Preparatory Problems

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Contact Address

Prof. Arvind Kumar
Homi Bhabha Centre for Science Education
Tata Institute of Fundamental Research
V. N. Purav Marg, Mankhurd, Mumbai - 400088
INDIA

Tel. No : 91 - 22 - 5562132 ; 5567711
Fax : 91 - 22 - 5565660 ; 5566803

E- mail : icho33@hbcse.tifr.res.in
arvindk@hbcse.tifr.res.in

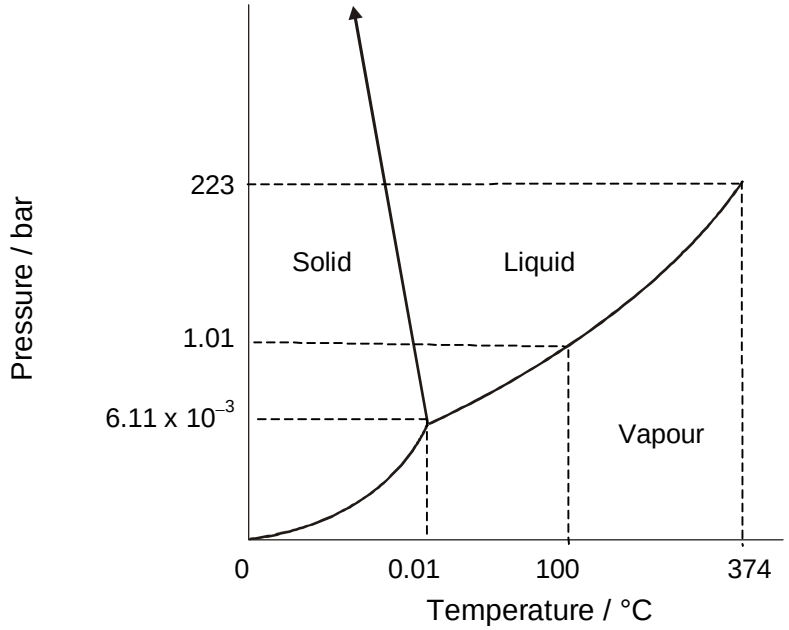
www.hbcse.tifr.res.in/icho

Theoretical Problems

Problem 1 Water

Water, the commonest substance around us, is an excellent system to understand many concepts of thermodynamics. It exists in three different phases: solid (ice), liquid and vapour. [At high pressures, different solid phases of ice exist, but we do not consider them here.] The phase diagram for water, which gives the pressure versus temperature curves for its different phases in equilibrium, is shown below :

A. Phase diagram



Phase diagram of water (not to scale)

a. At what temperature and pressure do all the three phases of water coexist in equilibrium?

b. What is the effect of decrease of pressure on boiling point of water and melting point of ice, as seen from the phase diagram?

c. The liquid-vapour coexistence curve ends at the point P_c = 223 bar and T_c = 374^{o}C. What is the significance of this point?

d. What is the phase of water at T = 300 K, P = 12.0 bar; T = 270 K, P = 1.00 bar?

e. Below what value of pressure will ice, when heated isobarically, sublimate to vapour?

f. At a certain temperature and pressure on the liquid-vapour co-existence line, the molar volumes of water in the two phases are

$\overline{V}_{\ell} = 3.15 \times 10^{-5}\ m^3$ $\qquad$ $\overline{V}_{v} = 15.8 \times 10^{-5}\ m^3$

For 1.00 mole of water in a 0.100 litre vessel at this temperature and pressure, determine the volume fractions in liquid and vapour phases.

B. Clausius – Clapeyron equation

a. Explain your answer to part **A. b** above on the basis of the Clapeyron equation.

b. Autoclaves used for medical sterilisation need to have a temperature of 120°C of boiling water to kill most bacteria. Estimate the pressure required for the purpose. The molar enthalpy change of vaporisation of water is 40.66 kJ mol^{-1} at the normal boiling point. Indicate the assumptions made in your estimate.

c. The molar enthalpy change of fusion at normal freezing point (273.15 K) is 6008 J mol^{-1}. Estimate the pressure at which water and ice are in equilibrium at – 0.200°C. Density of ice = 917 kg m^{-3} and density of water = 1000 kg m^{-3}. Indicate the assumptions made in your estimate.

C. Irreversible condensation

a. Consider 28.5 g of supercooled (liquid) water at –12.0°C and 1.00 bar. Does this state lie on the P - T plane of the phase diagram?

b. This metastable state suddenly freezes to ice at the same temperature and pressure. Treat the metastable state as an equilibrium state and calculate the heat released in the process. Molar heat capacities, assumed constant, are :

$\overline{C}_{p(ice)} = 76.1\,JK^{-1}mol^{-1}$

$\overline{C}_{p(liquid\ water)} = 37.15\,JK^{-1}mol^{-1}$

$\Delta\overline{H}_{(fusion)} = -333.5\,J\,g^{-1}$

c. Determine the total entropy change of the universe in the process and assure yourself that the answer is consistent with the Second Law of Thermodynamics. Take the surroundings to be at –12.0°C.

Problem 2 van der Waals gases

The ideal gas equation PV = nRT implies that the compressibility factor

$$Z = \frac{PV}{nRT} = 1$$

However, the compressibility factor is known to deviate from 1 for real gases. In order to account for the behavior of real gases, van der Waals proposed the following equation of state :

$$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$$

where a and b are constants, characteristic of the gas. The constant a is a measure of the intermolecular force and b that of the size of the molecules.

a. Show on the basis of van der Waals equation that

i. at sufficiently high temperatures, Z is greater than unity for all pressures. At high temperatures and low pressures, Z approaches the value for an ideal gas.

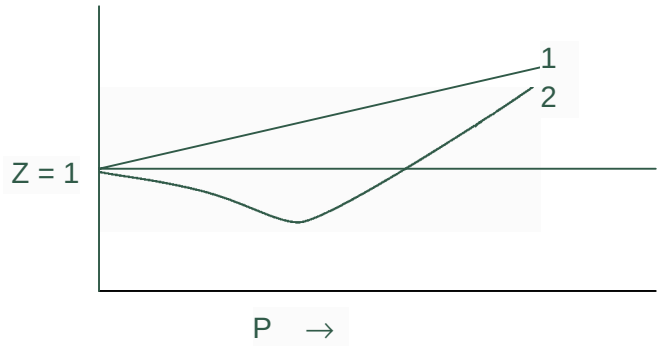
ii. at lower temperatures, Z can be less than unity.

iii. for a = 0, Z increases linearly with pressure.

b. At a certain temperature, the variation of Z with P for He and N_2 is shown schematically in the following figure.

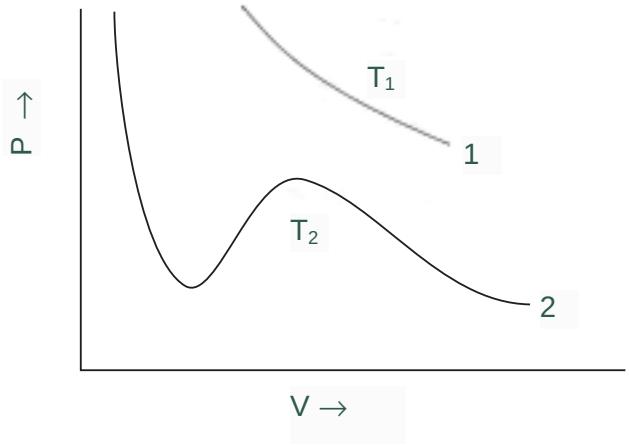
For He, $a = 3.46 \times 10^{-2}$ bar L^2 mol^{-2} and $b = 2.38 \times 10^{-2}$ $Lmol^{-1}$

For N_2, $a = 1.37$ bar L^2 mol^{-2} and $b = 3.87 \times 10^{-2}$ $Lmol^{-1}$



Identify the graph corresponding to He and N_2.

c. Two P-V isotherms of a van der Waals gas are shown below schematically. Identify the one that corresponds to a temperature lower than the critical temperature (T_c) of the gas.



d. For a given P, the three roots of van der Waals equation in V coincide at a certain temperature T = T_c. Determine T_c in terms of a and b, and use the result to show that N_2 is liquefied more readily than He.

e. Determine the work done by 1 mol of N_2 gas when it expands reversibly and isothermally at 300 K from 1.00 L to 10.0 L, treating it as a van der Waals gas.

Problem 3 Rates and reaction mechanisms

The observed rate law for a chemical reaction can arise from several different mechanisms. For the reaction

$$H_2 + I_2 \longrightarrow 2\,HI$$

the observed rate law is

$$-\frac{d[H_2]}{dt} = k\,[H_2]\,[I_2]$$

For a long time it was believed that the above reaction took place as it was written down; that is, it was a bimolecular elementary reaction. It is now considered that several mechanisms compete. Below a certain temperature, two alternative mechanisms have been proposed :

(1) $I_2 = 2I$ K : equilibrium constant

$I + I + H_2 \xrightarrow{k_1} 2HI$

(2) $I_2 = (I_2)_d$ K' : equilibrium constant

$(I_2)_d + H_2 \xrightarrow{k_1} 2HI$

where $(I_2)_d$ represents a dissociative state of I_2. The first step in each mechanism is fast and the second slow.

a. Show that both mechanisms are consistent with the observed rate law.

b. The values of the rate constant k for the reaction at two different temperatures are given in the table :

T(K)	k (L mol^{-1} s^{-1})
373.15	8.74×10^{-15}
473.15	9.53×10^{-10}

i. Determine the activation energy E_a.

ii. The bond dissociation energy of I_2 is 151 kJ mol^{-1}. Justify why the second step in each mechanism is rate determining.

c. The change in internal energy (ΔU) for the reaction is – 8.2 kJ mol^{-1}. Determine the activation energy for the reverse reaction.

d. The activation energy for a reaction can even be negative. An example is the gas phase recombination of iodine atoms in the presence of argon:

$$I + I + Ar \longrightarrow I_2 + Ar\,,$$

whose activation energy is about – 6 kJ mol^{-1}.

One of the proposed mechanisms of this reaction is :

$I + Ar + Ar = IAr + Ar$ K" : equilibrium constant

$IAr + I \xrightarrow{k_3} I_2 + Ar$

where IAr is a very loosely bound species.

i. Assume that the second step is rate determining and obtain the rate law for the reaction.

ii. Give a possible explanation of why the activation energy for the iodine recombination is negative.

