

# Preparatory Problems

33rd IChO  
2001



33rd International  
Chemistry Olympiad

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Mumbai

India



## **Secretariat 33rd International Chemistry Olympiad**

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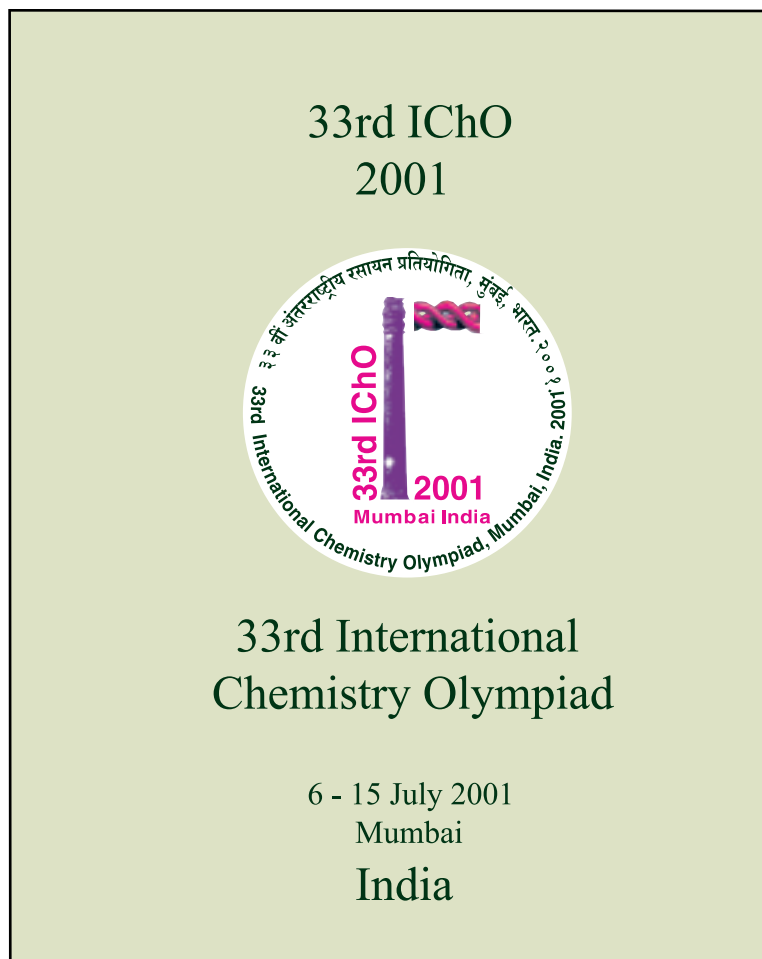
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# Preparatory Problems



Edited by

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33<sup>rd</sup> International Chemistry Olympiad

Edited by Savita Ladage and Arvind Kumar

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### **Homi Bhabha Centre for Science Education**

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**From the 33<sup>rd</sup> IChO Secretariat**

It was only in October 2000 that the idea of India hosting the 33<sup>rd</sup> IChO was finally confirmed. A National Scientific Committee (NSC) was constituted immediately under the chairmanship of Prof N. Sathyamurthy to look after the academic aspects of the 33<sup>rd</sup> IChO. It is a measure of the skills and competence of the NSC members that this set of preparatory problems is ready in such a short time. I cannot adequately thank Prof. N. Sathyamurthy and our distinguished colleagues of the NSC for their tremendous co-operation and efforts. Especially notable is the unremitting work of the chemistry olympiad cell of HBCSE led by Savita Ladage. On behalf of the organizers of the 33<sup>rd</sup> IChO, I express my appreciation and gratitude to all NSC members and the young chemists at the Centre who have provided them such excellent support.

I believe students and mentors of all participating countries will find this collection valuable. I send my greetings and best wishes to everyone. I hope the 33<sup>rd</sup> IChO turns out to be an exciting academic and cultural event, and we are looking forward to welcoming you all here in Mumbai.

**Arvind Kumar**

Chairperson  
National Organising Committee  
33<sup>rd</sup> IChO

## Preface

This collection of preparatory problems for the 33<sup>rd</sup> IChO aims to cover a fairly broad spectrum of topics from the syllabus of the International Chemistry Olympiad. We have endeavoured to see that they highlight significant facts and principles of chemistry and are set around interesting contexts, wherever possible. The practical problems involve both an understanding of chemical principles and the standard laboratory skills expected of students appearing at the chemistry olympiads. They do not require familiarity with handling microscale apparatus. The difficulty level varies from one problem to another; but with help from their teachers, students should be able to work through all problems and experiments in this collection and enhance their level of preparation for the contest. Safety practices and procedures in a chemistry laboratory have been stressed and students should be advised to go through them carefully. We hope this collection will be useful in general to all chemistry students and teachers.

Putting together this set of problems and experiments in the short span of three months has been a demanding task. It has been accomplished only because the National Scientific Committee (NSC) could draw upon the wide range of expertise of its members. The development of practical problems and the co-ordination of efforts in designing theoretical problems was mainly carried out at the Homi Bhabha Centre for Science Education (HBCSE), Mumbai. NSC greatly appreciates the dedicated work done by the chemistry olympiad cell of HBCSE (Savita Ladage and her supporting scientific colleagues, Swapna Narvekar and Rajesh Kumar). I am grateful to all NSC members for their expert help and wonderful co-operation.

On behalf of all the NSC members and on my own, I would like to express our appreciation of the untiring efforts of Professor Arvind Kumar in seeing that this document reached this stage.

I look forward to meeting all participants, observers and guests of the 33<sup>rd</sup> IChO in July this year in Mumbai. My greetings and best wishes to all !

**N.Sathyamurthy**

Chairperson  
National Scientific Committee  
33<sup>rd</sup> IChO

**33<sup>rd</sup> IChO National Scientific Committee**

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Mr. Rajesh Kumar	Homi Bhabha Centre for Science Education (TIFR), Mumbai



## SYLLABUS OF THE INTERNATIONAL CHEMISTRY OLYMPIAD

**Level 1:** These topics are included in the overwhelming majority of secondary school chemistry programs and need not be mentioned in the preparatory problems

**Level 2:** These topics are included in a substantial number of secondary school programs and maybe used without exemplification in the preparatory problems.

**Level 3:** These topics are not included in the majority of secondary school programs and can only be used in the competition if examples are given in the preparatory problems

**1 INORGANIC CHEMISTRY****1.1 Electronic configuration of atoms and ions**

1.1.1	main groups	1
1.1.2	transition metals	2
1.1.3	lanthanide and actinide metals	3
1.1.4	Pauli exclusion principle	1
1.1.5	Hund's rule	1

**1.2 Trends in the periodic table  
(main groups)**

1.2.1	electronegativity	1
1.2.2	electron affinity	2
1.2.3	first ionisation energy	2
1.2.4	atomic size	1
1.2.5	ionic size	2
1.2.6	highest oxidation number	1

**1.3 Trends in physical properties  
(main groups)**

1.3.1	melting point	1
1.3.2	boiling point	1
1.3.3	metal character	1
1.3.4	magnetic properties	2
1.3.5	thermal properties	3
1.3.6	law of Dulong and Petit	1
1.3.7	electrical conductivity	3

**1.4 Structures**

1.4.1	simple molecular structures	2
1.4.2	simple molecular structures with central atom exceeding octet rule	3
1.4.3	ionic crystal structures	3
1.4.4	metal structures	3
1.4.5	stereochemistry	3

**1.5 Nomenclature**

1.5.1	oxidation number	1
1.5.2	main group compounds	1
1.5.3	transition metal compounds	1
1.5.4	simple metal complexes	2
1.5.5	multicenter metal complexes	3

**1.6 Chemical calculations**

1.6.1	balancing equations	1
1.6.2	stoichiometric calculations	1
1.6.3	mass and volume relations	1
1.6.4	empirical formula	1
1.6.5	Avogadro's number	1
1.6.6	concentration calculations	1

**1.7 Isotopes**

1.7.1	counting of nucleons	1
1.7.2	radioactive decay	1
1.7.3	nuclear reactions (alpha, beta, gamma, neutrino)	2

**1.8 Natural cycles**

1.8.1 nitrogen	2
1.8.2 oxygen	2
1.8.3 carbon	2

**1.9 s-Block****1.9.1 Products of reactions of group I and II metals**

1.9.1.1 with water, basicity of the products	1
1.9.1.2 with halogens	1
1.9.1.3 with oxygen	2
1.9.2 heavier s-block elements are more reactive	1
1.9.3 lithium combines with H <sub>2</sub> and N <sub>2</sub> forming LiH and Li <sub>3</sub> N	2

**1.10 p-Block**

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1.10.2 properties of metal hydrides	3
1.10.3 acid-base properties of CH <sub>4</sub> , NH <sub>3</sub> , H <sub>2</sub> O, H <sub>2</sub> S, and hydrogen halides HX	1
1.10.4 NO reacts with O <sub>2</sub> to form NO <sub>2</sub>	1
1.10.5 equilibrium between NO <sub>2</sub> and N <sub>2</sub> O <sub>4</sub>	1
1.10.6 products of reaction of NO <sub>2</sub> with water	1
1.10.7 HNO <sub>2</sub> and its salts are reductants	1
1.10.8 HNO <sub>3</sub> and its salts are oxidants	1
1.10.9 N <sub>2</sub> H <sub>4</sub> is a liquid and reductant	3
1.10.10 there exist acids like H <sub>2</sub> N <sub>2</sub> O <sub>2</sub> , HN <sub>3</sub>	3
1.10.11 reactions of HNO <sub>3</sub> with different metals and reductants	3
1.10.12 reaction of Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> with iodine	2
1.10.13 other thioacids, polyacids, peroxyacids	3
1.10.14 B(III), Al(III), Si(IV), P(V), S(IV), S(VI), O(-II), F(-I), Cl(-I), Cl(I), Cl(III), Cl(V), Cl(VII) are normal oxidation states of 2nd and 3rd row elements in compounds with halogens and in oxoanions	1
1.10.15 compounds of non-metals with other oxidation states	3
1.10.16 the preferred oxidation states are Sn(II), Pb(II) and Bi(III)	2

1.10.17 products of reactions of non-metal oxides with water and stoichiometry of resulting acids	1
1.10.18 reactions of halogens with water	2
1.10.19 reactivity and oxidising power of halogens decrease from F <sub>2</sub> to I <sub>2</sub>	1
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1.11.1 common oxidation states of the common d-block metals are Cr(III), Cr(VI), Mn(II), Mn(IV), Mn(VII), Fe(II), Fe(III), Co(II), Ni(II), Cu(I), Cu(II), Ag(I), Zn(II), Hg(I), and Hg(II)	1
1.11.2 colours of the listed common ions in aqueous solutions	2
1.11.3 other oxidation states and chemistry of other d-block elements	3
1.11.4 Cr, Mn, Fe, Co, Ni, Zn dissolve in dilute HCl; Cu, Ag, Hg do not dissolve	1
1.11.5 products of dissolution are (2+) cations	2
1.11.6 passivation of Cr, Fe (and also Al)	2
1.11.7 Cr(OH) <sub>3</sub> and Zn(OH) <sub>2</sub> are amphoteric, other common hydroxides are not	1
1.11.8 MnO <sub>4</sub> <sup>-</sup> , CrO <sub>4</sub> <sup>2-</sup> , Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> are strong oxidants	1
1.11.9 products of reduction of MnO <sub>4</sub> <sup>-</sup> depending on pH	2
1.11.10 polyanions other than Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	3

**1.12 Other inorganic problems**

1.12.1 industrial production of H <sub>2</sub> SO <sub>4</sub> , NH <sub>3</sub> , Na <sub>2</sub> CO <sub>3</sub> , Na, Cl <sub>2</sub> , NaOH,	1
1.12.2 chemistry of lanthanides and actinides	3
1.12.3 chemistry of noble gases	3

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2.1.3 chemical equilibria expressed in terms of partial pressures	2

