature on the rate constant of a reaction? [1 mark]

Solution:

Concept:

- The Arrhenius equation is $k = Ae^{-E_a/(RT)}$, where k is the rate constant, A is the frequency factor, E_a is activation energy, R is the gas constant and T is absolute temperature.
- For a reaction with positive activation energy, increasing temperature increases the fraction of collisions having sufficient energy to react.

Step 1: Apply the temperature dependence On raising T, the magnitude of the negative exponent $-E_a/(RT)$ decreases. The exponential factor therefore increases, so the rate constant increases.

Step 2: State the usual experimental trend For many reactions, the rate constant becomes approximately two to three times its initial value for a temperature rise of $10\,\text{K}$. This is a useful approximate trend; the exact change depends on the activation energy.

Step 3: Conclusion The rate constant generally increases with an increase in temperature, according to the Arrhenius equation.

Quick Tip to Solve: Use absolute temperature in the Arrhenius equation; a higher temperature makes the negative exponent smaller in magnitude.

12(b). For a reaction $\text{A} + \text{B} \longrightarrow \text{Product}$, the rate law is given by, Rate $= k[A]^2[B]^{1/2}$. What is the order of the reaction? [1 mark]

Solution:

Concept:

- For a rate law Rate $= k[A]^x[B]^y$, the overall order is the sum $x + y$ of the concentration exponents.

Quick Tip to Solve: Add the powers in the rate law, including fractional powers; do not substitute the stoichiometric coefficients.

- Order is determined from the experimentally obtained rate law. It can be an integer, zero or a fraction.

Step 1: Read the individual orders In the given rate law Rate $= k[A]^2[B]^{1/2}$, the order with respect to A is 2, and the order with respect to B is $1/2$. These exponents show how the rate depends on each reactant concentration.

Step 2: Add the exponents The overall order is therefore

$$n = 2 + \frac{1}{2} = \frac{5}{2} = 2.5.$$

Do not add the coefficients in the equation $\mathrm{A^+B} \longrightarrow \mathrm{Product}$: its coefficients do not determine the order of a general reaction.

Step 3: Conclusion The overall order of the reaction is $\boxed{5/2}$, or 2.5.

Quick Tip to Solve: Add the powers in the rate law, including fractional powers; do not substitute the stoichiometric coefficients.

12(c). How order and molecularity are different for complex reactions? [1 mark]

Solution:

Concept:

- Order is the sum of the powers of reactant concentrations in the experimentally determined rate law.
- Molecularity is the number of reacting species participating together in a single elementary step; it is a positive integer.

Step 1: Define order for a complex reaction A complex reaction occurs through several elementary steps. Its overall rate law, and hence its order, is determined experimentally and depends on the mechanism. The order may be zero, fractional or integral; it need not match the coefficients in the overall equation.

Step 2: Identify where molecularity applies Molecularity is assigned separately to each elementary step of the mechanism. It is not defined for the overall complex reaction, because the net equation does not represent a single collision involving all the species. Thus an overall order cannot generally be equated with molecularity.

Step 3: Conclusion For a complex reaction, overall order is experimentally defined, whereas molecularity applies only to its individual elementary steps and has no overall value.

Quick Tip to Solve: For a multistep reaction, discuss overall order but assign molecularity only to a specified elementary step.

12(d). A first order reaction has a rate constant $2 \times 10^{-3}\,\mathrm{s}^{-1}$. How long will 6 g of this reactant take to reduce to 2 g? [2 marks]

Solution:

Concept:

- The integrated rate law for a first-order reaction is $t = \dfrac{2.303}{k} \log \dfrac{[A]_0}{[A]_t}$, where k is the rate constant and $[A]_0, [A]_t$ are initial and remaining concentrations.
- At constant volume, concentration is proportional to the mass of the same reactant, so $[A]_0/[A]_t = m_0/m_t$. A rate constant in s^{-1} gives time in seconds.

Step 1: Form the reactant ratio The initial mass is $m_0 = 6\,\mathrm{g}$, and the remaining mass is $m_t = 2\,\mathrm{g}$. Hence

$$\frac{[A]_0}{[A]_t} = \frac{6}{2} = 3.$$

The amount remaining enters the denominator; the $4\,\mathrm{g}$ consumed does not.

Step 2: Substitute into the first-order rate law Using $k = 2 \times 10^{-3}\,\mathrm{s}^{-1}$ and $\log 3 = 0.4771$,

$$\begin{aligned} t &= \frac{2.303}{2 \times 10^{-3}} \log 3 \\ &= \frac{2.303 \times 0.4771}{0.002} \\ &= 549.38\,\mathrm{s}. \end{aligned}$$

This is about $9.16\,\mathrm{min}$. The result is larger than one half-life, as the remaining fraction $1/3$ is below $1/2$.

Step 3: Conclusion The time required is approximately $\boxed{5.49 \times 10^2\,\mathrm{s}}$, or $9.16\,\mathrm{min}$.

Quick Tip to Solve: For first-order decay, use initial mass divided by remaining mass inside the logarithm; keep the time unit consistent with the rate constant.

OR

12(d). The half life for radioactive decay of ^{14}C is 6930 years. An archaeological artifact containing wood had only 75% of the ^{14}C found in a living tree. Find the age of the sample.
[log 4 = 0.6021, log 3 = 0.4771, log 2 = 0.3010, log 10 = 1] [2 marks]

Solution:

Concept:

- Radioactive decay follows first-order kinetics: $k = \dfrac{2.303}{t} \log \dfrac{N_0}{N}$, where N_0 is the initial amount of radioactive carbon and N is its amount after time t.
- For first-order decay, $t_{1/2} = \dfrac{2.303 \log 2}{k}$. The half-life and the sample's age must be expressed in the same time unit.

Step 1: Express the fraction of carbon remaining Taking the radioactive carbon content of living wood

Quick Tip to Solve: For 75% remaining, use the ratio $N_0/N = 4/3$ and $\log(4/3) = \log 4 - \log 3$; divide by $\log 2$ to express the age as a fraction of the half-life.

as N_0, the artifact has $N = 0.75N_0$. Thus $N_0/N = 4/3$. The stated 75% is the amount remaining, so it must not be used as the fraction decayed. The logarithm needed in the decay equation is

$$\log \frac{N_0}{N} = \log 4 - \log 3 = 0.6021 - 0.4771 = 0.1250.$$

Step 2: Use the half-life to calculate the elapsed time Eliminate the rate constant between the first-order decay equation and the half-life equation:

$$t = \frac{t_{1/2}}{\log 2} \log \frac{N_0}{N} = \frac{6930}{0.3010} \times 0.1250 = 2877.9 \text{ years}.$$

The age is less than the half-life, as expected: more than half of the initial radioactive carbon is still present in the wood.

Step 3: Conclusion The archaeological wood sample is approximately 2.88×10^3 years old (about 2878 years).

Quick Tip to Solve: For 75% remaining, use the ratio $N_0/N = 4/3$ and $\log(4/3) = \log 4 - \log 3$; divide by $\log 2$ to express the age as a fraction of the half-life.