Problem 4 Enzyme catalysis

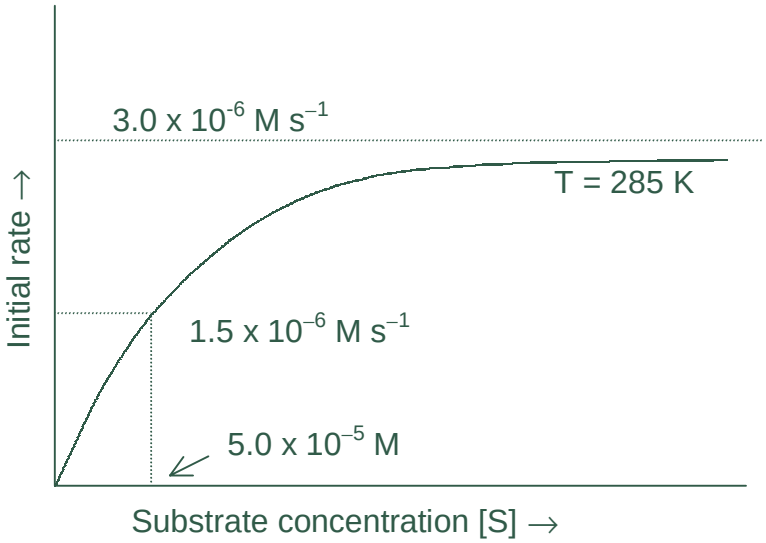
Enzymes play a key role in many chemical reactions in living systems. Some enzyme-catalysed reactions are described in a simple way by the Michaelis-Menten mechanism, as given below.

$$E + S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

where E stands for the enzyme, S stands for the substrate on which it acts and P, the end product of the reaction. k_1 and k_1' are the forward and backward rate constants for the first step and k_2 the forward rate constant for the second step.

Ignore the backward rate for the second step. Also assume that the enzyme equilibrates with its substrate very quickly.

a. In an experiment, the initial rate (of formation of P) is determined for different concentrations of the substrate, keeping the total concentration of enzyme fixed at 1.5 x 10^{-9} M. The following graph is obtained.



i. The graph is linear for small [S] and it approaches a constant value for large [S]. Show that these features are consistent with the Michaelis-Menten mechanism. (Use steady state approximation for the intermediate step.)

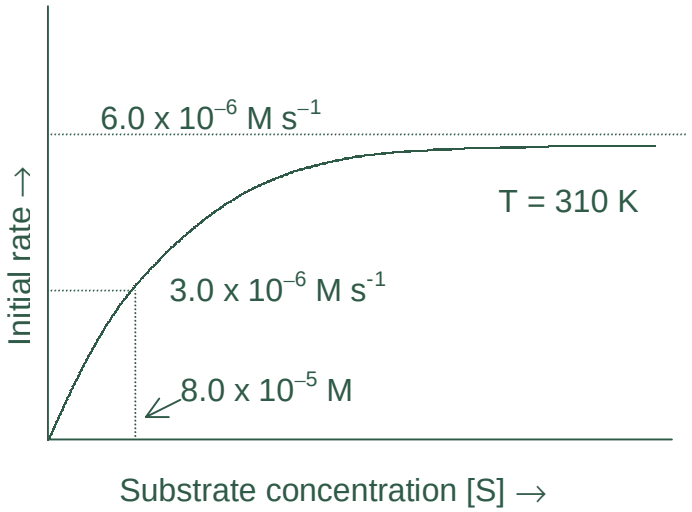
ii. Determine the rate constant k_2 for the second step.

iii. Predict the initial rate on the basis of the Michaelis-Menten mechanism for the substrate concentration [S] = 1.0×10^{-4} M.

iv. Determine the equilibrium constant for the formation of the enzyme - substrate complex ES.

b. The experiment above studied at 285 K is repeated for the same total enzyme concentration at a different temperature (310 K), and a similar graph is obtained, as shown below.

Determine the activation energy for the conversion of ES to E and P.



c. One interesting application of the ideas above is the way enzyme catalysed reactions inactivate antibiotics. The antibiotic penicillin is, for example, inactivated by the enzyme penicillinase secreted by certain bacteria. This enzyme has a single active site. Suppose, for simplicity, that the rate constants obtained in a above apply to this reaction. Suppose further that a dose of 3.0 μmol of the antibiotic triggers the release of 2.0×10^{-6} μmol of the enzyme in a 1.00 mL bacterial suspension.

i. Determine the fraction of the enzyme that binds with the substrate (penicillin) in the early stage of the reaction.

ii. Determine the time required to inactivate 50% of the antibiotic dose.

d. To control the inactivation of penicillin, suppose a substance is introduced which has a similar structure to penicillin and is able to occupy the enzyme site, but is otherwise completely unreactive. This naturally inhibits the enzyme-catalysed reaction. The degree of inhibition i is defined by

$$i = 1 - \frac{r}{r_0}$$

where r and r_0 are the initial rates of reaction with and without the inhibitor respectively.

Consider again the Michaelis-Menten type of mechanism to describe the situation :

$$E + S \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} ES$$

$$E + I \underset{k_3'}{\overset{k_3}{\rightleftharpoons}} EI$$

$$ES \xrightarrow{k_2} E + P$$

i. Show that the degree of inhibition decreases with increase in concentration of the substrate (for constant concentration of the inhibitor), and the inhibitor ceases to be effective for large substrate concentrations. (This is known as *competitive inhibition*.)

ii. For low substrate concentration of penicillin, determine the concentration of the inhibitor that reduces the rate of the inactivation of penicillin by a factor of 4. The dissociation constant of enzyme-inhibitor complex is given to be 5.0×10^{-5}.

Problem 5 Schrödinger equation

The simplest Schrödinger equation, describing a free particle confined to move in a one-dimensional 'rigid box' brings out a most basic fact: quantization arises due to boundary conditions on the wave function.

a. An electron of mass m is confined to move in a line along the x-axis from x = 0 to x = L. Between the two ends it experiences no force.

i. Write down the (time-independent) Schrödinger equation for the wave function ψ of an electron.

ii. Which of the following are possible wave functions of an electron in one-dimensional rigid box :

e^{-kx}

$\cos \frac{n\pi x}{L}$

$\sin kx$

$\sin \frac{n\pi x}{L}$

where k is any real number and n is a positive integer ?

iii. For the acceptable wave functions of the electron in (ii) above, show that the energies are given by

$$E_n = \frac{h^2 n^2}{8 m L^2}$$

iv. Plot schematically the wave function of the electron in the ground and the first two excited states. What is the number of nodes (in the region between x = 0 to L) of the wave function with energy E_n?

v. Normalize the ground state wave function of the electron.
(The integral of the square of the modulus of a normalized wave function over all space is unity.)

b. An interesting example of this one-dimensional model in chemistry is the motion of an electron in a conjugated system of single and double bonds. The molecule 1,3-butadiene has four π electrons assumed to move freely in a line consisting of three carbon-carbon bonds, each of approximately the same length (1.4×10^{-10} m), with an additional length of 1.4×10^{-10} m at each end. Using the aufbau principle, determine a scheme to fill the electrons in the available energy levels. Calculate the lowest excitation energy of the system.

c. 'Boundary conditions' on wave functions result in quantization of not only energy but also other physical quantities, such as angular momentum.
The wave function corresponding to the value $h\lambda/2\pi$ for the z-component of angular momentum (L_z) is:
$\psi(\phi) = e^{i\lambda\phi}$,
where ϕ is the (azimuthal) angle in the x-y plane measured relative to the x-axis. Use the condition that this function is single valued at every point in space and show that this implies that λ is quantized. Give the quantized values of angular momentum projection along the z-axis.

Problem 6 Atomic and molecular orbitals

Orbitals are one-electron wave functions, whether they refer to electronic motion in an atom (atomic orbitals) or in a molecule (molecular orbitals) or a solid. Each orbital corresponds to a certain probability distribution of finding an electron in different regions of space.

A. Atomic orbitals

a. The 1s orbital of hydrogen atom is given by

$$\psi_{1s} = e^{-r/a_o},$$

where a_o is the Bohr radius ($a_o = 5.3 \times 10^{-11}$ m) and r is the radial co-ordinate (distance of a point in space from the centre).

i. Normalize the given wave function.

ii. At what distance from the nucleus is the electron most likely to be found?

b. The wave functions for 2s, $2p_z$ and $3d_z^2$ states are given below :

$$\psi_{2s} = (2 - \frac{r}{a_o})\, e^{-\frac{r}{2a_o}}$$

$$\psi_{2p_z} = \left(\frac{r}{a_o}\right) \cos\theta\ e^{-\frac{r}{2a_o}}$$

$$\psi_{3d_{z^2}} = \left(\frac{r^2}{a_o^2}\right)(3\cos^2\theta - 1)\, e^{-\frac{r}{3a_o}}$$

What are the nodal surfaces of these orbitals?

c. It turns out that the solution of Schrödinger equation for a one-electron atom yields exactly the 'good old' formula of Bohr for quantized energies:

$$E_n = -\frac{(13.6\ \text{eV})Z^2}{n^2}$$

where, for convenience, the numerical value of the combination of constants appearing in the formula has been put in units of eV .

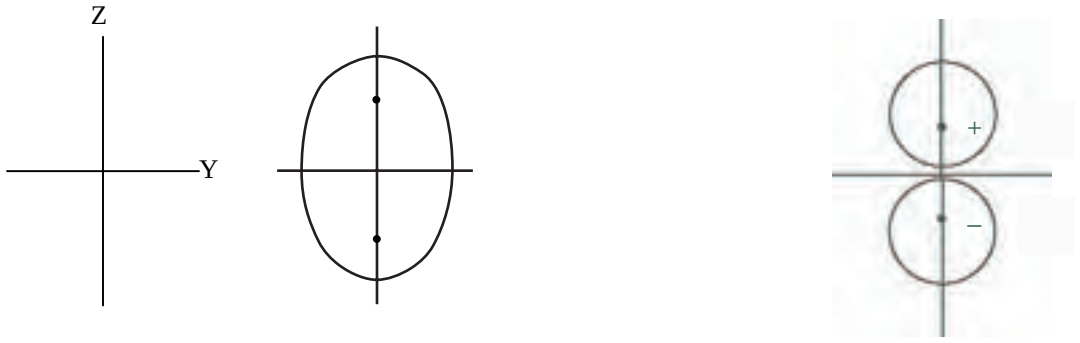
It is fun using this formula for a neutral helium atom, but we must exercise some care. In a helium atom, each electron 'sees' the nucleus screened by the other electron. That is, the effective charge of the nucleus 'seen' by each electron decreases from its bare value Z=2 to some other value, say, Z_{eff} . The ionization energy for a helium atom in its ground state is known experimentally to be 24.46 eV. Estimate Z_{eff} .