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2.2.2	Broensted-Lowry theory, conjugated acids and bases	1	2.4.11	calculation of rate constant for 1st order reaction	2
2.2.3	definition of pH	1	2.4.12	calculation of rate constant for second, third order reaction	3
2.2.4	ionic product of water	1	2.4.13	calculation of activation energy from experimental data	3
2.2.5	relation between $K_a$ and $K_b$ for conjugated acids and bases	1	2.4.14	basic concepts of collision theory	3
2.2.6	hydrolysis of salts	1	2.4.15	basic concepts of transition state theory	3
2.2.7	solubility product - definition	1	2.4.16	opposing, parallel and consecutive reactions	3
2.2.8	calculation of solubility (in water) from solubility product	1	<b>2.5 <u>Thermodynamics (First law)</u></b>		
2.2.9	calculation of pH for weak acid from $K_a$	1	2.5.1	system and its surroundings	2
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2.4.5	1st order reactions: time dependence of concentration	2	2.7.2	van der Waals gas law	3
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3.1.2 naming (IUPAC)	1	3.6.2 exchange of halogens	3
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<b>3.1.4 substitution (e.g. with Cl<sub>2</sub>)</b>		3.6.4 ionic mechanism of substitution	2
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3.8.4.4 addition of NaHSO<sub>3</sub> 2  
3.8.4.5 addition of NH<sub>2</sub>OH 2  
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3.8.4.8 Cannizzaro (PhCH<sub>2</sub>OH  
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3.10.2 equivalence of oxygen atoms in  
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3.10.3.2 preparation from nitriles 2  
3.10.3.3 products of reaction with  
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3.10.3.5 isotopes in mechanism  
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3.10.3.7 preparation of acid chlorides 2  
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3.10.3.11 oxalic acid, name and formula 1  
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- 3.11.4 identification of primary/sec./tert./  
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3.12.3 preparation of soaps 1  
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3.12.7 phenol + aldehydes 3  
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3.12.9 polymers cross linking 3  
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- 4.1.1 ionic structure of amino acids 1  
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4.1.3 20 amino acids (classification in  
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4.1.4 20 amino acids (names and  
structures) 3  
4.1.5 ninhydrin reaction (including  
equation) 3  
4.1.6 separation by chromatography 3

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4.2.3	sequence analysis	3	4.5.11 photosynthesis (products only)	2
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4.2.8	quaternary structure	3	4.6.2 intermediate compounds in the cycle	3
4.2.9	separation of proteins (molecule size and solubility)	3	4.6.3 formation of water and ATP (no details)	3
4.2.10	metabolism of proteins (general)	3	4.6.4 FMN and cytochromes	3
4.2.11	proteolysis	3	4.6.5 calculation of ATP amount for 1 mole of glucose	3
4.2.12	transamination	3	<b>4.7 <u>Nucleic acids and protein synthesis</u></b>	
4.2.13	four pathways of catabolism of amino acids	3	4.7.1 pyrimidine, purine	2
4.2.14	decarboxylation of amino acids	3	4.7.2 nucleosides and nucleotides	3
4.2.15	urea cycle (only results)	3	4.7.3 formulas of all pyrimidine and purine bases	3
<b>4.3 <u>Fatty acids and fats</u></b>				
4.3.1	IUPAC names from C <sub>4</sub> to C <sub>18</sub>	2	4.7.4 difference between ribose and 2-deoxyribose	3
4.3.2	trivial names of most important (ca. 5) fatty acids	2	4.7.5 base combination CG and AT	3
4.3.3	general metabolism of fats	2	4.7.6 base combination CG and AT – (hydrogen bonding structure)	3
4.3.4	beta-oxidation of fatty acids (formulas and ATP balance)	3	4.7.7 difference between DNA and RNA	3
4.3.5	fatty acids and fats anabolism	3	4.7.8 difference between mRNA and tRNA	3
4.3.6	phosphoglycerides	3	4.7.9 hydrolysis of nucleic acids	3
4.3.7	membranes	3	4.7.9 semiconservative replication of DNA	3
4.3.8	active transport	3	4.7.11 DNA-ligase	3
<b>4.4 <u>Enzymes</u></b>				
4.4.1	general properties, active centres	2	4.7.12 RNA synthesis (transcription) without details	3
4.4.2	nomenclature, kinetics, coenzymes, function of ATP, etc.	3	4.7.13 reverse transcriptase	3
<b>4.5 <u>Saccharides</u></b>				
glucose and fructose:				
4.5.1	- chain formulas	2	4.7.14 use of genetic code	3
4.5.2	- Fischer projections	2	4.7.15 start and stop codons	3
4.5.3	- Haworth formulas	3	4.7.16 translation steps	3
4.5.4	osazones	3	<b>4.8 <u>Other biochemical problems</u></b>	
4.5.5	maltose as reducing sugar	2	4.8.1 hormones, regulation	3
4.5.6	difference between starch and cellulose	2	4.8.2 hormones, feedback	3
4.5.7	difference between alpha- and		4.8.3 insulin, glucagon, adrenaline	3
			4.8.4 mineral metabolism (no details)	3
			4.8.5 ions in blood	3

4.8.6 buffers in blood	3	7.7 molecular orbital diagram: H <sub>2</sub> molecule	2
4.8.7 haemoglobin; function and skeleton	3	7.8 molecular orbital diagram: N <sub>2</sub> and O <sub>2</sub> molecules	3
4.8.8 haemoglobin; diagram of oxygen absorption	3	7.9 bond orders in O <sub>2</sub> , O <sub>2</sub> <sup>+</sup> , O <sub>2</sub> <sup>-</sup>	3
4.8.9 steps in clotting the blood	3	7.9 unpaired electrons and paramagnetism	2
4.8.10 antigens and antibodies	3	7.10 Hückel theory for aromatic compounds	3
4.8.11 blood groups	3	7.12 Lewis acids and bases	2
4.8.12 acetyl choline, structure and functions	3	7.13 hard and soft Lewis acids	3

## OTHER PROBLEMS

### 5. Analytical chemistry

5.1 choice of indicators for acidimetry	1
5.2 titration curve; pH (strong and weak acid)	2
5.3 EMF (redox titration)	2
5.4 calculation of pH of simple buffer solution	2
5.5 identification of Ag <sup>+</sup> , Ba <sup>2+</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>	1
5.6 identification of Al <sup>3+</sup> , NO <sub>2</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , Bi <sup>3+</sup>	2
5.7 identification of VO <sub>3</sub> <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , Ti <sup>4+</sup>	3
5.8 use of flame tests for identification of K, Ca a Sr	1
5.9 Beer-Lambert law	2

### 6. Complexes

6.1 writing down complexation reactions	1
6.2 definition of coordination number	1
6.3 prediction of coordination number of complex ions and molecules	3
6.4 complex formation constants (definition)	2
6.5 E <sub>g</sub> and T <sub>2g</sub> terms: high and low spin octahedral complexes	3
6.6 calculation of solubility of AgCl in NH <sub>3</sub> (from K <sub>s</sub> and constants β)	3
6.7 cis and trans forms	3

### 7. Theoretical chemistry

7.1 energy levels of hydrogen atom (formula)	2
7.2 square of the wave function and probability	3
7.3 understanding the simplest Schrödinger equation	3
7.4 n, l, m quantum numbers	2
7.5 shape of p-orbitals	2
7.6 d orbital stereoconfiguration	3

### 8. Instrumental methods of determining structure

#### 8.1 UV-VIS spectroscopy

8.1.1 identification of aromatic compound	3
8.1.2 identification of chromophore	3

#### 8.2 Mass spectra

recognition of:

8.2.1- molecular ion	3
8.2.2- fragments with a help of a table	3
8.2.3 typical isotope distribution	3

#### 8.3 Infrared spectra

8.3.1 interpretation using a table of group frequencies	3
8.3.2 recognition of hydrogen bonds	3
8.3.3 Raman spectroscopy	3

#### 8.4 NMR

8.4.1 interpretation of simple spectrum (like ethanol)	3
8.4.2 spin-spin coupling	3
8.4.3 coupling constants	3
8.4.4 identification of o- and p- substituted benzene	3
8.4.5 <sup>13</sup> C- NMR	3

#### 8.5 X-rays

8.5.1 Bragg law	3
8.5.2 electron density diagram	3
8.5.3 coordination number	3
8.5.4 unit cell	3

structures:

8.5.5- of NaCl	3
8.5.6- of CsCl	3
8.5.7- close-packed (2 types)	3
8.5.8 determining of the Avogadro constant from X-ray data	3

## 8.6 Polarimetry

8.6.1 calculation of specific rotation angle	3
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## Syllabus for the Experimental Part of the IChO Competition

- Level 1** is assigned to the basic experimental activities which are supposed to be mastered by competitors very well.
- Level 2** is assigned to the activities which are parts of school experimental exercises in developed countries and the authors of IChO tasks may incorporate them into the tasks without being bounded to mention it in advance.
- Level 3** is assigned to such activities which are not in the chemistry syllabus in the majority of participating countries and the authors are obliged to mention them in the set of preparatory tasks.

- |  |  |   |
|--|--|---|
| <b>1. <u>Synthesis of inorganic and organic compounds</u></b>              | 1.25 washing of precipitates on a filter   | 2 |
| 1.1 heating with burners and hotplates                                     | 1.26 drying of precipitates on a filter with appropriate solvents                            | 2 |
| 1.2 heating of liquids   | 1.27 recrystallization of substances from aqueous solution                                   | 1 |
| 1.3 handling the work with inflammable substances and materials            | 1.28 recrystallization of substances from a known organic solvent                            | 2 |
| 1.4 measuring of masses (analytical balance)                               | 1.29 practical choice of an appropriate solvent for recrystallization of a substance         | 3 |
| 1.5 measuring of volumes of liquids (measuring cylinder, pipette, burette) | 1.30 drying of substances in a drying box  | 2 |
| 1.6 preparation of solutions from a solid compound and solvent             | 1.31 drying of substances in a desiccator  | 2 |
| 1.7 mixing and dilution of solutions                                       | 1.32 connecting and using of a gas washing bottle  | 2 |
| 1.8 mixing and stirring of liquids   | 1.33 extraction with an immiscible solvent   | 1 |
| 1.9 using mixer and magnetic stirrer                                       |  |   |
| 1.10 using a dropping funnel   |  |   |
| 1.11 syntheses in flat bottom vessels – general principles                 |  |   |
| 1.12 syntheses in round bottom vessels – general principles                | <b>2. <u>Identification of inorganic and organic compounds- general principles</u></b>       |   |
| 1.13 syntheses in a closed apparatus – general principles                  | 2.1 test-tube reactions  | 1 |
| 1.14 using microscale equipment for synthesis                              | 2.2 technique of reactions performed in a dot dish and on a filter paper                     | 1 |
| 1.15 apparatus for heating of reaction mixture under reflux                | 2.3 group reactions of some cations and anions specified by the organizer                    | 2 |
| 1.16 apparatus for distillation of liquids at normal pressure              | 2.4 selective reactions of some cations and anions specified by the organizer                | 2 |
| 1.17 apparatus for distillation of liquids at reduced pressure             | 2.5 specific reactions of some cations and anions specified by the organizer                 | 3 |
| 1.18 apparatus for steam distillation                                      | 2.6 identification of elements by flame coloration (using a platinum wire/MgO rod, Co-glass) | 2 |
| 1.19 filtration through flat paper filter                                  | 2.7 using a hand spectroscope/   |   |
| 1.20 filtration through a folded paper filter                              |  |   |
| 1.21 handling a water vacuum pump  |  |   |
| 1.22 filtration through a Büchner funnel                                   |  |   |
| 1.23 suction through a glass filter  |  |   |
| 1.24 washing of precipitates by decantation                                |  |   |

- Bunsen spectroscope 3
- 2.8 melting point determination with Kofler  
or similar type of apparatus 3
- 2.9 qualitative evidence of basic functional  
groups of organic substances  
specified by the organizer 2
- 2.10 exploitation of some specific reactions  
for identification of organic compounds  
(specified by the organizer) 3

### 3. Determination of some inorganic and organic compounds - general principles

- 3.1 quantitative determinations using  
precipitation reactions 2
- 3.2 igniting of a precipitate in a crucible 1
- 3.3 quantitative volumetric  
determinations 1
- 3.4 rules at titrating 1
- 3.5 use of a pipetting ball 1
- 3.6 preparation of a standard solution 2
- 3.7 alkalimetric and acidimetric  
determinations 2
- 3.8 color transitions of indicators at a  
alkalimetric and acidimetric  
determinations 2
- 3.9 direct and indirect determinations  
(back titration) 3
- 3.10 manganometric determinations 3
- 3.11 iodometric determinations 3
- 3.11 other types of determinations on  
basis of redox reactions 3
- 3.13 complexometric determinations 3
- 3.14 color transitions of solutions  
at complexometric determinations 3
- 3.15 volumetric determinations  
on basis of precipitation reactions 3
- 3.16 thermometric titration 3

### 4. Special measurements and procedures

- 4.1 measuring with a pH-meter 2
- 4.2 chromatography on thin layers 3
- 4.3 column chromatography 3
- 4.4 separation on ion exchanger 3
- 4.5. measuring of UV-VIS absorbances  
with a spectral photometer 3
- 4.6. performing of conductivity  
measurements 3

### 5. Evaluation of results

- 5.1 Estimation of experimental errors  
(significant figures, plots scales) 1

### 6. If the organizer wants to apply a technique which is not mentioned in the above syllabus, this technique is set to level 3 automatically.