B. Molecular orbitals

Molecular orbitals of a hydrogen molecule ion (H_2^+) can be approximately written as linear combinations of atomic orbitals centered around the two nuclei of the molecule. Consider the (unnormalized) molecular orbitals constructed in this manner from the 1s and 2s orbitals of two hydrogen atoms, say, A and B:

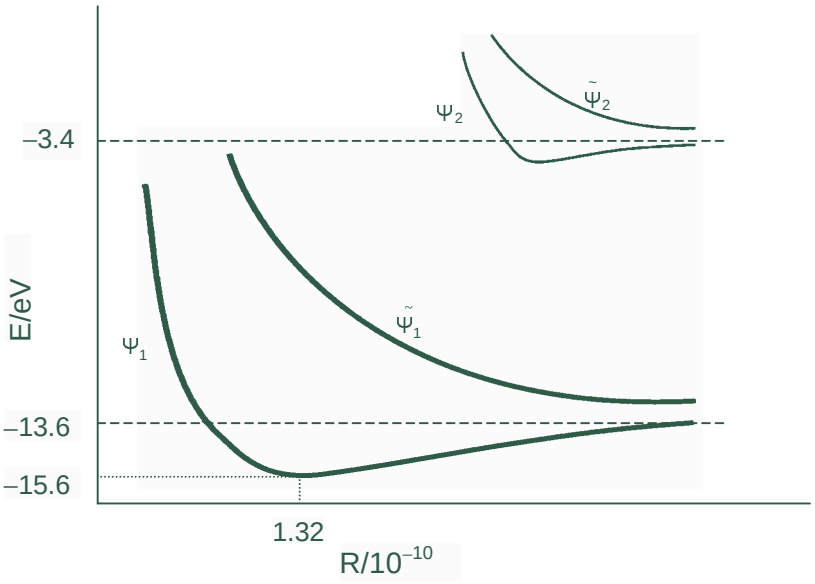
$$\psi_1 = \psi_{1s}^A + \psi_{1s}^B$$
$$\tilde{\psi}_1 = \psi_{1s}^A - \psi_{1s}^B$$
$$\psi_2 = \psi_{2s}^A + \psi_{2s}^B$$
$$\tilde{\psi}_2 = \psi_{2s}^A - \psi_{2s}^B$$

Taking the z-axis along the line joining the two nuclei, the orbital contours of ψ_1 and $\tilde{\psi}_1$ are shown schematically below :



Similar orbital contours (curves on which the value of ψ is constant) can be drawn for ψ_2 and $\tilde{\psi}_2$.

The energies of these wave functions as a function of internuclear distance are shown below schematically:



a. Identify the bonding and antibonding orbitals. State qualitatively what makes one orbital bonding and another antibonding.

b. Determine the values of the equilibrium internuclear distance R_e and the dissociation energy D of the ground state of H_2^+.

c. If the molecular ion H_2^+ is excited to the state ψ_2, to what atomic states will it dissociate?

In the following questions, assume that the energy versus internuclear distance graphs for the orbitals of H_2 and He_2 are similar to the one shown for H_2^+.

d. Explain why the ground state total electron spin of the neutral H_2 molecule is zero.

e. Write down the electronic configuration of the first excited state of H_2 molecule. Predict if it will stay bound or dissociate.

f. It is difficult to obtain He_2 in its ground state, but it has been observed in its excited states. Explain how this is possible.

Problem 7 Fission

a. Consider the following fission reactions of ^{235}U by thermal neutrons :

$$^{235}_{92}U + n \rightarrow {}^{94}_{38}Sr + {}^{140}_{(...)}Xe + (.....)$$

$$^{235}_{92}U + n \rightarrow {}^{141}_{56}Ba + (....) + 3n$$

Identify the missing species and numbers.

b. Consider the first of the reactions above. The unstable fission fragments undergo successive β-decays giving Zr and Ce. Write down the net nuclear reaction and calculate the total energy released in MeV. You are given the following data on atomic masses :

$m(^{235}U) = 235.0493\ u$

$m(^{94}Zr) = 93.9063\ u$

$m(^{140}Ce) = 139.9054\ u$

$m_n = 1.00866\ u$

$1u = 931.5\ MeV/c^2$

c. 1 kg of natural uranium metal was put in a nuclear research reactor. When the total energy released reached 1 Mega Watt Day (MWd), it was removed from the reactor. What would be the percentage abundance of ^{235}U in the uranium metal at that time, if it is 0.72% in natural uranium. Your result in **b.** above may be taken to be the average energy released per fission. Assume that all the energy is due to fission of ^{235}U only.

Problem 8 Radioactive decay

The radioactive isotope ^{210}Bi is the daughter product of ^{210}Pb and decays by β - emission to ^{210}Po, which is also radioactive. ^{210}Po decays by α-emission to the stable ^{206}Pb.

$$^{210}Pb \xrightarrow[T_{1/2} = 22.3\ y]{\beta} {}^{210}Bi \xrightarrow[T_{1/2} = 5.01\ d]{\beta} {}^{210}Po \xrightarrow[T_{1/2} = 138.4\ d]{\alpha} {}^{206}Pb$$

A sample of radiochemically pure ^{210}Bi was freshly isolated from ^{210}Pb and was allowed to stand for the growth of ^{210}Po. The radioactivity of the freshly purified ^{210}Bi sample was 100 μCi. (1 Ci = 3.7 x 10^{10} disintegration per second)

a. What is the initial mass of the sample (^{210}Bi)?

b. Calculate the time it takes for the amount of ^{210}Po in the sample to grow to its maximum value. How much is the maximum amount of ^{210}Po?

c. Determine the α-disintegration rate of ^{210}Po and β-disintegration rate of ^{210}Bi at that time.

Problem 9 Redox reactions

a. A solution containing Sn^{2+} ions is titrated potentiometrically with Fe^{3+}. The standard reduction potentials for $Sn^{4+/2+}$ and $Fe^{3+/2+}$ are given below.

$Sn^{4+} + 2e^- = Sn^{2+}$ $\quad E° = 0.154$ V

$Fe^{3+} + e^- = Fe^{2+}$ $\quad E° = 0.771$ V

i. Write down the overall reaction and calculate the standard free energy change of the overall reaction.

ii. Determine the equilibrium constant of the reaction.

b. If 20 mL of 0.10 M Sn^{2+} is titrated with 0.20 M Fe^{3+} solution, calculate the voltage of the cell

i. when 5 mL of Fe^{3+} solution is added.

ii. at the equivalence point.

iii. when 30 mL Fe^{3+} of the solution is added.

The saturated calomel electrode ($E°_{S.C.E} = 0.242$ V) is used as the reference electrode in the titration.

c. One of the important analytical methods for estimation of Cu^{2+} is iodometric titration. In this reaction Cu^{2+} is reduced to Cu^+ by I^- and the liberated I_2 is then titrated with standard $Na_2S_2O_3$ solution. The redox reaction is as follows:

$2Cu^{2+} + 4I^- \rightarrow 2CuI_{(s)} + I_{2\,(aq)}$

Electrode potentials of the relevant half-cells are:

$Cu^{2+} + e^- = Cu^+$ $\quad E° = 0.153$ V

$I_2 + 2e^- = 2I^-$ $\quad E° = 0.535$ V

A consideration of the electrode potentials would indicate that reduction of Cu^{2+} by I^- is not a spontaneous reaction. However, in the iodometric titration this reaction does take place. Let us try to understand the anomaly:

i. CuI has low solubility in water with $K_{sp} \approx 1.1 \times 10^{-12}$. Calculate the effective E° value for the equilibrium $CuI_{(s)} = Cu^+ + I^-$.

ii. Using the result in **i.**, calculate the effective E° value for the reduction of Cu^{2+} by I^-. What does this value suggest about the spontaneity of the reaction?

iii. Calculate the equilibrium constant of the reduction reaction in **ii**.

Problem 10 Solubility of sparingly soluble salts

Two important factors that affect the solubility of a sparingly soluble salt are pH and the presence of a complexing agent. Silver oxalate is one such salt, which has low solubility in water (2.06×10^{-4} at pH = 7.0). Its solubility is affected by pH as the anion oxalate reacts with hydronium ions, and also by a complexing agent such as ammonia as the cation silver forms complexes with ammonia.

a. Calculate the solubility of silver oxalate in acidified water with pH = 5.0. The first and second dissociation constants for oxalic acid are 5.6×10^{-2} and 6.2×10^{-5} respectively.

b. In the presence of ammonia in aqueous solution, silver ion forms two complexes $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$. The values of the stepwise stability constants for the formation of these complexes are 1.59×10^3 and 6.76×10^3. What is the solubility of silver oxalate in an aqueous solution that contains 0.02 M NH_3 and has pH = 10.8?

Problem 11 Spectrophotometry

a. Manganese and chromium in steel can be determined simultaneously by absorption spectral method. Dichromate and permanganate ions in 1M H_2SO_4 ($Cr_2O_7^{2-}$ and MnO_4^-) absorb at 440nm and 545nm. At these wavelengths, molar absorptivity of MnO_4^- is 95 $Lmol^{-1}cm^{-1}$ and 2350 $Lmol^{-1}cm^{-1}$ respectively and that of $Cr_2O_7^{2-}$ is 370 $Lmol^{-1}cm^{-1}$ and 11 $Lmol^{-1}cm^{-1}$ respectively.

A steel sample, weighing 1.374g was dissolved and Mn and Cr in the resulting solution oxidised to MnO_4^- and $Cr_2O_7^{2-}$. The solution was diluted with 1M H_2SO_4 to 100.0mL in a volumetric flask. The transmittances of this solution were measured with a cell of 1.0cm path length and with 1.0M H_2SO_4 as blank. The observed transmittances at 440nm and 545nm respectively were 35.5% and 16.6%.

Calculate from these data the percentage of Mn and Cr in the steel sample. Assume that Beer's law is valid for each ion and that the absorption due to one ion is unaffected by the presence of the other ion .

b. Cobalt (II) forms a single complex CoL_3^{2+} with an organic ligand L and the complex absorbs strongly at 560nm. Neither Co(II) nor ligand L absorbs at this wavelength. Two solutions with the following compositions were prepared:

Solution 1 $[Co(II)] = 8 \times 10^{-5}$ and $[L] = 2 \times 10^{-5}$.

Solution 2 $[Co(II)] = 3 \times 10^{-5}$ and $[L] = 7 \times 10^{-5}$.

The absorbances of solution 1 and solution 2 at 560nm, measured with a cell of 1.0cm path length, were 0.203 and 0.680 respectively. It may be assumed that in solution 1, all the ligand is consumed in the formation of the complex. From these data calculate the

i. molar absorptivity of the complex CoL_3^{2+}

ii. stability constant for the formation of the complex CoL_3^{2+}.

Problem 12 Reactions in buffer medium

An organic nitro-compound (RNO_2) is electrolytically reduced in an aqueous acetate buffer solution having total acetate concentration ($HOAc + OAc^-$) 0.500 and pH = 5.0. 300 mL of the buffered solution containing 0.01M RNO_2 was reduced completely. The dissociation constant for acetic acid is 1.75×10^{-5} at 25 °C. The reduction reaction is

$$RNO_2 + 4H^+ + 4e^- \longrightarrow RNHOH + H_2O$$

Calculate the pH of the solution on completion of the reduction of RNO_2.

Problem 13 Identification of an inorganic compound

Some observations related to an unknown inorganic substance **A** are presented below.

- **A** is a yellowish – white deliquescent solid and it sublimes on heating. It has a molecular weight of 266.
- **A** reacts violently with water, forming solution **B**.
- When a solution of NH_4Cl and NH_4OH is added to solution **B**, a white gelatinous precipitate is obtained.
- A sample of **B** also gives a curdy white precipitate **C** on addition of dilute nitric acid and silver nitrate solution. This white precipitate **C** readily dissolves when dilute NH_4OH is added, though a gelatinous white precipitate **D** is formed in its place with excess NH_4OH.
- Precipitate **D** is filtered off and is dissolved in excess NaOH to give a clear solution **E**.
- When CO_2 is passed through solution **E**, compound **D** is reprecipitated.
- Substance **A** dissolves unchanged in dry ether. When this solution is reacted with LiH, a product **F** is formed. If LiH is used in excess, **F** transforms to **G**.

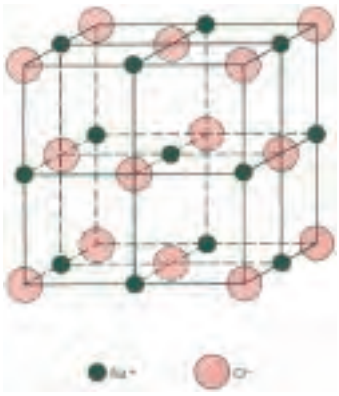
a. Identify the unknown compound **A**.

b. Write down the appropriate chemical equations for the given reactions and identify the different products from **B** to **G**.

Problem 14 Ionic and metallic structures

Modern methods of structural analysis using X-rays provide valuable information about the three dimensional arrangement of atoms, molecules or ions in a given crystal structure.

a. Crystal structure of rock salt (NaCl) is given below.



i. What is the type of crystal lattice presented in the diagram?

ii. What is the coordination number of a sodium ion in this structure?

iii. What is the number of formula units of NaCl per unit cell?

iv. Calculate the r_{Na^+} / r_{Cl^-} limiting radius ratio for this structure.

v. Why is the array of chloride ions slightly expanded, with the nearest Cl-Cl distance being 400pm, compared to the close packed value of 362 pm?

vi. What happens when the cation radius in the structure shown above is progressively increased till the cation/anion radius ratio reaches a value of 0.732?

vii. What is the range of cation/anion radius ratio for which the structure like that of NaCl is stable?

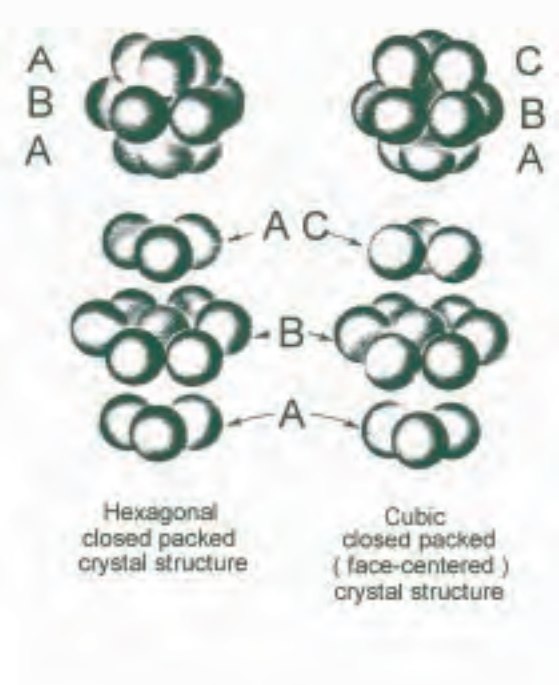
b. The Cu - K_α X-ray(λ = 154pm) reflection from (200) planes of sodium chloride crystal is observed at 15.8°. Given that the radius of the chloride ion is 181 pm, calculate

i. the separation between adjacent 200 planes of NaCl.

ii. the length of the unit cell edge (lattice constant) of NaCl.

iii. the radius of the sodium ion.

c. The diagram of a cubic close packing (*ccp*) and a hexagonal close packing (*hcp*) lattice arrangement (assuming rigid sphere model) is given below.



i. Describe the difference between the *ccp* and *hcp* lattice arrangements.

ii. Calculate the packing fraction for a *ccp* arrangement.

iii. Will the coordination number, and the packing fraction in a *hcp* arrangement be the same as that in a *ccp* arrangement?

d. Nickel (at.wt. 58.69) crystallizes in the *ccp* structure. X-ray diffraction studies indicate that its unit cell edge length is 352.4 pm. Given that the density of Nickel is 8.902 g cm^{-3}, calculate

i. the radius of the nickel atom.

ii. the volume of the unit cell.

iii. the Avogadro number.

Problem 15 Compounds of nitrogen

a. Nitrogen forms a number of oxides. One of the important oxides of nitrogen is NO_2, a red-brown colored reactive gas**.**

i. Draw the Lewis structure of NO_2 and predict its shape using valence shell electron pair repulsion theory.

ii. Using VSEPR, predict the shapes of the NO_2^- and NO_2^+ ions. Compare the shapes of these two ions with that of NO_2.

b. Consider two other compounds of nitrogen, trimethylamine (Me_3N) and trisilylamine $(H_3Si)_3N$. The observed bond angles at nitrogen in these compounds are 108° and 120° respectively. Explain the difference in the bond angles.

c. Both nitrogen and boron form trifluorides. The bond energy in BF_3 is 646 kJ/mole and that in NF_3 is only 280 kJ/mole. Account for the difference in bond energies.

d. The boiling point of NF_3 is –129°C while that of NH_3 is –33°C. Ammonia acts as a Lewis base whereas NF_3 does not. The observed dipole moment of NF_3 (0.24 D) is much less than that of NH_3 (1.46 D), even though fluorine is much more electronegative than hydrogen.

i. Explain the differences between boiling points and basicities of NF_3 and NH_3.

ii. Account for the low dipole moment of NF_3.

e. The reaction of aqueous sodium nitrate with sodium amalgam as well as that of ethyl nitrite with hydroxylamine in presence of sodium ethoxide give the same product. This product is the salt of a weak unstable acid of nitrogen. Identify the acid and write down its structure. This acid isomerises into a product, which finds use in propellant formulations. Write the structure of the isomer.

Problem 16 Structure elucidation with stereochemistry

Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid) is the primary acid of citrus fruits, which contributes to their sour taste. Commercial manufacturing of citric acid involves fermentation of molasses or starch using the fungus *Aspergillus niger* at pH 3.5. It is widely used in food, soft drinks and as a mordant in dyeing. It is also an important biochemical intermediate.

a. What transformation will citric acid undergo when warmed with concentrated sulfuric acid at 45-50°C? Give the structure and IUPAC name of the product obtained. Which type of organic acids would undergo a similar reaction?

After warming citric acid with sulfuric acid, anisole (methoxybenzene) is added to the reaction mixture and product **A** ($\mathbf{C_{12}H_{12}O_5}$) is obtained.

- On heating with acetic anhydride, **A** forms an anhydride.
- 118 mg of **A** requires 20 mL of 0.05 N KOH for neutralisation.
- Reaction with bromine indicates that the same amount of compound **A** requires 80 mg of bromine, to give an addition product.

b. Deduce the structure of **A**.

c. Identify the possible isomers of **A** in this reaction and give their structures, absolute configurations and the IUPAC names.

d. In the bromination reaction, how many stereoisomers of **A** will be obtained? Draw their Fischer projections.

e. Assign absolute configurations to the stereocentres in all the stereoisomers formed in **d.**

Instead of anisole, if phenol and resorcinol are separately added to the reaction mixture, compounds **B** and **C** are obtained, respectively. **B** does not give any coloration with neutral $FeCl_3$, but **C** does. Under identical reaction conditions, the yield of compound **C** is much higher than that of **B**.

f. Give appropriate structures for **B** and **C**.

g. What is the difference between the reactions leading to the formation of **A** and **B**?