**Values of Some Fundamental Constants**

Avogadro number       $N_A$     =  $6.022 \times 10^{23} \text{ mol}^{-1}$

Faraday constant       $F$       =  $96485 \text{ C mol}^{-1}$

Gas constant           $R$       =  $8.314 \text{ J. K}^{-1} \cdot \text{mol}^{-1}$

Planck's constant       $h$       =  $6.626 \times 10^{-34} \text{ J.s}$

Mass of electron       $m_e$     =  $9.110 \times 10^{-31} \text{ kg}$

**Notes:**

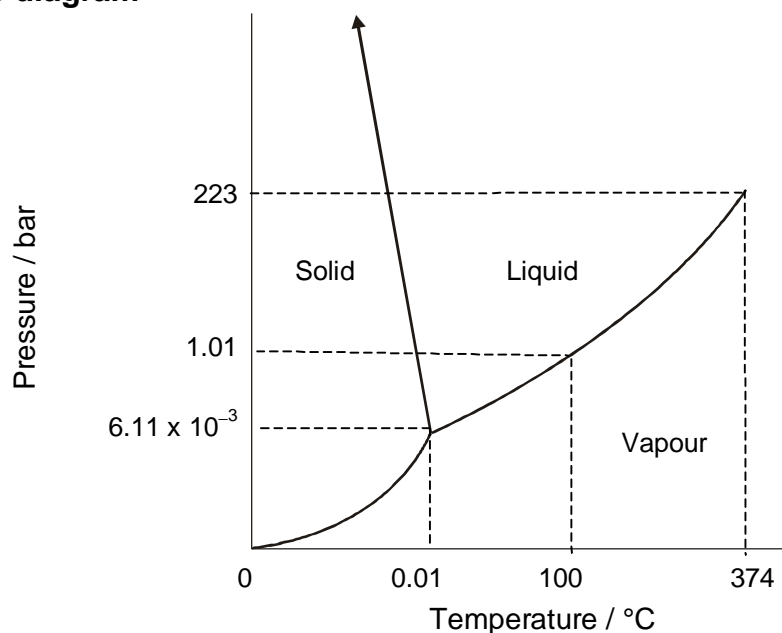
1. The symbol  $[X]$  denotes concentration of X. It may carry the unit  $\text{mol L}^{-1}$  or, in some places, may denote concentration relative to the standard concentration of 1M, in which case it is dimensionless. The particular usage should be obvious from the context. All equilibrium constants are dimensionless.
2. The knowledge of mathematics required for the contest problems of the 33rd IChO will be no more than that indicated by the problems in this collection.

## 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)

- At what temperature and pressure do all the three phases of water coexist in equilibrium?
- What is the effect of decrease of pressure on boiling point of water and melting point of ice, as seen from the phase diagram?
- The liquid-vapour coexistence curve ends at the point  $P_c = 223$  bar and  $T_c = 374^\circ\text{C}$ . What is the significance of this point?
- 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, sublime 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

$$\bar{V}_l = 3.15 \times 10^{-5} \text{ m}^3 \quad \bar{V}_v = 15.8 \times 10^{-5} \text{ m}^3$$

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<sup>-1</sup> 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<sup>-1</sup>. Estimate the pressure at which water and ice are in equilibrium at – 0.200°C. Density of ice = 917 kg m<sup>-3</sup> and density of water = 1000 kg m<sup>-3</sup>. 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 :

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

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

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

- 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  $-12.0^{\circ}\text{C}$ .

## 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 :

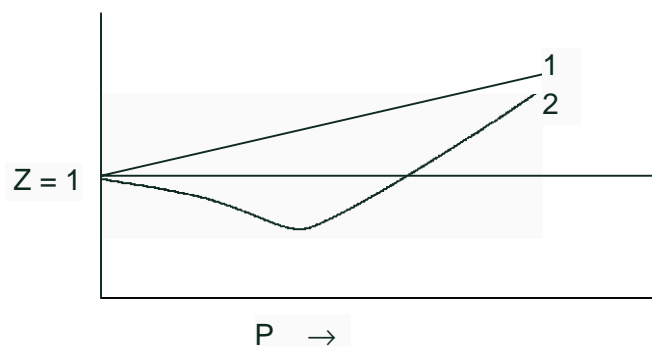
$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

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  $\text{N}_2$  is shown schematically in the following figure.

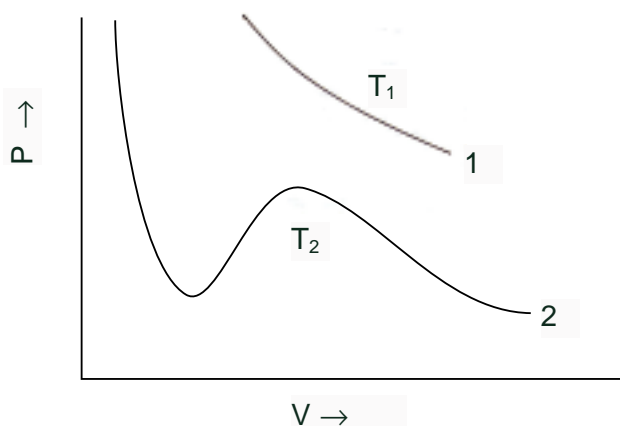
For He,  $a = 3.46 \times 10^{-2} \text{ bar L}^2 \text{ mol}^{-2}$  and  $b = 2.38 \times 10^{-2} \text{ Lmol}^{-1}$

For  $\text{N}_2$ ,  $a = 1.37 \text{ bar L}^2 \text{ mol}^{-2}$  and  $b = 3.87 \times 10^{-2} \text{ Lmol}^{-1}$



Identify the graph corresponding to He and N<sub>2</sub>.

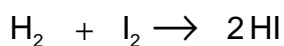
- c. Two P-V isotherms of a van der Waals gas are shown below schematically. Identify the one that corresponds to a temperature lower than the critical temperature ( $T_c$ ) of the gas.



- 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<sub>2</sub> is liquefied more readily than He.
- e. Determine the work done by 1 mol of N<sub>2</sub> 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

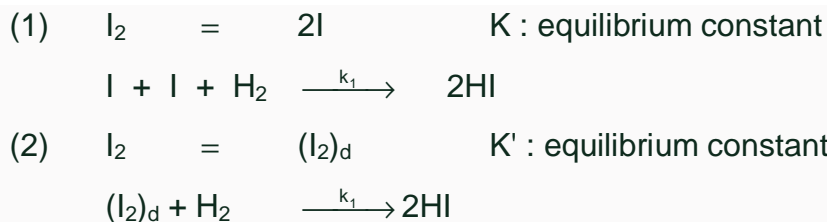




the observed rate law is

$$-\frac{d[\text{H}_2]}{dt} = k [\text{H}_2] [\text{I}_2]$$

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 :



where  $(\text{I}_2)_d$  represents a dissociative state of  $\text{I}_2$ . 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 :

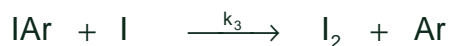
T(K)	$k$ ( $\text{L mol}^{-1} \text{s}^{-1}$ )
373.15	$8.74 \times 10^{-15}$
473.15	$9.53 \times 10^{-10}$

- i. Determine the activation energy  $E_a$ .
- ii. The bond dissociation energy of  $\text{I}_2$  is  $151 \text{ kJ mol}^{-1}$ . Justify why the second step in each mechanism is rate determining.
- c. The change in internal energy ( $\Delta U$ ) for the reaction is  $-8.2 \text{ kJ mol}^{-1}$ . 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:



whose activation energy is about  $-6 \text{ kJ mol}^{-1}$ .

One of the proposed mechanisms of this reaction is :



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

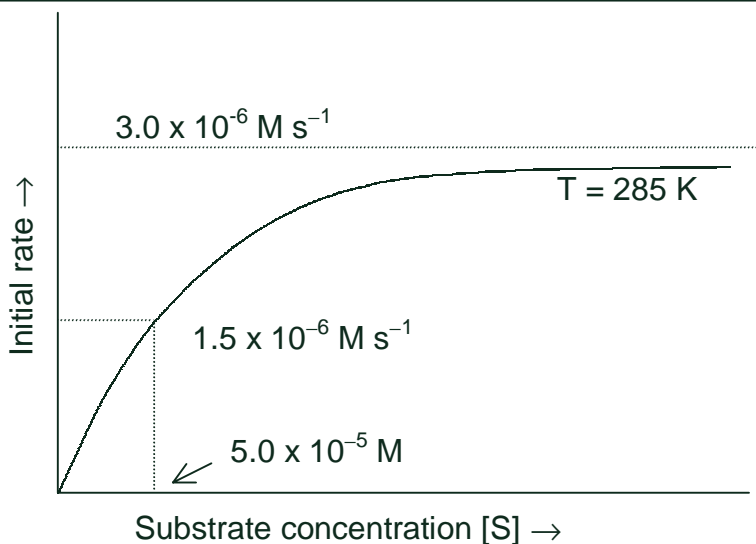
Enzymes play a key role in many chemical reactions in living systems. Some enzyme-catalysed reactions are described in a simple way by the Michaelis-Menten mechanism, as given below.



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.

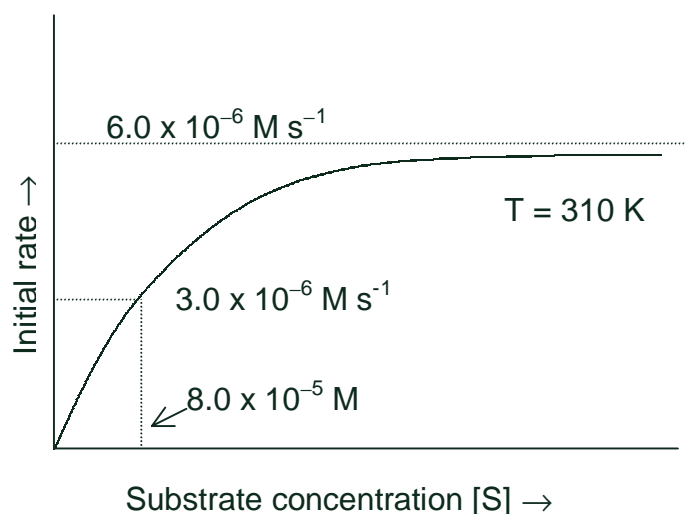
Ignore the backward rate for the second step. Also assume that the enzyme equilibrates with its substrate very quickly.

- 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  $1.5 \times 10^{-9} \text{ M}$ . 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  $[S] = 1.0 \times 10^{-4} \text{ M}$ .
  - 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.

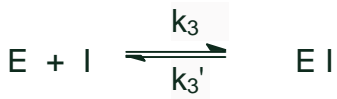


- c. One interesting application of the ideas above is the way enzyme catalysed reactions inactivate antibiotics. The antibiotic penicillin is, for example, inactivated by the enzyme penicillinase secreted by certain bacteria. This enzyme has a single active site. Suppose, for simplicity, that the rate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



- 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  $5.0 \times 10^{-5}$ .