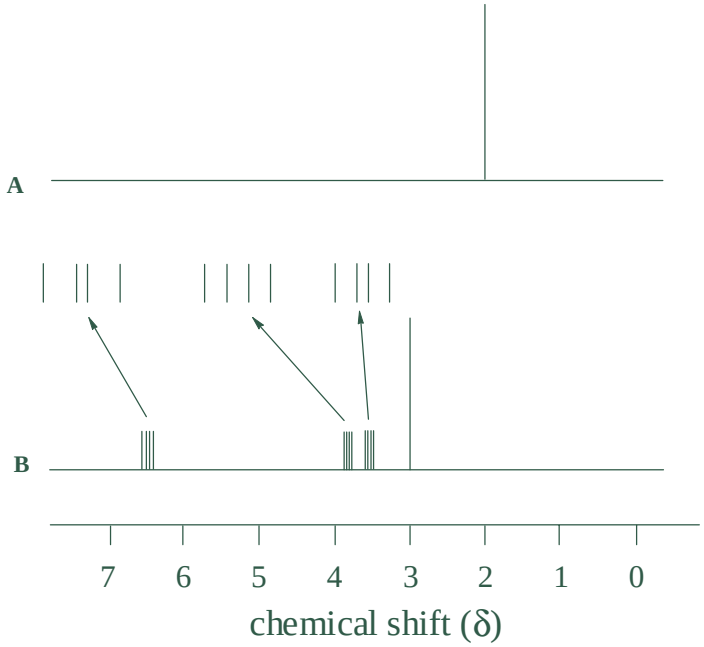
h. Why is the yield of **C** higher than that of **B?**

Problem 17 Organic spectroscopy and structure determination

The following observations were recorded for identifying two compounds **A** and **B**.

Both have the molecular formula $\mathbf{C_3H_6O}$. Schematic ^{1}H-NMR spectra of these compounds at 400 MHz are presented in the following figure. The peak positions and the relative intensities of the different lines in the ^{1}H-NMR spectrum of **B** are given in the accompanying Table (Note: the values have been altered slightly from the experimental values to facilitate analysis.)

One of these compounds reacts with malonic acid to form a compound known as Meldrum's acid, with the molecular formula $\mathbf{C_6H_8O_4}$, which gives peaks between 0 and 7.0 δ in its ^{1}H-NMR spectrum. The IR spectrum shows a peak in the region 1700 - 1800 cm^{-1}. It condenses with an aromatic aldehyde in the presence of a base.



^{1}H-NMR schematic spectra of A and B at 400 MHz

Peak positions and relative intensities of individual lines in the ^{1}H NMR spectrum (400 MHz) of B

Line	(ppm)	Relative intensity	Line	(ppm)	Relative intensity
1	6.535	1	8	3.870	1
2	6.505	1	9	3.525	1
3	6.495	1	10	3.505	1
4	6.465	1	11	3.495	1
5	3.930	1	12	3.475	1
6	3.910	1	13	3.000	12
7	3.890	1			

a. Label the unknown compounds in the bottles with IUPAC names, using the NMR spectra given in the figure.

b. In the ^{1}H-NMR spectrum of **B**, assign the peak positions to specific protons.

c. Calculate the spin-spin coupling constants for protons of compound **B**.

d. Convert the peak positions of the first four lines into Hz (refer to theTable). What will be the peak positions of these lines in Hz, if the spectrum is recorded on a 600 MHz instrument?

e. Draw the possible structure of Meldrum's acid.

f. Meldrum's acid has $pK_a = 4.83$. Explain the acidity of Meldrum's acid.

g. Give the structure of the condensation product of Meldrum's acid with an aromatic aldehyde.

Problem 18 Polymer synthesis

Ethylene finds extensive application in the manufacture of polymers and bulk chemicals. It is produced on a large scale by thermal and catalytic cracking of alkanes obtained from natural gas and petroleum.

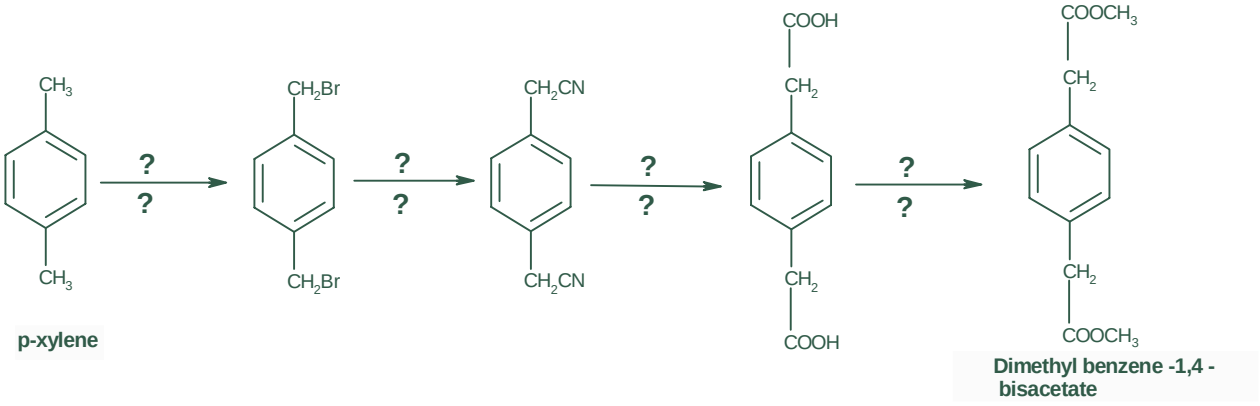
In the presence of silver catalyst, ethylene reacts with oxygen to give **P**. Compound **P** on heating with acidified water forms **Q**. ^{1}H-NMR spectrum of **P** has only one signal while that of **Q** contains two signals.

a. Identify and draw the structures for compounds **P** and **Q.**

Compound **R** is obtained when **P** and **Q** react with each other. **R** reacts with $SOCl_2$ to give **S**. On heating with alcoholic KOH, **S** gives **T**, an anaesthetic under the name "vinethene".

b. Identify compounds **R**, **S** and **T.**

Another compound dimethyl benzene-1,4-*bis*(acetate) can be synthesised from p-xylene. Such a synthesis requires use of proper reagents so that desired intermediate compounds and the final product are obtained. Various intermediate compounds obtained in the synthesis of dimethyl benzene-1,4-*bis*(acetate) along with their structures are shown below.



c. Identify the reagents used in this synthesis of dimethyl benzene –1,4-*bis*(acetate).

d. How many peaks would you expect in the ^{1}H-NMR spectrum of dimethyl benzene –1,4-*bis*(acetate)?

When dimethyl benzene-1,4-*bis*(acetate) (synthesised from p-xylene) and compound **R** (obtained from ethylene) are heated together a polymer is formed.

e. Draw the structure of the polymer.

f. What happens when this polymer is treated with

- aq KOH (heat), then H^+ / H_2O?
- $LiAlH_4$?

g. Inadvertently, an excess of dimethyl benzene-1,4-*bis*(acetate) was heated with glycerol and a different polymer was obtained. What is the likely structure of this polymer? Will it be suitable for drawing fibres?

Problem 19 Organic synthesis involving regioselection

One crucial problems in organic synthesis concerns the synthesis of a specific disubstituted benzene through an electrophilic substitution reaction on a monosubstituted benzene. This problem is elegantly tackled in a synthesis of Tramadol, an analgesic drug **($C_{16}H_{25}NO_2$)**, described below. The first step in this synthesis invovles :

A gives two equal intensity peaks at 172 and 174 in the highest m/z region of its mass spectrum. It gives a mixture of three isomeric mononitro derivatives on nitration under mild conditions.

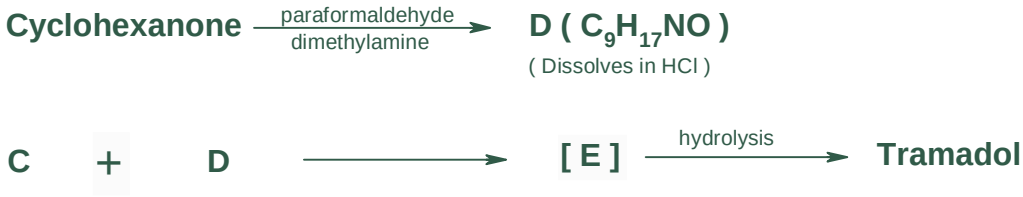
a. Draw the structure for compound **A**. What is the regioselection observed in the reaction of phenol to form **A**? State the significance of this reaction.

Consider the following reaction

Mass spectrum of **B** shows equal intensity peaks at 186 and 188 in the highest m/z region.

b. Give structures of compounds **B** and **C**. How does the reactivity of **B** change on its conversion to **C**?

Another intermediate compound **D** required for the synthesis of Tramadol is obtained as follows



c. Show the structures of compound **D** and the final product Tramadol.

d. Give the structures of the possible stereoisomers of Tramadol.

Problem 20 Carbon acids

Keto esters are bifunctional reactive molecules and are important synthons for the synthesis of aliphatic and heterocyclic compounds.

a. Two isomeric keto esters **X** and **Y** have the same molecular formula **$C_5H_8O_3$**. Deduce their possible structures

Each ester is first reacted with benzyl bromide in the presence of CH_3ONa, and the resulting products are treated with 1 or 2 equivalent of a strong base (such as lithium diisopropyl amide, LDA) followed by 1 equivalent of CH_3I.

The products at the end of the second step are then hydrolysed by aq.HCl.

b. Write down the reaction sequences involved.

c. At the end of the reaction, the final product of keto ester **X** is a neutral compound (molecular formula $\mathbf{C_{11}H_{14}O}$) whereas keto ester **Y**, gives a keto acid (molecular formula $\mathbf{C_{12}H_{14}O_3}$). Explain.

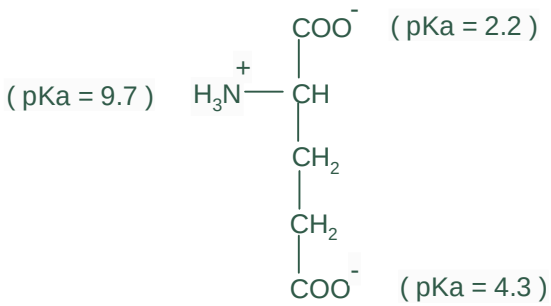
d. Keto ester **X** gives different products depending upon the amount of LDA used. Explain what happens when

i. 1 equivalent of LDA is used.

ii. 2 equivalents of LDA are used.

Problem 21 Amino acids and enzymes

Amino acids are the building blocks of proteins. The presence of $-NH_2$ and -COOH groups makes amino acids amphoteric in nature. Certain amino acid side chains in proteins are critically important for their reactivity and catalytic role. Glutamic acid is one such amino acid, whose structure is shown below.

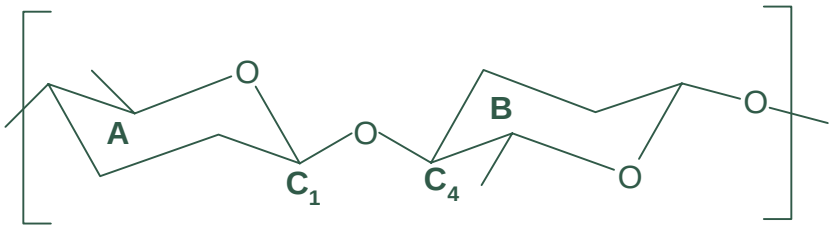


a. Why is the pK_a of the α-COOH group lower than that of the γ-COOH ?

b. Calculate the percent of γ-COOH group that remains unionized at pH 6.3.

c. Glutamic acid is subjected to paper electrophoresis at pH = 3.25. Will it move towards the anode (+) or cathode (-) ? Why ?

Hydrolysis of polysaccharides like chitin, cellulose and peptidoglycan is a common biochemical process. This involves the hydrolysis of a glycosidic bond like the β-1, 4 linkage shown below.

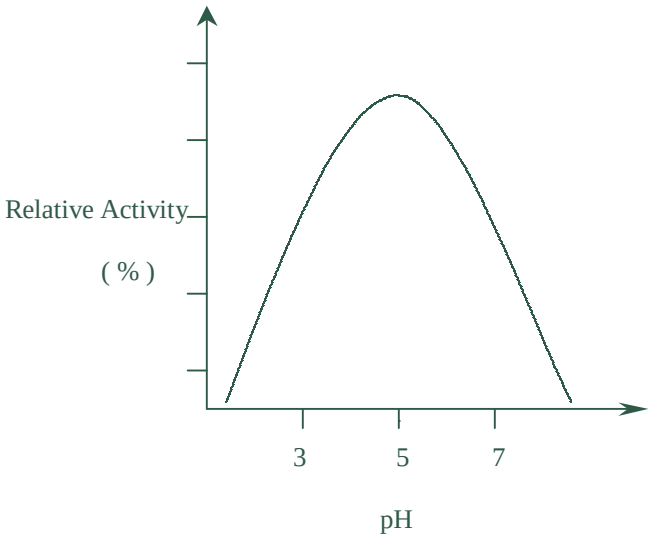


β-1, 4 linkage

One such hydrolysis reaction is catalysed by lysozyme.

d. Suppose the lysozyme catalyzed reaction is performed in ^{18}O enriched water, do you expect the ^{18}O to be incorporated into the product? If yes, where?

The pH-activity profile of lysozyme is shown in the figure



e. Explain this pH behavior in terms of two carboxylates (Asp-52 and Glu-35) present at the lysozyme active site (note : ionizable groups on the substrate are not involved). Write the ideal state of ionization at the lysozyme active site at pH 5.0.

f. The pK_a of Glu-35 in lysozyme active site is 6.0 and not 4.3 as found in the free amino acid. Which of the following local effects is likely to be involved?

1. Enhanced negative charge

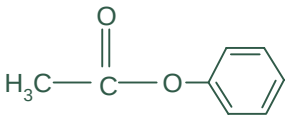
2. Enhanced positive charge

3. Enhanced polarity

4. Diminished polarity

Organic model reactions have helped to understand many features of enzyme catalytic mechanisms. When a reaction is made intramolecular (like the enzyme catalysts do!), rate acceleration takes place as if the apparent reactant concentration felt at the site is enormously raised. The carboxylate group assisted hydrolysis of three phenylacetates and their rate constants (k) are shown below.

(1)



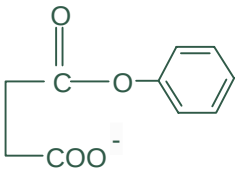
+

$k_1 = 0.002\ s^{-1}$

(when $[CH_3COO^-] = 1\ M$)

(pseudo first order)

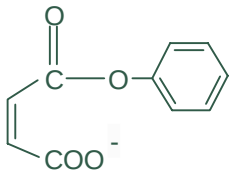
(2)



$k_2 = 0.4\ s^{-1}$

(first order)

(3)



$k_3 = 20\ s^{-1}$

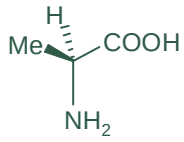
(first order)

g. Calculate the effective local concentration of the COO^- group felt in (2) and (3) above.

h. Why do you see a higher rate in (3) than in (2) ?

Problem 22 Coenzyme chemistry

The protective outer cell wall in bacteria has D-alanine as one of the building blocks. However, metabolically only L-amino acids are available. Bacteria make D-alanine by inverting the L-alanine. The structure of L-alanine is given below :

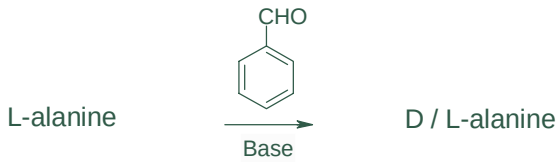


L-alanine

The abstraction of α-proton from L-alanine and reprotonation of the resultant carbanion from the opposite side appears to be a simple process. However, it is not easy to deprotonate alanine unless its NH_2 group is masked and C_α-H is activated as an acid.

Both these steps are brought about by the coenzyme *pyridoxal phosphate* (PLP) in the presence of the enzyme *alanine racemase*. The following observations made in certain model reactions will help you appreciate the role of PLP as the coenzyme.

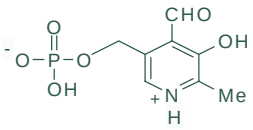
Under favorable experimental conditions, benzaldehyde can be used as a reagent to racemize alanine. In other words, it can mask the amine group and activate the C_α-H of alanine making it more acidic.



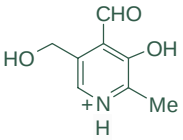
a. Propose a stepwise mechanism for this base catalyzed racemisation of L-alanine involving benzaldehyde as the reagent.

Compared to benzaldehyde, PLP is a somewhat complex molecule. With the help of a few carefully designed aromatic aldehydes, good insight about the role of PLP as a coenzyme can be obtained.

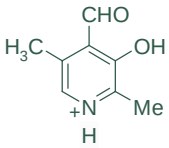
A few relevant structures are presented below. Underneath each, there is an indication about its activity.



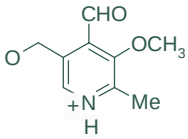
PLP (1)
Active



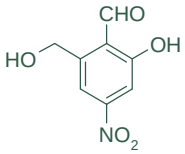
Pyridoxal (2)
Active



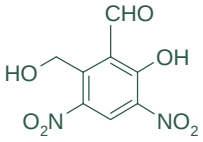
(3)
Active



(4)
Inactive



(5)
Active



(6)
Inactive

b. Based on this information, what inferences can you draw about the structural requirements for PLP to act as a coenzyme?

c. A trivalent metal ion is actually critically needed for any of the above shown compounds to display PLP-like activity without the involvement of the enzyme. Suggest a plausible explanation for the role of the metal ion.

d. PLP is quite a versatile coenzyme. It participates in a variety of biologically important reactions. The activity of PLP is due to its functioning as an electron sink that stabilizes carbanions.

An important illustration of catalytic versatility of PLP is in the biosynthesis of the neurotransmitter gamma amino butyric acid (GABA). As shown below, GABA is

made in a single step from L-glutamic acid. Suggest a mechanism explaining the role of PLP as the coenzyme in this particular reaction.

Glutamic Acid GABA

e. In yet another PLP mediated reaction, L-serine serves as a one-carbon donor in a complex process of nucleotide biosynthesis. The enzyme *serine hydroxymethyltransferase* degrades L-serine with the help of PLP into the simpler amino acid glycine. An important metabolic intermediate (X) is obtained as the side product in this reaction. Identify the one carbon metabolic intermediate formed by analyzing its PLP based mechanism.

L-Serine Glycine

Problem 23 Protein folding

The link between amino acid sequence of a protein (the primary structure) and its precise three-dimensional fold (the tertiary structure) remains one of the most important unsolved mysteries of modern science.

All protein backbones are identical: planar amide units are linked via tetrahedral methylene bridges, the so called α-carbons. Each α-carbon carries an R group of a specific α-amino acid (see the following diagram).

A unique sequence of amino acids characterizes a particular protein, determining how it folds and functions.

a. Every amide group in the polypeptide backbone, including its flanking α-carbons, is a planar unit. Explain.

b. The α-carbons across each amide unit occur in a *trans* geometrical arrangement. However, in case of the amino acid proline, both *cis* and *trans* amide arrangements are almost equally favored. Why?

c. The conformational choices of amino acid residues in a polypeptide chain are stereochemically controlled. For nineteen of the genetically coded amino acids, the conformational choice is largely restricted to the α (folded) and β (extended) regions of the Ramachandran diagram. For the amino acid glycine, however, the conformational choices are much wider. Explain.

d. When a linear polypeptide folds forming a globular protein, an amino acid residue may assume α or β conformation. However it is observed that consecutive residues generally assume α or β conformation, rather than a random combination of α and β. Explain.

e. In an aqueous environment polypeptides generally fold into compact globular protein structures. The reason is (select one)

1. The R groups in polypeptides are largely polar.
2. The R groups in polypeptides are largely nonpolar.
3. Both polar and nonpolar R groups occur in comparable proportion.

Justify your answer.

f. The pattern of R group polarities has an important role in determining whether α-helix or β-sheet will form when a polypeptide folds in water at an apolar surface. Explain the role of R group polarities.

Problem 24 Protein sequencing

Sequencing of a protein (polypeptide) involves the following steps: a) purification, (b) determination of N-terminal amino acid, (c) cleavage of the polypeptide chain by chemical or enzymatic methods, (d) isolation of the peptide fragments and (e) determination of their sequence by an automated sequencing machine (sequenator). It is also possible to sequence the mixture of peptide fragments without resolving it.

The final sequence could be determined by constructing overlapping sequences after analyzing the information on the positional data on amino acids in different fragments.

A small protein, made up of 40 amino acid residues was sequenced as follows :

- Edman degradation involves treatment with phenyl isothiocyanate, subsequent hydrolysis and spectrophotometric identification of the modified amino acid. This procedure identified aspartic acid (Asp) as the N-terminal residue.

- The protein was cleaved with CNBr (cyanogen bromide) which cleaves the peptide bond between methionine and any other amino acid on its C-terminal side. The resulting peptide fragments were not separated. This mixture of peptides was analyzed on the protein sequenator. Therefore, the sequenator would detect as many amino acids in the given position as the number of fragments. The results are shown in Table 1(a).