### 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  $\psi$  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

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

- 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  $\pi$  electrons assumed to move freely in a line consisting of three carbon-carbon bonds, each of approximately the same length ( $1.4 \times 10^{-10}$  m), with an additional length of  $1.4 \times 10^{-10}$  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  $\phi$  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  $\lambda$  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

$$\psi_{1s} = e^{-r/a_0},$$

where  $a_0$  is the Bohr radius ( $a_0 = 5.3 \times 10^{-11}$  m) and  $r$  is the radial coordinate (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 :

$$\psi_{2s} = \left(2 - \frac{r}{a_0}\right) e^{-\frac{r}{2a_0}}$$

$$\psi_{2p_z} = \left(\frac{r}{a_0}\right) \cos \theta e^{-\frac{r}{2a_0}}$$

$$\psi_{3d_z^2} = \left(\frac{r^2}{a_0^2}\right) (3 \cos^2 \theta - 1) e^{-\frac{r}{3a_0}}$$

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,  $Z_{\text{eff}}$ . The ionization energy for a helium atom in its ground state is known experimentally to be 24.46 eV. Estimate  $Z_{\text{eff}}$ .

## B. Molecular orbitals

Molecular orbitals of a hydrogen molecule ion ( $\text{H}_2^+$ ) 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:

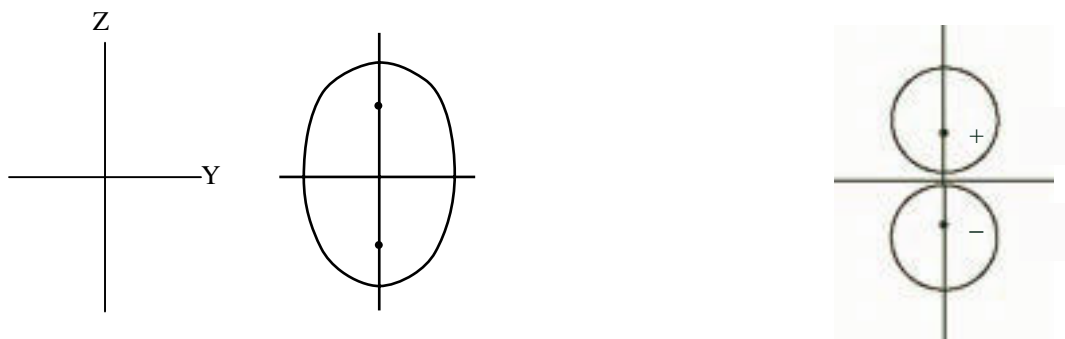
$$\psi_1 = \psi_{1s}^A + \psi_{1s}^B$$

$$\tilde{\psi}_1 = \psi_{1s}^A - \psi_{1s}^B$$

$$\psi_2 = \psi_{2s}^A + \psi_{2s}^B$$

$$\tilde{\psi}_2 = \psi_{2s}^A - \psi_{2s}^B$$

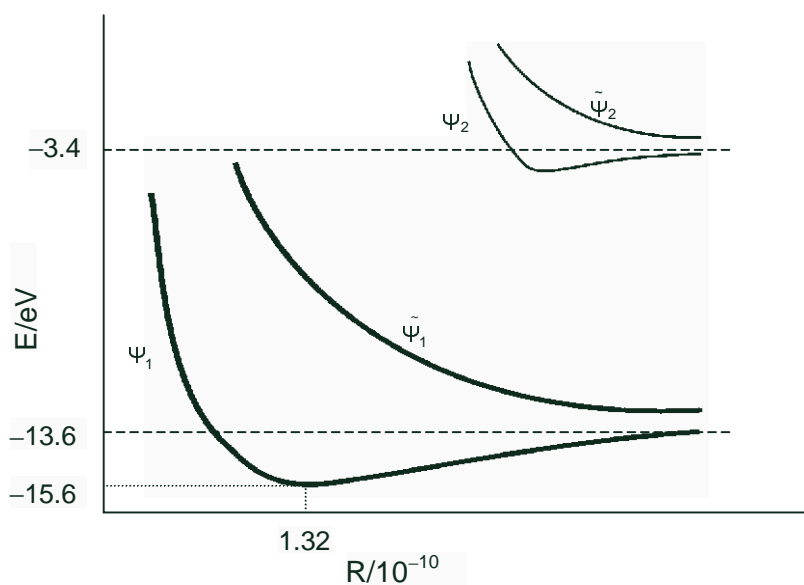
Taking the z-axis along the line joining the two nuclei, the orbital contours of  $\psi_1$  and  $\tilde{\psi}_1$  are shown schematically below :



Similar orbital contours (curves on which the value of  $\psi$  is constant) can be drawn for  $\psi_2$  and  $\tilde{\psi}_2$ .

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





- Identify the bonding and antibonding orbitals. State qualitatively what makes one orbital bonding and another antibonding.
- Determine the values of the equilibrium internuclear distance  $R_e$  and the dissociation energy  $D$  of the ground state of  $H_2^+$ .
- If the molecular ion  $H_2^+$  is excited to the state  $\psi_2$ , 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  $H_2^+$ .

- Explain why the ground state total electron spin of the neutral  $H_2$  molecule is zero.
- Write down the electronic configuration of the first excited state of  $H_2$  molecule. Predict if it will stay bound or dissociate.
- 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

- Consider the following fission reactions of  $^{235}_{92}\text{U}$  by thermal neutrons :



Identify the missing species and numbers.

- b.** Consider the first of the reactions above. The unstable fission fragments undergo successive  $\beta$ -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 :

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

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

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

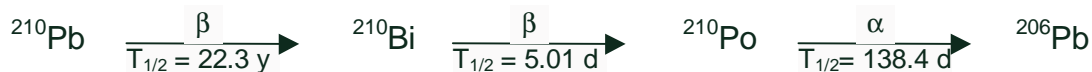
$$m_n = 1.00866 \text{ u}$$

$$1 \text{ u} = 931.5 \text{ MeV}/c^2$$

- 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  $^{235}\text{U}$  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  $^{235}\text{U}$  only.

### Problem 8 Radioactive decay

The radioactive isotope  $^{210}\text{Bi}$  is the daughter product of  $^{210}\text{Pb}$  and decays by  $\beta$ -emission to  $^{210}\text{Po}$ , which is also radioactive.  $^{210}\text{Po}$  decays by  $\alpha$ -emission to the stable  $^{206}\text{Pb}$ .



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

- a.** What is the initial mass of the sample ( $^{210}\text{Bi}$ )?
- b.** Calculate the time it takes for the amount of  $^{210}\text{Po}$  in the sample to grow to its maximum value. How much is the maximum amount of  $^{210}\text{Po}$ ?

- c. Determine the  $\alpha$ -disintegration rate of  $^{210}\text{Po}$  and  $\beta$ -disintegration rate of  $^{210}\text{Bi}$  at that time.

### Problem 9 Redox reactions

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



- 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  $\text{Sn}^{2+}$  is titrated with 0.20 M  $\text{Fe}^{3+}$  solution, calculate the voltage of the cell
- i. when 5 mL of  $\text{Fe}^{3+}$  solution is added.
  - ii. at the equivalence point.
  - iii. when 30 mL  $\text{Fe}^{3+}$  of the solution is added.

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

- c. One of the important analytical methods for estimation of  $\text{Cu}^{2+}$  is iodometric titration. In this reaction  $\text{Cu}^{2+}$  is reduced to  $\text{Cu}^{+}$  by  $\text{I}^{-}$  and the liberated  $\text{I}_2$  is then titrated with standard  $\text{Na}_2\text{S}_2\text{O}_3$  solution. The redox reaction is as follows:



Electrode potentials of the relevant half-cells are:



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

- i.  $\text{CuI}$  has low solubility in water with  $K_{\text{sp}} \approx 1.1 \times 10^{-12}$ . Calculate the effective  $E^\circ$  value for the equilibrium  $\text{CuI}_{(\text{s})} = \text{Cu}^+ + \text{I}^-$ .
- ii. Using the result in i., calculate the effective  $E^\circ$  value for the reduction of  $\text{Cu}^{2+}$  by  $\text{I}^-$ . 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 ( $2.06 \times 10^{-4}$  at  $\text{pH} = 7.0$ ). 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  $\text{pH} = 5.0$ . The first and second dissociation constants for oxalic acid are  $5.6 \times 10^{-2}$  and  $6.2 \times 10^{-5}$  respectively.
- b. In the presence of ammonia in aqueous solution, silver ion forms two complexes  $\text{Ag}(\text{NH}_3)^+$  and  $\text{Ag}(\text{NH}_3)_2^+$ . The values of the stepwise stability constants for the formation of these complexes are  $1.59 \times 10^3$  and  $6.76 \times 10^3$ . What is the solubility of silver oxalate in an aqueous solution that contains  $0.02 \text{ M NH}_3$  and has  $\text{pH} = 10.8$ ?

### Problem 11 Spectrophotometry

- a. Manganese and chromium in steel can be determined simultaneously by absorption spectral method. Dichromate and permanganate ions in  $1 \text{ M H}_2\text{SO}_4$  ( $\text{Cr}_2\text{O}_7^{2-}$  and  $\text{MnO}_4^-$ ) absorb at  $440 \text{ nm}$  and  $545 \text{ nm}$ . At these wavelengths, molar absorptivity of  $\text{MnO}_4^-$  is  $95 \text{ Lmol}^{-1}\text{cm}^{-1}$  and  $2350 \text{ Lmol}^{-1}\text{cm}^{-1}$  respectively and that of  $\text{Cr}_2\text{O}_7^{2-}$  is  $370 \text{ Lmol}^{-1}\text{cm}^{-1}$  and  $11 \text{ Lmol}^{-1}\text{cm}^{-1}$  respectively.

A steel sample, weighing 1.374g was dissolved and Mn and Cr in the resulting solution oxidised to  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$ . The solution was diluted with 1M  $\text{H}_2\text{SO}_4$  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  $\text{H}_2\text{SO}_4$  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  $\text{CoL}_3^{2+}$  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     $[\text{Co(II)}] = 8 \times 10^{-5}$     and     $[\text{L}] = 2 \times 10^{-5}$  .

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

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  $\text{CoL}_3^{2+}$
- ii.    stability constant for the formation of the complex  $\text{CoL}_3^{2+}$ .

## Problem 12 Reactions in buffer medium

An organic nitro-compound ( $\text{RNO}_2$ ) is electrolytically reduced in an aqueous acetate buffer solution having total acetate concentration ( $\text{HOAc} + \text{OAc}^-$ ) 0.500 and  $\text{pH} = 5.0$ . 300 mL of the buffered solution containing 0.01M  $\text{RNO}_2$  was reduced completely. The dissociation constant for acetic acid is  $1.75 \times 10^{-5}$  at 25 °C. The reduction reaction is



Calculate the pH of the solution on completion of the reduction of  $\text{RNO}_2$ .

**Problem 13 Identification of an inorganic compound**

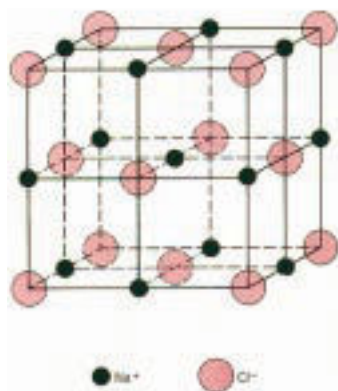
Some observations related to an unknown inorganic substance **A** are presented below.

- ◆ **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  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  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  $\text{NH}_4\text{OH}$  is added, though a gelatinous white precipitate **D** is formed in its place with excess  $\text{NH}_4\text{OH}$ .
  - ◆ Precipitate **D** is filtered off and is dissolved in excess  $\text{NaOH}$  to give a clear solution **E**.
  - ◆ When  $\text{CO}_2$  is passed through solution **E**, compound **D** is reprecipitated.
  - ◆ Substance **A** dissolves unchanged in dry ether. When this solution is reacted with  $\text{LiH}$ , a product **F** is formed. If  $\text{LiH}$  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**

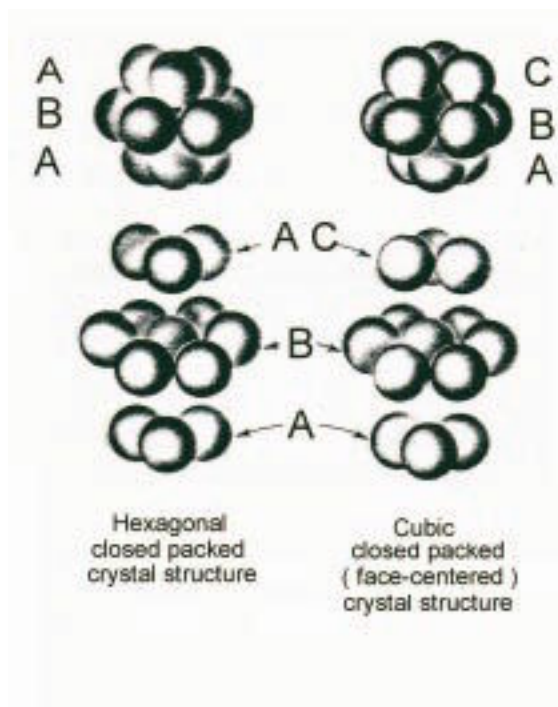
Modern methods of structural analysis using X-rays provide valuable information about the three dimensional arrangement of atoms, molecules or ions in a given crystal structure.

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  $r_{\text{Na}^+} / r_{\text{Cl}^-}$  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 -  $K_{\alpha}$  X-ray ( $\lambda = 154\text{pm}$ ) reflection from (200) planes of sodium chloride crystal is observed at  $15.8^\circ$ . 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  $8.902 \text{ g cm}^{-3}$ , 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  $\text{NO}_2$ , a red-brown colored reactive gas.



- i. Draw the Lewis structure of  $\text{NO}_2$  and predict its shape using valence shell electron pair repulsion theory.
  - ii. Using VSEPR, predict the shapes of the  $\text{NO}_2^-$  and  $\text{NO}_2^+$  ions. Compare the shapes of these two ions with that of  $\text{NO}_2$ .
- b. Consider two other compounds of nitrogen, trimethylamine ( $\text{Me}_3\text{N}$ ) and trisilylamine ( $(\text{H}_3\text{Si})_3\text{N}$ ). The observed bond angles at nitrogen in these compounds are  $108^\circ$  and  $120^\circ$  respectively. Explain the difference in the bond angles.
- c. Both nitrogen and boron form trifluorides. The bond energy in  $\text{BF}_3$  is 646 kJ/mole and that in  $\text{NF}_3$  is only 280 kJ/mole. Account for the difference in bond energies.
- d. The boiling point of  $\text{NF}_3$  is  $-129^\circ\text{C}$  while that of  $\text{NH}_3$  is  $-33^\circ\text{C}$ . Ammonia acts as a Lewis base whereas  $\text{NF}_3$  does not. The observed dipole moment of  $\text{NF}_3$  (0.24 D) is much less than that of  $\text{NH}_3$  (1.46 D), even though fluorine is much more electronegative than hydrogen.
  - i. Explain the differences between boiling points and basicities of  $\text{NF}_3$  and  $\text{NH}_3$ .
  - ii. Account for the low dipole moment of  $\text{NF}_3$ .
- 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** ( $C_{12}H_{12}O_5$ ) 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**.

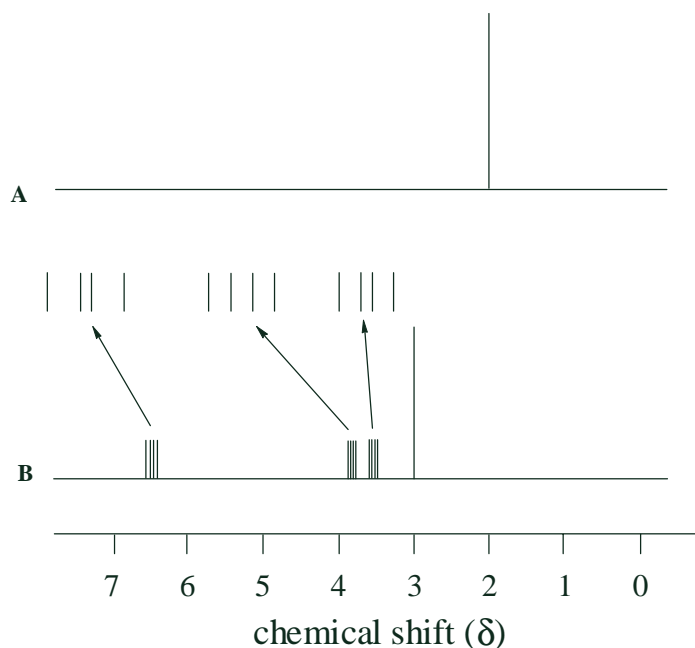
- f. Give appropriate structures for **B** and **C**.
- g. What is the difference between the reactions leading to the formation of **A** and **B**?
- h. Why is the yield of **C** higher than that of **B**?

### Problem 17 Organic spectroscopy and structure determination

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

Both have the molecular formula **C<sub>3</sub>H<sub>6</sub>O**. Schematic <sup>1</sup>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 <sup>1</sup>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 **C<sub>6</sub>H<sub>8</sub>O<sub>4</sub>**, which gives peaks between 0 and 7.0 δ in its <sup>1</sup>H-NMR spectrum. The IR spectrum shows a peak in the region 1700 - 1800 cm<sup>-1</sup>. It condenses with an aromatic aldehyde in the presence of a base.



<sup>1</sup>H-NMR schematic spectra of **A** and **B** at 400 MHz

**Peak positions and relative intensities of individual lines in the <sup>1</sup>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			

- Label the unknown compounds in the bottles with IUPAC names, using the NMR spectra given in the figure.
- In the <sup>1</sup>H-NMR spectrum of **B**, assign the peak positions to specific protons.
- Calculate the spin-spin coupling constants for protons of compound **B**.
- Convert the peak positions of the first four lines into Hz (refer to the Table). What will be the peak positions of these lines in Hz, if the spectrum is recorded on a 600 MHz instrument?
- Draw the possible structure of Meldrum's acid.
- Meldrum's acid has pK<sub>a</sub> = 4.83. Explain the acidity of Meldrum's acid.
- 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**. <sup>1</sup>H-NMR spectrum of **P** has only one signal while that of **Q** contains two signals.

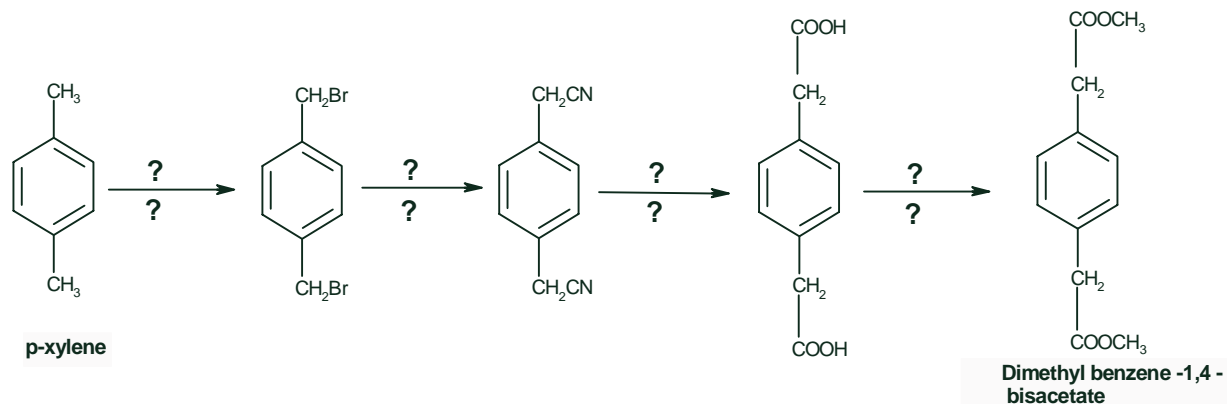
a. Identify and draw the structures for compounds **P** and **Q**.

Compound **R** is obtained when **P** and **Q** react with each other. **R** reacts with SOCl<sub>2</sub> 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  $^1\text{H-NMR}$  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  $\text{H}^+ / \text{H}_2\text{O}$ ?
  - $\text{LiAlH}_4$ ?
- 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 ( $\text{C}_{16}\text{H}_{25}\text{NO}_2$ ), described below. The first step in this synthesis involves :



**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.

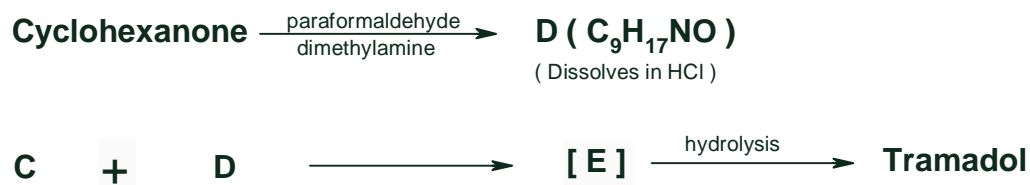
Consider the following reaction



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  $\text{C}_5\text{H}_8\text{O}_3$ . Deduce their possible structures

Each ester is first reacted with benzyl bromide in the presence of  $\text{CH}_3\text{ONa}$ , 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  $\text{CH}_3\text{I}$ .

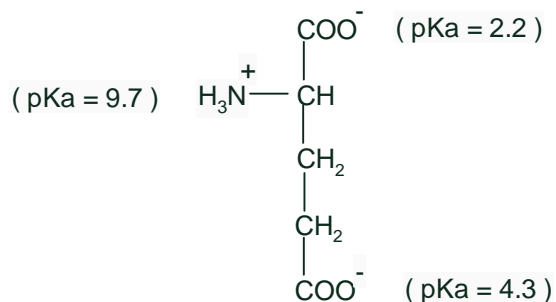
The products at the end of the second step are then hydrolysed by aq.HCl.

- 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  $\text{C}_{11}\text{H}_{14}\text{O}$ ) whereas keto ester **Y**, gives a keto acid (molecular formula  $\text{C}_{12}\text{H}_{14}\text{O}_3$ ). Explain.
- d. Keto ester **X** gives different products depending upon the amount of LDA used. Explain what happens when
- 1 equivalent of LDA is used.
  - 2 equivalents of LDA are used.

### Problem 21 Amino acids and enzymes

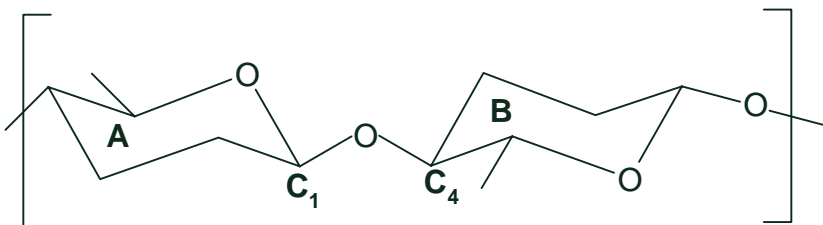
Amino acids are the building blocks of proteins. The presence of  $-\text{NH}_2$  and  $-\text{COOH}$  groups makes amino acids amphoteric in nature. Certain amino acid side chains in proteins are critically important for their reactivity and catalytic role. Glutamic acid is one such amino acid, whose structure is shown below.



- Why is the  $\text{pK}_a$  of the  $\alpha$ -COOH group lower than that of the  $\gamma$ -COOH ?
- Calculate the percent of  $\gamma$ -COOH group that remains unionized at pH 6.3.
- 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  $\beta$ -1, 4 linkage shown below.



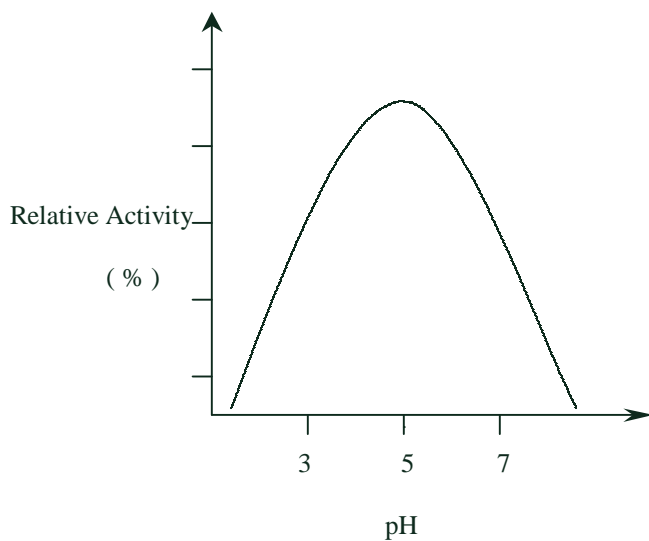


$\beta$ -1, 4 linkage

One such hydrolysis reaction is catalysed by lysozyme.