- The protein was digested with a proteolytic enzyme trypsin. This enzyme cleaves the peptide bond between a basic amino acid (Arg or Lys) and the next C-terminal residue. The resulting mixture of peptides was also analyzed as above. The results are shown in Table 1(b).

Given this information:

a. Deduce the amino acid sequence *common* to the first fragment (N-terminal) obtained by CNBr and trypsin treatments.

b. Deduce the sequence of the first fragment generated by CNBr treatment.

c. Deduce the entire sequence in the original polypeptide. Indicate the CNBr-labile and trypsin-labile sites in this sequence.

d. What percentage of the total residues are basic amino acids?

e. If the polypeptide were to exist as an α helix, what will be the length of this α helical structure?

Table 1. Data from protein sequenator .

Treatment	Position number							
	1	2	3	4	5	6	7	8
a) CNBr: (Met)	Arg Asp Glu Gly	Gln Pro Thr Tyr	Asn Pro Ser Tyr	Arg His Ilu Val	Asn Ilu Leu Phe	Arg His Trp Val	Ala Gly Phe Thr	Ala Lys Met Tyr
b) Trypsin: (Arg or Lys)	Asp Gly Gly Phe Tyr	Cys His Pro Pro Tyr	His Met Thr Tyr	Ala Asn Glu Val	Ilu Leu Thr Trp	Arg Phe Ser Ser	Cys Lys Ilu	Glu Leu

f. What will be the size of the DNA segment (exon) coding for this polypeptide of 40 amino acids? Give the size in base pairs as well as in daltons. (consider average molecular weight of a nucleotide in DNA = 330).

g. Assuming that the DNA corresponding to the exon contains equal numbers of Adenine and Cytosine, calculate the number of H-bonds which will hold this double helix.

Practical Problems

Safety Regulations

The following regulations apply to all laboratories used for the Olympiad. Participating students must be well acquainted with these regulations and should study them seriously. These rules will be strictly followed in the 33rd IChO practical examination. Students who break any of these rules will be given only one warning before they are disqualified from the practical examination.

If any questions arise concerning safety procedures during the practical examination, students should not hesitate to ask the nearest instructor for directions.

All students are required to sign a statement agreeing that they have read and understood the rules prior to the examination.

Rules for personal safety

a. For eye protection, safety goggles must be worn in the laboratories at all times. If the student wears contact lenses, full protection goggles, which provide total seal around eyes, must be worn. All students are requested to bring their safety goggles, but we shall have some in reserve.

b. A long sleeved, knee length laboratory coat is recommended. Long pants and closed-toed shoes must be worn for individual safety. Loose clothing, open style shoes and sandals are prohibited. Long hair must be contained. Each student will have to get her/his own necessary items for herself/himself.

c. Prior to the examination, the demonstrator-in-charge will check all protective equipments to ensure that they are in order.

d. Pipetting by mouth is strictly forbidden.

e. Eating, drinking or smoking in the laboratory is strictly prohibited.

Accidents and first aid

In any chemistry laboratory, accidents can take place due to spillage of chemicals, broken glasswares and fire. Any injury, illness, or incident, however minor, must be reported to the instructor immediately so that proper corrective action can be taken up.

a. Chemicals: Every chemical in the laboratory must be handled with utmost care. Chemicals can be corrosive, flammable or poisonous. Each student should read the safety notes related to the chemicals given in the task before handling them. The following general precautions must be always followed in the laboratory :

- Chemicals should never be tasted. Use pipette bulbs or pipette fillers all the time.
- Spillage on the skin: For any spillage of chemicals, the first step is to flush the skin under cold tap water for 10 to 15 minutes and then seek first aid/or medical help as appropriate. Organic materials tend to get absorbed on the skin, so wash the skin with warm water and soap, after cleaning it with cold water. Contaminated clothing should be removed at the earliest.
- Chemicals in the eye: The proper use of safety goggles will reduce the risk of any eye injury. Even so, if there is any splash of chemicals into the eyes, wash your eyes with cold water for 15 minutes and then look for appropriate medical attention.

b. Fire: Many chemicals are flammable, and hence no open flames are permitted when such chemicals are in use. You should get familiar with the location of the nearest fire extinguisher and fire blanket.

c. Glassware: Glass is a very hard but brittle material, and can break under stress or strain. Please handle the glasswares very carefully. If breakage occurs it is essential that any particles or splinters, specially from the wounds, are removed at the earliest. The injuries must be inspected by the demonstrator-in-charge.

Please report and clean up any breakage of the glassware. Necessary replacements can be obtained from the instructor.

d. Waste Materials: Do not dispose of chemicals in the sink. Please follow all disposal rules provided in the task notes. Waste collection containers will be provided wherever necessary.

e. Care of Benches and Apparatus: Each student is responsible for her/his section of the bench. Any spillage of chemicals or water must be wiped immediately. Concentrated acid spills must be first neutralized with sodium bicarbonate and then washed with plenty of water. Your working area must be kept clean at all times. Chemicals spilled on the ground must be washed and broken glassware must be swept off immediately. Mops, brooms, dust-pans etc will be available from the preparation room.

Some important information regarding the 33rd IChO practical examination

- Time duration for the practical examination would be four and a half hours instead of five hours.
- The examination may consist of three **independent** experimental tasks. The time duration for each task may vary from one to one and a half hour.
- The examination will be conducted in two batches. Students No.1 and 2 from each team will be part of the first batch; students No.3 and 4 will be part of the second batch.
- Students of both batches will get a new set of apparatus for the examination.
- The apparatus for the examination will include both plasticware and glassware.
- The examination will not involve use of microscale apparatus.

Problem 25 Determination of aspirin in the given sample

Acetyl salicylic acid ($CH_3COO.C_6H_4.COOH$) undergoes hydrolysis when boiled gently with aqueous NaOH, which forms a basis for its estimation.

Chemicals and solutions

- Plain aspirin tablets
- 0.1 M Hydrochloric acid **R** : 34, 37 **S** : 26, 45
- 1 M Sodium hydroxide **R** : 35 **S** : 2, 26, 37, 39
- Borax(AR Grade) **S** : 22, 24, 25
- Phenol red indicator **S** : 22, 24, 25

Preparation of 0.1 M HCl solution

9 mL of concentrated HCl is diluted to 1000 mL using freshly prepared distilled water in a standard volumetric flask.

Preparation of 1 M NaOH solution.

Weigh rapidly approximately 10.5 g of NaOH in a small beaker. Dissolve it in minimum amount of distilled water. Transfer the solution in a 250 mL flask and dilute the solution using boiled out distilled water.

Procedure

Standardisation of HCl

Weigh 0.15 g of Borax accurately and transfer it quantitatively in a clean 250 mL conical flask ; add 50 mL of distilled water to the flask. Titrate the resulting solution with HCl, using methyl red indicator until the colour changes from yellow to red.

- ***Calculate the concentration of the HCl solution.***

Blank titration

Dilute the 25 mL of 1 M NaOH solution in a 250 mL standard flask using freshly boiled distilled water. Pipette out 25 mL of the diluted NaOH solution and titrate it against the HCl solution using phenol red as indicator until the colour changes from red to yellow.

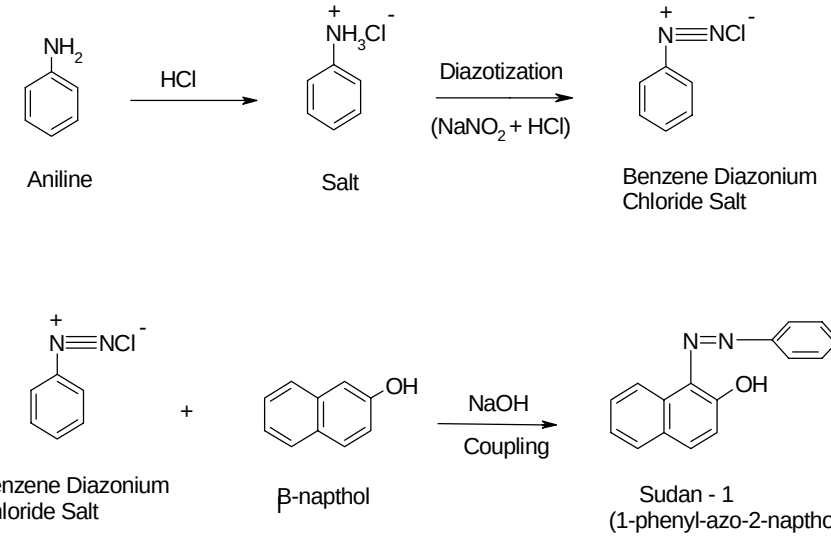
Titration of sample aliquot

Weigh accurately about 1.5 g of the crushed tablet sample and transfer it quantitatively in a 250 mL beaker. Add 25 mL of 1 M NaOH solution with the help of pipette and swirl the content. Boil the mixture gently on a water bath for 15 min and then cool the solution. Transfer the solution to a 250 mL standard flask. Dilute the solution up to the mark with distilled water and mix well. Titrate 25 mL of the diluted solution against the standardised HCl solution using phenol red indicator until the colour changes from red to yellow.

- ***Write down the appropriate chemical reaction for hydrolysis of acetyl salicylic acid.***
- ***Calculate the percentage of aspirin in the sample.***

Problem 26 Synthesis of 1-phenyl-azo-2-naphthol ($C_{16}H_{12}ON_2$)

Reactions



Chemicals and solutions

• Aniline	**R** : 23, 24, 25, 33	**S** : 28, 36, 37, 45
• Concentrated HCl	**R** : 34, 37	**S** : 26, 45
• Solid Sodium Nitrite	**R** : 8, 25	**S** : 44
• β - naphthol	**R** : 20, 22	**S** : 24, 25
• Ethyl Alcohol		
• Urea		**S** : 22, 24, 25
• Sodium Hydroxide	**R** : 35	**S** : 2, 26, 37, 39

Preparation of diazonium salt

Take 1 mL of aniline in a clean 50 mL beaker. Add approximately 5 mL of distilled water to aniline. Place the beaker in an ice-bath. Slowly add 2.5 mL of conc. HCl. Stir the solution with a glass rod to obtain a clear solution. Cool this solution in the ice-bath.

Weigh accurately 0.5 g of sodium nitrite ($NaNO_2$) and transfer it quantitatively in a 15 (or 25) mL test tube. Add 5mL of distilled water (to the test tube) to dissolve $NaNO_2$. Cool the resulting $NaNO_2$ solution in an ice-bath.