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

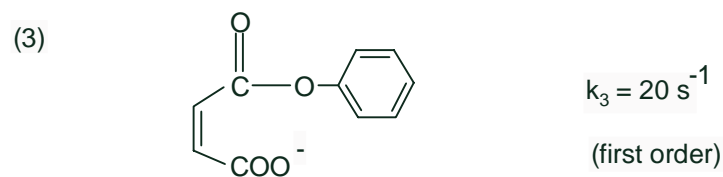
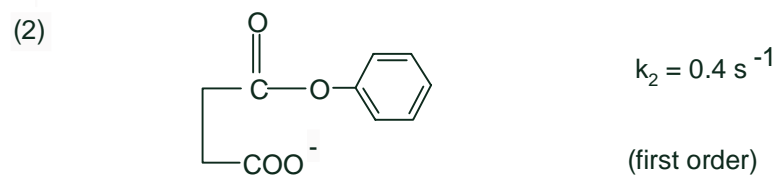
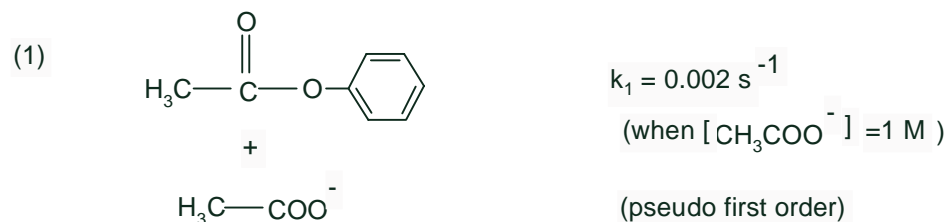
The pH-activity profile of lysozyme is shown in the figure



- 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  $\text{pK}_a$  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

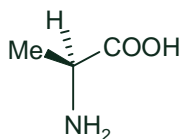
Organic model reactions have helped to understand many features of enzyme catalytic mechanisms. When a reaction is made intramolecular (like the enzyme catalysts do!), rate acceleration takes place as if the apparent reactant concentration felt at the site is enormously raised. The carboxylate group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



- g.** Calculate the effective local concentration of the  $\text{COO}^-$  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 :

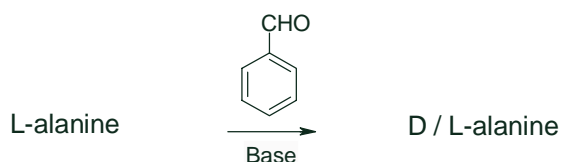


L-alanine

The abstraction of  $\alpha$ -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  $\text{NH}_2$  group is masked and  $\text{C}_\alpha\text{-H}$  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.

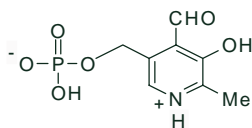
Under favorable experimental conditions, benzaldehyde can be used as a reagent to racemize alanine. In other words, it can mask the amine group and activate the  $\text{C}_\alpha\text{-H}$  of alanine making it more acidic.



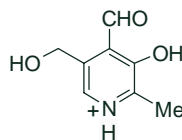
- a. Propose a stepwise mechanism for this base catalyzed racemisation of L-alanine involving benzaldehyde as the reagent.

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.

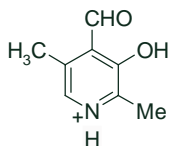
A few relevant structures are presented below. Underneath each, there is an indication about its activity.



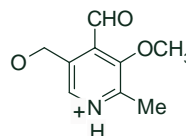
PLP (1)  
Active



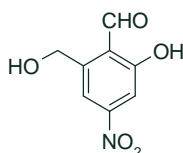
Pyridoxal (2)  
Active



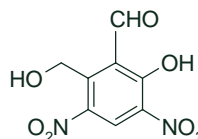
(3)  
Active



(4)  
Inactive



(5)  
Active

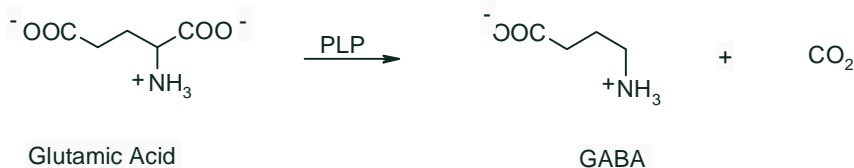


(6)  
Inactive

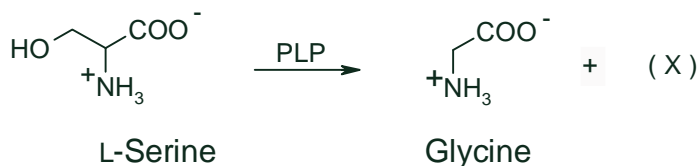
- b.** Based on this information, what inferences can you draw about the structural requirements for PLP to act as a coenzyme?
- c.** A trivalent metal ion is actually critically needed for any of the above shown compounds to display PLP-like activity without the involvement of the enzyme. Suggest a 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.



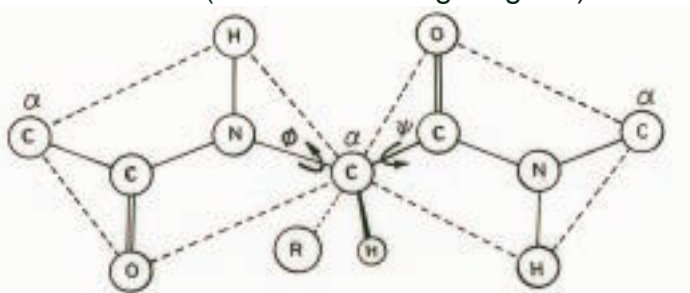
- e. In yet another PLP mediated reaction, L-serine serves as a one-carbon donor in a complex process of nucleotide biosynthesis. The enzyme *serine hydroxymethyltransferase* degrades L-serine with the help of PLP into the simpler amino acid glycine. An important metabolic intermediate (X) is obtained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



### 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  $\alpha$ -carbons. Each  $\alpha$ -carbon carries an R group of a specific  $\alpha$ -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  $\alpha$ -carbons, is a planar unit. Explain.
- b. The  $\alpha$ -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  $\alpha$  (folded) and  $\beta$  (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  $\alpha$  or  $\beta$  conformation. However it is observed that consecutive residues generally assume  $\alpha$  or  $\beta$  conformation, rather than a random combination of  $\alpha$  and  $\beta$ . 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  $\alpha$ -helix or  $\beta$ -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  $\alpha$  helix, what will be the length of this  $\alpha$  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 33<sup>rd</sup> 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 33<sup>rd</sup> 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.



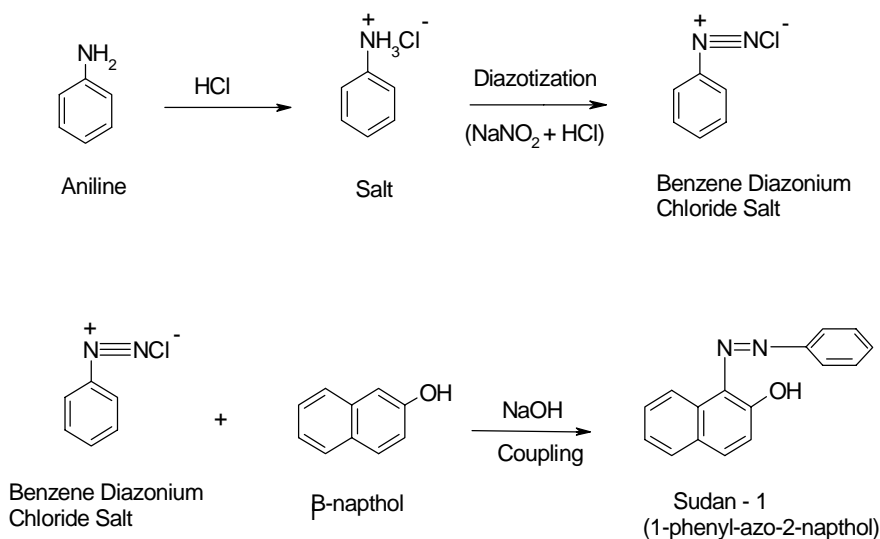
**Blank titration**

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<sub>16</sub>H<sub>12</sub>ON<sub>2</sub>)****Reactions**



**Coupling reaction**

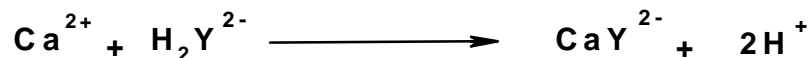
Weigh 0.75 g of powdered  $\beta$ -naphthol in a 50 mL beaker. Add 5 mL of 10% NaOH solution and 5 mL of distilled water to the beaker. Stir well with glass rod to obtain a clear solution. This solution is also cooled in an ice-bath to 0°C.

The ice cooled filtrate containing diazotised salt is added dropwise to the ice cooled solution of  $\beta$ -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    **R** : 36                      **S** : 22, 24  
(prepared from A.R. grade  $\text{CaCl}_2$ )
- 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<sub>2</sub>EDTA and quantitatively transfer the same to 500 mL volumetric flask. Add distilled water to the flask to dissolve Na<sub>2</sub>EDTA 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<sub>2</sub>EDTA 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<sub>2</sub>SO<sub>4</sub>. **R** : 35 **S** : 2, 26, 30
- 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> **S** : 22, 24, 25



**Preparation of 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>:**

Weigh 25 g of AR grade Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> 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<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**

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<sub>2</sub>SO<sub>4</sub> (check the pH with pH paper).



**Preparation of 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**

Weigh 25 g of AR grade Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>S<sub>2</sub>O<sub>3</sub>**

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<sub>2</sub>S<sub>2</sub>O<sub>3</sub> 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 :  $NH_4Fe(SO_4)_2 \cdot 12H_2O$  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  $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  per 100 mL of the sample solution.*



## Worked Solutions to Problems

### 1. Water

#### A. Phase diagram

- a. The three phases of water coexist in equilibrium at a unique temperature and pressure (called the triple point):

$$T_{\text{tr}} = 273.16 \text{ K} = 0.01 \text{ }^{\circ}\text{C} \quad P_{\text{tr}} = 6.11 \times 10^{-3} \text{ bar}$$

- b. If pressure decreases, boiling point decreases, but melting point increases (slightly).
- c. Beyond this point, there is no distinction between liquid and vapour phases of water. Put alternatively, it is possible to have liquid to vapour transition by a continuous path going around the critical point. (In contrast, solid-liquid transition is discontinuous.)
- d.  $T = 300\text{K}$ ,  $P = 12.0 \text{ bar}$  : liquid phase  
 $T = 270\text{K}$ ,  $P = 1.00 \text{ bar}$  : solid phase
- e. Below  $P = 6.11 \times 10^{-3} \text{ bar}$ , ice heated isobarically will sublime to vapour.
- f. If  $x_l$  and  $x_v$  are the mole fractions of water in liquid and vapour phases,

$$V = x_l \bar{V}_l + x_v \bar{V}_v = x_l \bar{V}_l + (1 - x_l) \bar{V}_v$$

$$\therefore x_l = \frac{\bar{V}_v - V}{\bar{V}_v - \bar{V}_l} = 4.6 \times 10^{-1}$$

$$\frac{V_l}{V} = \frac{x_l \bar{V}_l}{V} = 0.140$$

$$\frac{V_v}{V} = 1 - 0.14 = 0.860$$

**B. Clausius – Clapeyron equation**

$$\text{a. } \frac{dP}{dT} = \frac{\Delta\bar{H}}{T\Delta\bar{V}}$$

$\Delta\bar{H}$  = molar enthalpy change in phase transition

$\Delta\bar{V}$  = molar change in volume in phase transition.

*For ice-liquid water transition :*

$\Delta\bar{H} > 0$        $\Delta\bar{V} < 0$ , since ice is less dense than water.

$$\therefore \frac{dP}{dT} < 0$$

Since  $|\Delta\bar{V}|$  is not large, the P-T curve for this transition is steep, with a negative slope. Thus decrease of pressure increases the melting point slightly.

*For liquid water - vapour transition*

$\Delta\bar{H} > 0$        $\Delta\bar{V} < 0$

$$\therefore \frac{dP}{dT} > 0$$

Decrease of pressure decreases the boiling point.

**b.** Clausius - Clapeyron equation for (solid) liquid - vapour transition is

$$\frac{dP}{dT} = \frac{P \Delta\bar{H}_{\text{vap}}}{RT^2}$$

This equation follows from the Clapeyron equation under the assumptions:

1. Vapour follows ideal gas law.
2. Molar volume of the condensed phase is negligible compared to molar volume of vapour phase.
3. If further  $\Delta\bar{H}_{\text{vap}}$  is assumed to be constant (no variation with T), the eq. is integrated to give

$$\ln \frac{P_2}{P_1} = \frac{\Delta\bar{H}_{\text{vap}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$



$$\begin{aligned} \text{Here } P_1 &= 1.01 \text{ bar}, & T_1 &= 373.15 \text{ K} \\ T_2 &= 393.15 \text{ K} & \Delta \bar{H}_{\text{vap}} &= 40.66 \text{ kJ mol}^{-1} \\ R &= 8.31 \text{ J K}^{-1} \text{ mol}^{-1} \\ \therefore P_2 &= 2.01 \text{ bar} \end{aligned}$$

The estimate is based on assumptions 1, 2 and 3.

c. For ice - liquid water equilibrium, use Clapeyron equation

At  $T_1 = 273.15 \text{ K}$ ,  $P_1 = 1.01 \text{ bar}$

1. Assume that for a small change in  $T$ ,  $\frac{\Delta \bar{H}}{\Delta \bar{V}}$  is constant.

Integrating the Clapeyron equation above

$$P_2 - P_1 = \frac{\Delta \bar{H}}{\Delta \bar{V}} \ln \left( \frac{T_2}{T_1} \right)$$

$T_2 = 272.95 \text{ K}$ ,  $\Delta \bar{H}_{(\text{fusion})} = 6008 \text{ J mol}^{-1}$

$$\Delta \bar{V} = \left( \frac{1}{1.00} - \frac{1}{0.917} \right) \times 18.015 = -1.63 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$$

$$P_2 - P_1 = 27.0 \text{ bar}$$

$$P_2 = 28.0 \text{ bar}$$

The estimate is based on assumption 1.

### C. Irreversible condensation

a. On the P-T plane, this equilibrium state is a solid phase (ice). Water in liquid phase at this temperature and pressure is not an equilibrium state - it is a supercooled state that does not lie on the given P-T plane.

b. Treating the metastable state as equilibrium state, we can go from the supercooled liquid state to the solid state at the same temperature and pressure by a sequence of 3 reversible steps.

1. Supercooled liquid at  $-12.0^\circ\text{C}$  to liquid at  $0^\circ\text{C}$

$$q_1 = \text{number of moles} \times \bar{C}_p (\text{liquid water}) \times \text{change of temperature}$$

$$\frac{28.5\text{g}}{18.015\text{ g mol}^{-1}} \times 76.1\text{ J K}^{-1}\text{ mol}^{-1} \times 12.0\text{ K} = 1445\text{ J}$$

2. *liquid at 0°C to ice at 0°C*

$$q_2 = 28.5\text{ g} \times (-333.5)\text{ J g}^{-1} = -9505\text{ J}$$

3. *Ice at 0°C to ice at -12.0°C*

$$q_3 = \text{number of moles} \times \bar{C}_p (\text{liquid water}) \times \text{change of temp.}$$

$$= \frac{28.5}{18.015\text{ g mol}^{-1}} \times 37.15\text{ J K}^{-1}\text{ mol}^{-1} \times (-12.0\text{ K})$$

$$= -705.3\text{ J}$$

$$\therefore q = q_1 + q_2 + q_3 = -8765\text{ J}$$

Since all the steps are at the constant pressure of 1.00 bar,

$$q = \Delta H$$

But  $\Delta H$  is independent of the path, i.e., it depends only on the end points.

Thus for the irreversible condensation of supercooled liquid to ice

$$q = \Delta H = -8765\text{ J}$$

- c. The actual irreversible path between the two end states of the system is replaced by the sequence of three reversible steps, as above. For each reversible step,  $\Delta S$  can be calculated.

$$\Delta S_1 = n \int_{T_1}^{T_2} \frac{\bar{C}_p}{T} dT = n \bar{C}_p \ln \frac{T_2}{T_1}$$

$$\Delta S_1 = \frac{28.5\text{ g}}{18.015\text{ g mol}^{-1}} \times 76.1\text{ J K}^{-1}\text{ mol}^{-1} \times \ln \frac{273.15}{261.15}$$

$$= 5.41\text{ J K}^{-1}$$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{-9505}{273.15} = -34.79 \text{ JK}^{-1}$$

$$\Delta S_3 = \frac{28.5 \text{ g}}{18.015 \text{ g mol}^{-1}} 37.15 \text{ J K}^{-1} \text{ mol}^{-1} \ln \frac{261.15}{273.15}$$

$$= -2.64 \text{ J K}^{-1}$$

$$\Delta S_{\text{system}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = -32.02 \text{ J K}^{-1}$$

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T_{\text{sur}}} = \frac{8765}{261.15} = 33.56 \text{ JK}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{sur}} = 1.54 \text{ JK}^{-1}$$

The entropy of the universe increases in the irreversible process, as expected by the Second Law of Thermodynamics.

## 2. van der Waals gases

a. For a van der Waals gas

$$Z = \frac{PV}{nRT} = 1 + \frac{bP}{RT} - \frac{na}{VRT} + \frac{n^2 ab}{V^2 RT}$$

The ratio of the magnitudes of the second and third terms on the right side is :

$$\frac{b}{na} PV \approx \frac{b}{a} RT, \quad \text{taking } PV = nRT \text{ up to zeroth order.}$$

The ratio of the magnitudes of the fourth and third terms on the right side is :

$$\frac{nb}{V} \approx \frac{bP}{RT}$$

i. From the ratios above, it follows that at sufficiently high temperature for any given pressure, the second term dominates the third and fourth terms. Therefore,

$$Z \cong 1 + \frac{bP}{RT} > 1$$

For small P, Z nearly equals unity.

ii. At lower temperatures, the third term can be greater (in magnitude) than the second term. It may be greater (in magnitude) than the fourth term also, provided  $P$  is not too large. Since the third term has a negative sign, this implies that  $Z$  can be less than unity.

iii. For  $a = 0$

$$Z = 1 + \frac{bP}{RT}$$

which shows that  $Z$  increases linearly with  $P$ .

b. Helium has negligible value of  $a$ . Graph (1) corresponds to He and (2) corresponds to  $N_2$ .

c. Above  $T > T_c$ , only one phase (the gaseous phase) exists, that is the cubic equation in  $V$  has only one real root. Thus isotherm (2) corresponds to  $T < T_c$ .

d. At  $T = T_c$ , the three roots coincide at  $V = V_c$ . This is an inflexion point.

$$\left. \frac{dP}{dV} \right|_{V_c} = \left. \frac{d^2P}{dV^2} \right|_{V_c} = 0$$

The first condition gives

$$\frac{RT_c}{(V_c - nb)^2} = \frac{2na}{V_c^3} \quad (1)$$

The second condition gives

$$\frac{RT_c}{(V_c - nb)^3} = \frac{3na}{V_c^4} \quad (2)$$

These equations give

$$V_c = 3nb \text{ and } T_c = \frac{8a}{27bR}$$

$$\text{For He, } T_c = 5.2\text{K}$$

$$\text{For } N_2, T_c = 128\text{K}$$

Since,  $T_c(N_2)$  is greater than  $T_c(\text{He})$ ,  $N_2$  is liquefied more readily than He.

e.

$$W = \int_{V_1}^{V_2} P dV$$

$$= \int_{V_1}^{V_2} \left( \frac{RT}{V-b} - \frac{a}{V^2} \right) dV$$

$$= RT \ln \left( \frac{V_2-b}{V_1-b} \right) + a \left( \frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$= 56.7 \text{ L bar mol}^{-1}$$

### 3. Rates and reaction mechanisms

a. Mechanism 1 :

$$\frac{1}{2} \frac{d[\text{HI}]}{dt} = k_1 [\text{I}]^2 [\text{H}_2]$$

Since the first step is fast, there is a pre - equilibrium :

$$K = \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$\therefore \frac{d[\text{HI}]}{dt} = 2k_1 K [\text{I}_2][\text{H}_2] = k [\text{H}_2][\text{I}_2]$$

Mechanism 2 :

$$\frac{1}{2} \frac{d[\text{HI}]}{dt} = k_2 [\text{I}_2]_d [\text{H}_2]$$

$$K' = \frac{[\text{I}_2]_d}{[\text{I}_2]}$$

$$\therefore \frac{d[\text{HI}]}{dt} = 2k_2 K' [\text{I}_2][\text{H}_2] = k [\text{H}_2][\text{I}_2]$$

Both mechanisms are consistent with the observed rate law.

b. i.  $k = A e^{-E_a/RT}$

$$E_a \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = R \ln \frac{k_2}{k_1}$$

With the given numerical values,

$$E_a = 170 \text{ kJ mol}^{-1}$$

- ii. The activation energy is greater than the bond dissociation energy of  $I_2$ . Hence the second step is rate determining in both the mechanisms.
- c. The activation energy  $E_a'$  for the reverse reaction is

$$\begin{aligned} E_a' &= E_a - \Delta U \\ &= 170 + 8.2 = 178.2 \text{ kJ mol}^{-1} \end{aligned}$$

- d. i.

$$\frac{d[I_2]}{dt} = k_3 [IAr][I]$$

$$K'' = \frac{[IAr][Ar]}{[I][Ar]^2}$$

$$\begin{aligned} \therefore \frac{d[I_2]}{dt} &= K'' k_3 [I]^2 [Ar] \\ &= k [I]^2 [Ar] \end{aligned}$$

- ii. A possible reason why this is negative is that  $E_{a3}$  is positive and less in magnitude than  $|\Delta H^\circ|$ , while  $\Delta H^\circ$  is negative.

$$\begin{aligned} k &= k_3 K'' \\ &= A_3 e^{-E_{a3}/RT} e^{-\Delta G^\circ/RT} \\ \text{we know } \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ \therefore k &= A_3 e^{\frac{\Delta S^\circ}{R}} e^{-(E_{a3} + \Delta H^\circ)/RT} \end{aligned}$$

The activation energy for the overall reaction is  $E_{a3} + \Delta H^\circ$

#### 4. Enzyme catalysis

- a. i. The differential rate equations for the Michaelis-Menten mechanism are

$$\frac{d[ES]}{dt} = k_1 [E][S] - k_1' [ES] - k_2 [ES] \quad (1)$$

$$\frac{d[P]}{dt} = k_2 [ES] \quad (2)$$

In the steady-state approximation,  $\frac{d[ES]}{dt} = 0$  (3)

Eq. (1) then gives  $[ES] = \frac{k_1 [E][S]}{k_1 + k_2}$  (4)

Now  $[E]_0 = [E] + [ES]$  (5)

where  $[E]_0$  is the total enzyme concentration. Eqs. (4) and (5) gives

$$[ES] = \frac{[E]_0 [S]}{K_m + [S]} \quad (6)$$

where  $K_m = \frac{k_1 + k_2}{k_1}$  is the Michaelis-Menten constant.

From eq. (2),  $\frac{d[P]}{dt} = \frac{k_2 [E]_0 [S]}{K_m + [S]}$  (7)

Since the backward rate is ignored, our analysis applies to the initial rate of formation of P and not close to equilibrium. Further, since the enzyme concentration is generally much smaller than the substrate concentration,  $[S]$  is nearly equal to  $[S]_0$  in the initial stage of the reaction.

Thus, according to the Michaelis-Menten mechanism, the initial rate versus substrate concentration is described by eq. (7), where  $[S]$  is replaced by  $[S]_0$ .

For  $[S] \ll K_m$ ,

$$\text{Initial rate} = \frac{k_2}{K_m} [E]_0 [S] \quad (8)$$

i.e., initial rate varies linearly with  $[S]$ .