Allow both the solutions to attain 0°C temperature. Add sodium nitrite solution in a dropwise manner to the aniline solution with continuous stirring. (During addition, the temperature of the reaction mixture should not rise above 10°C.)

The presence of excess nitrous acid in the reaction mixture is checked using starch iodide paper.

To decompose the excess nitrous acid formed, add a small portion of solid urea. The solution is then filtered. The filtrate contains the diazonium salt.

Coupling reaction

Weigh 0.75 g of powdered β-naphthol in a 50 mL beaker. Add 5 mL of 10% NaOH solution and 5 mL of distilled water to the beaker. Stir well with glass rod to obtain a clear solution. This solution is also cooled in an ice-bath to 0°C.

The ice cooled filtrate containing diazotised salt is added dropwise to the ice cooled solution of β-naphthol with constant stirring. At this stage, an orange-red dye will start precipitating. After the addition of the solution is complete, filter the dye using buchner funnel. Cold water is used for washing the precipitate. Dry the product and record the yield.

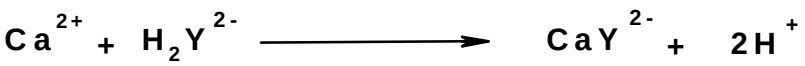
Determination of melting point

Recrystallise a small portion of the organic dye prepared using ethyl alcohol. Gently heat the solution in a water bath (careful!) to dissolve the dye. Filter the hot solution. Cool the filtrate and filter the recrystallised product using Buchner funnel and suction.

- ***Record the weight of the crude product***
- ***Record the melting point of the recrystallised product***.

Problem 27 Determination of calcium in a sample solution

Reaction



Chemical and solutions

- Sample solution containing calcium (prepared from A.R. grade $CaCl_2$) **R** : 36 **S** : 22, 24
- Patton and Reeders indicator

- KOH solution. **R** : 35 **S** : 26, 37, 39, 45
- EDTA disodium salt **R** : 36, 37, 38 **S** : 26, 36

Preparation of 0.01 M EDTA:

Weigh 1.861 g of AR grade Na_2EDTA and quantitatively transfer the same to 500 mL volumetric flask. Add distilled water to the flask to dissolve Na_2EDTA and make up the solution to 500 mL mark with distilled water.

Procedure

Dilute the given sample solution to 100 mL in a 100 mL volumetric flask using distilled water. Pipette out 25 mL of the diluted sample solution in a clean conical flask. Add 25 mL of distilled water and adjust the pH using freshly prepared KOH solution to 12. Check the pH with pH paper. Add a pinch of solid indicator and titrate with Na_2EDTA solution till the colour changes from wine red to blue.

- ***Calculate the amount of calcium in mmoles in 100 mL of the diluted sample*** **solution**

Problem 28 Estimation of methyl ketone by back titration

Methyl ketones like acetone can be estimated by iodinating with excess of standard iodine in an alkaline medium. The unreacted iodine is then back titrated with standard sodium thiosulphate solution.

Chemicals and solutions

- 0.1N Iodine solution **R** : 20, 21 **S** : 23, 25
- 0.1N NaOH **R** : 35 **S** : 2, 26, 37, 39
- Concentrated HCl **R** : 34, 37 **S** : 26, 45
- 1 N H_2SO_4. **R** : 35 **S** : 2, 26, 30
- 0.1 M $Na_2S_2O_3$ **S** : 22, 24, 25

Preparation of 0.1 M $Na_2S_2O_3$:

Weigh 25 g of AR grade $Na_2S_2O_3$ and quantitatively transfer it to a 1 L volumetric flask. Prepare the solution using freshly boiled distilled water. Add 3 drops of chloroform while preparing the solution. Avoid exposure to light.

Preparation of 0.1 N I_2 solution

Dissolve 20 g of iodate-free potassium iodide in 30 - 40 mL of distilled water in a 1 L volumetric flask. Weigh 12.7 g iodine and quantitatively transfer to the concentrated potassium iodide solution. Shake the flask well until all the iodine dissolves and then dilute up to the mark with distilled water.

Procedure

Standardisation of $Na_2S_2O_3$

Weigh out accurately 0.14 to 0.15 g of dry potassium iodate. Dissolve it in 25 mL of distilled and freshly boiled water and add 2 g of iodate free potassium iodide. Add 5 mL of 1N sulphuric acid. Titrate the liberated iodine with thiosulphate solution with constant shaking. When the colour of the solution is pale yellow add 200 mL of distilled water and 2 mL of starch indicator. Continue the titration until the colour changes from blue to colourless.

Determination of ketone

Weigh accurately 0.2 g of the given acetone sample in a clean 50 mL beaker and add minimum amount of distilled water. Transfer the acetone solution to a 250 mL standard volumetric flask. Add distilled water to the flask to prepare acetone solution in water and make up the solution to 250 mL mark with distilled water. Pipette out 10 mL of the acetone solution in a clean conical flask. Add 10 mL of 10% aqueous sodium hydroxide, and stopper the flask. Shake the flask for 10 min. At the end of 10 minutes, add 35 mL of 0.1 N Iodine solution from the burette. Swirl the content, preferably using magnetic stirrer for 5 minutes, and keep it standing for 15 minutes.

Yellow crystals of iodoform will appear. Acidify the solution with H_2SO_4 (check the pH with pH paper).

Titrate the solution against the standardised sodium thiosulphate using starch indicator.

- ***Write down the appropriate chemical reactions for iodination of acetone.***
- ***Calculate the amount of acetone in the given sample solution.***

Problem 29 Determination of phenol in the given sample.

Reactions

$KBrO_3 + 5KBr + 6HCl \rightarrow 6KCl + 3H_2O + 3Br_2 \uparrow$

$C_6H_5OH + 3Br_2 \rightarrow C_6H_2OHBr_3 + 3HBr$

$3Br_2 + 6KI \rightarrow 6KBr + 3I_2 \uparrow$

$6Na_2S_2O_3 + 3I_2 \rightarrow 3Na_2S_2O_3 + 6NaI$

Chemicals and solutions

- 0.3g phenol **R** : 24, 25, 34 **S** : 2, 28, 44
- 0.02M $KBrO_3$ **R** : 9 **S** : 24, 25, 27
- 3M H_2SO_4 **R** : 35 **S** : 2, 26, 30
- KBr
- KI **S** : 22, 24, 25
- 1 M $Na_2S_2O_3$ **S** : 24, 25, 28
- Starch indicator.

Preparation of 0.1 M $Na_2S_2O_3$

Weigh 25 g of AR grade $Na_2S_2O_3$ in a small beaker. Quantitatively transfer it to a 1 L volumetric flask. Prepare the solution using freshly boiled distilled water. Add 3 drops of chloroform while preparing the solution. Avoid exposure to light.

Standardisation of $Na_2S_2O_3$

Weigh out accurately 0.14 to 0.15 g of dry potassium iodate. Dissolve it in 25 mL of fresh, boiled distilled water and add 2 g of iodate free potassium iodide. Add 5 mL of 1N sulphuric acid. Titrate the liberated iodine with thiosulphate solution with constant shaking. When the colour of the solution is pale yellow add 200 mL of distilled water and 2 mL of starch indicator. Continue the titration until the colour changes from blue to colourless.

Procedure

Dissolve the given sample of phenol to 250 mL with distilled water. Take 25 mL of the phenol solution into 250 mL stoppered conical flask. Add 25 mL of standard potassium bromate solution and 0.5 g of potassium bromide. Add 5 mL of 3M sulphuric acid. Stopper the flask immediately. Mix the reagents and let them stand for 15 min (avoid exposure to light). Then, add 2.5 g of potassium iodide rapidly. Re-stopper the flask immediately and swirl the contents of the flask to dissolve the solid.

Titrate the liberated iodine with standard 0.1M $Na_2S_2O_3$ from the burette using starch indicator.

- ***Calculate the amount of phenol per 250 mL of the solution.***

Problem 30 Determination of amount of Fe (III) present in the given sample

Fe (III) in the sample solution is first reduced to Fe (II) in HCl medium using stannous chloride. Excess of stannous chloride is oxidized by addition of mercury (II) chloride. The Fe(II) is then titrated with standard potassium dichromate solution.

Chemicals and solutions

• Sample solution	**R** : 36, 38	**S** : 26, 36
• 0.1N $K_2Cr_2O_7$ solution	**R** : 45, 36, 37, 38, 43	**S** : 53, 22, 28
• Equimolar H_2SO_4 &	**R** : 35	**S** : 2, 26, 30
H_3PO_4 acid mixture	**R** : 34	**S** : 26, 45
• Conc. HCl	**R** : 34, 37	**S** : 26, 45
• 5% $HgCl_2$	**R** : 26, 27, 28	**S** : 13, 28, 45
• 3% $SnCl_2$ solutions	**R**: 22, 36, 37, 38	**S** : 26, 36,
• Diphenylamine indicator.	**R** : 23, 24, 25, 33	**S** : 28, 36, 37, 45

Note : $NH_4Fe(SO_4)_2.12H_2O$ is used to prepare the sample solution

Preparation of 0.1N $K_2Cr_2O_7$ solution

Weigh accurately 1.225 g of pure $K_2Cr_2O_7$ and transfer it to a 250 mL volumetric flask. Prepare the solution using distilled water.

Procedure:

Dilute the given Fe(III) sample solution to 100 mL using the standard volumetric flask. Take 10 mL of the diluted sample solution in a clean conical flask. Add 2 mL of concentrated HCl and boil the solution. To the hot solution, add $SnCl_2$ solution dropwise till the reaction mixture becomes colourless. Add 2 - 3 drops of $SnCl_2$ in excess.

Cool the solution under tap water. Add 2 to 3 mL of $HgCl_2$ solution at once. A white precipitate is obtained at this stage. (If grey precipitate is obtained, reject the sample and start again.)

Add 2 to 3 mL of the acid mixture and 1 drop of the diphenylamine indicator and titrate it against $K_2Cr_2O_7$ solution. Continue the titration until a colour change from colourless to permanent blue or violet is observed.

- ***Write down the appropriate chemical reactions .***
- ***Calculate the amounts of Fe (III) and $NH_4Fe(SO_4)_2 12H_2O$ per 100 mL of the sample solution.***