For  $[S] \gg K_m$ ,

$$\text{Initial rate} = k_2 [E]_0 \quad (9)$$

i.e., for large substrate concentration, initial rate approaches a constant value  $k_2 [E]_0$ .

Thus the indicated features of the graph are consistent with Michaelis-Menten mechanism.

- ii. The asymptotic value of initial rate is  $k_2 [E]_0$

From the graph,

$$k_2 [E]_0 = 3.0 \times 10^{-6} \text{ M s}^{-1}$$

With  $[E]_0 = 1.5 \times 10^{-9} \text{ M}$

we get  $k_2 = 2.0 \times 10^3 \text{ s}^{-1}$

- iii. From eq. (7), for  $[S] = K_m$ , the initial rate is half the asymptotic value. From the graph, therefore,

$$K_m = 5.0 \times 10^{-5} \text{ M}$$

For  $[S] = 1.0 \times 10^{-4} \text{ M}$ , using eq. (7) again,

$$\text{Initial rate} = \frac{[2.0 \times 10^3 \text{ s}^{-1}] \times [1.5 \times 10^{-9} \text{ M}] \times [1.0 \times 10^{-4} \text{ M}]}{[5.0 \times 10^{-5} \text{ M}] + [1.0 \times 10^{-4} \text{ M}]}$$

$$= 2.0 \times 10^{-6} \text{ M s}^{-1}$$

- iv. We have  $K_m = \frac{k_1 + k_2}{k_1} = 5.0 \times 10^{-5} \text{ M}$

The enzyme equilibrates with the substrate quickly, that is the first step of equilibration between E, S and [ES] is very fast. This means that  $k_1^{\dagger}$  is much greater than  $k_2$ . Therefore, neglecting  $k_2$  above,

$$\frac{k_1^{\dagger}}{k_1} = 5.0 \times 10^{-5} \text{ M}$$

The equilibrium constant K for the formation of ES from E and S is,

$$\frac{K}{1\text{M}} = \frac{k_1}{k_1^{\dagger}} = 2.0 \times 10^{-5}$$

- b. From the graph at the new temperature,  $k_2 [E]_0 = 6.0 \times 10^{-6} \text{ M s}^{-1}$

i.e.,  $k_2 = \frac{6.0 \times 10^{-6} \text{ M s}^{-1}}{1.5 \times 10^{-9} \text{ M}} = 4.0 \times 10^3 \text{ s}^{-1}$



Using Arrhenius relation for temperature dependence of rate constant :

$$k = A e^{-\frac{E_a}{RT}} \quad (10)$$

where  $E_a$  is the molar activation energy.

$$\frac{k(T_1)}{k(T_2)} = e^{-\frac{E_a}{R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right]}$$

$$\text{i.e.} \quad E_a = R \frac{\ln \frac{k(T_2)}{k(T_1)}}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)} \quad (11)$$

$$\text{Now} \quad \frac{k_2(310)}{k_1(285)} = 2.0, \quad R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\therefore E_a = 20.4 \text{ kJ mol}^{-1}$$

- c. i.** The fraction of the enzyme that binds with the substrate is, from eq. (6):

$$\frac{[ES]}{[E]_0} = \frac{[S]}{K_m + [S]} \quad (12)$$

where  $[S]$  is nearly equal to  $[S]_0$  in the initial stage of the reaction.

$$\text{Now} \quad [S]_0 = \frac{3.0 \times 10^{-6} \text{ mol}}{1 \times 10^{-3} \text{ L}} = 3.0 \times 10^{-3} \text{ M}$$

$$\text{and} \quad K_m = 5.0 \times 10^{-5} \text{ M}$$

$$\therefore \frac{[ES]}{[E]_0} = \frac{3.0 \times 10^{-3} \text{ M}}{(5.0 \times 10^{-5} + 3.0 \times 10^{-3}) \text{ M}} = 0.98$$

Nearly the whole of the enzyme is bound with the substrate.

- ii.** From eq. (7),

Integrating the equation gives,

$$\frac{d[S]}{dt} = -\frac{k_2 [E]_0 [S]}{K_m + [S]}$$

$$K_m \ln \frac{[S]}{[S]_0} + [S] - [S]_0 = -k_2 [E]_0 t \quad (13)$$

If at  $t = T$ ,  $[S] = 1/2[S]_0$ ,

$$T k_2 [E]_0 = K_m \ln 2 + \frac{1}{2} [S]_0 \quad (14)$$

$$\text{Here } [E]_0 = \frac{2.0 \times 10^{-12} \text{ mol}}{1.0 \times 10^{-3} \text{ L}} = 2.0 \times 10^{-9} \text{ M}$$

$$k_2 = 2.0 \times 10^3 \text{ s}^{-1}, \quad K_m = 5.0 \times 10^{-5} \text{ M},$$

$$[S]_0 = 3.0 \times 10^{-3} \text{ M}$$

Substituting these values in eq. (14) gives

$$T = 384 \text{ s}$$

Thus 50% of the antibiotic dose is inactivated in 384 s.

**d. i.** The differential rate equations for the situation are :

$$\frac{d}{dt} [ES] = k_1 [E][S] - k_1^l [ES] - k_2 [ES] \quad (15)$$

$$\frac{d}{dt} [EI] = k_3 [E][I] - k_3^l [EI] \quad (16)$$

$$\frac{d}{dt} [P] = k_2 [ES] \quad (17)$$

where  $k_3$  and  $k_3^l$  are the forward and backward rate constants for the enzyme-inhibitor reaction.

Applying steady-state approximation to [ES] and [EI],

$$[ES] = \frac{k_1 [E][S]}{k_1^l + k_2} \quad (18)$$

$$\text{and } [EI] = \frac{k_3 [E][I]}{k_3^l} \quad (19)$$

$$\text{Now } [E]_0 = [E] + [ES] + [EI] \quad (20)$$

Eliminating [E] and [EI] from eqs. (18) to (20) gives :

$$[\text{ES}] = \frac{[\text{E}]_0 [\text{S}]}{[\text{S}] + K_m \left( 1 + \frac{[\text{I}]}{K_i (1\text{M})} \right)} \quad (21)$$

$$\frac{d[\text{P}]}{dt} = \frac{k_2 [\text{E}]_0 [\text{S}]}{[\text{S}] + K_m \left( 1 + \frac{[\text{I}]}{K_i (1\text{M})} \right)} \quad (22)$$

Here,  $K_i(1\text{M}) = \frac{k_3^l}{k_3}$  is the equilibrium constant for the dissociation of EI to E and I.

The degree of inhibition is  $i = 1 - \frac{r}{r_0}$

$$\text{Using eq. (22), } i = \frac{\frac{K_m}{K_i} \frac{[\text{I}]}{(1\text{M})}}{[\text{S}] + K_m \left( 1 + \frac{[\text{I}]}{K_i (1\text{M})} \right)} \quad (23)$$

For fixed [I],  $i$  decreases with increase in [S] (*competitive inhibition*).

and for large [S],  $i \rightarrow 0$ , i.e., the inhibitor ceases to play any role.

ii. For small [S]  $i = \frac{[\text{I}]}{K_i (1\text{M}) + [\text{I}]}$

$$\text{If } r = \frac{1}{4} r_0, \quad i = \frac{3}{4}$$

$$\text{i.e., } [\text{I}] = 3 K_i \times (1\text{M}) = 1.5 \times 10^{-4} \text{ M}$$

The inhibitor concentration required to reduce the rate of inactivation by a factor of 4 is  $1.5 \times 10^{-4} \text{ M}$ ; i.e.,  $0.15 \mu\text{mol}$  in a volume of  $1.00 \text{ mL}$ .

## 5. Schrödinger equation

a.

i. One-dimensional Schrödinger equation for a free particle of mass  $m$ :

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} = E\psi \quad \hbar = \frac{h}{2\pi}$$

where  $E$  stands for the energy of the particle and  $\psi$  its wave function.

ii. The boundary conditions are :

$$\psi(0) = \psi(L) = 0$$

Only  $\psi_n(x) = \sin \frac{n\pi x}{L}$  satisfies the required boundary conditions.

Other functions are not possible wave functions of the electron in a one-dimensional rigid box.

iii.

$$-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \sin \frac{n\pi x}{L} = \frac{\hbar^2\pi^2}{2mL^2} n^2 \sin \frac{n\pi x}{L}$$

$$\therefore E_n = \frac{\hbar^2\pi^2}{2mL^2} n^2 = \frac{h^2n^2}{8mL^2}$$

iv. Ground state ( $n = 1$ )

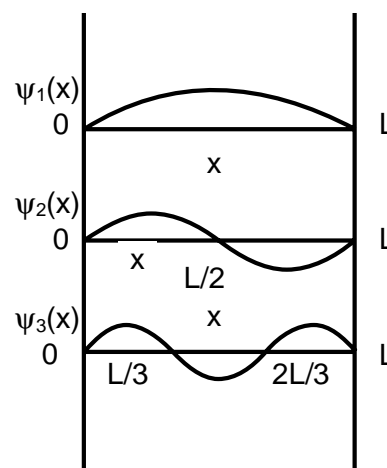
$$\psi_1(x) = \sin \frac{\pi x}{L}$$

First excited state ( $n = 2$ )

$$\psi_2(x) = \sin \frac{2\pi x}{L}$$

Second excited state ( $n = 3$ )

$$\psi_3(x) = \sin \frac{3\pi x}{L}$$



Number of nodes in  $\psi_n = n - 1$ , apart from the nodes at the end points.

v.

$$\begin{aligned}\psi_1^N(x) &= N \sin \frac{\pi x}{L} \\ 1 &= \int_{-\infty}^{\infty} |\psi_1^N(x)|^2 dx \\ &= N^2 \int_0^L \sin^2 \frac{\pi x}{L} dx = \frac{N^2}{2} \int_0^L \left(1 - \cos \frac{2\pi x}{L}\right) dx \\ &= N^2 \frac{L}{2} \\ \therefore N &= \sqrt{\frac{2}{L}} \quad (\text{N is chosen to be real}) \\ \psi_1^N(x) &= \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}\end{aligned}$$

b. In the example

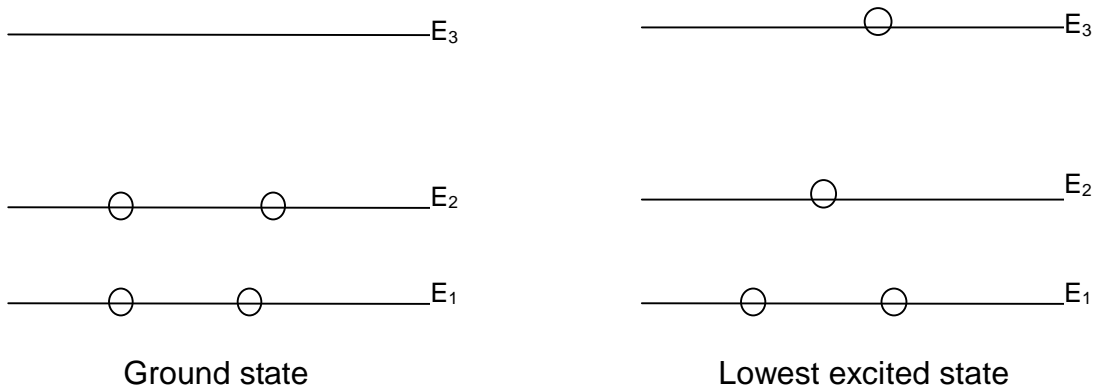
$$L = 5 \times 1.4 \times 10^{-10} \text{ m} = 7.0 \times 10^{-10} \text{ m}$$

The first three energy levels are:

$$E_1 = \frac{h^2}{8mL^2} = 1.22 \times 10^{-19} \text{ J}$$

$$E_2 = 4 E_1 = 4.88 \times 10^{-19} \text{ J}$$

$$E_3 = 9 E_1 = 10.98 \times 10^{-19} \text{ J}$$

In the ground state, the four electrons will occupy the levels  $E_1$  and  $E_2$ , each with two electrons.

The lowest excitation energy

$$E_3 - E_2 = 6.10 \times 10^{-19} \text{ J}$$

**c.** The condition that  $\psi(\phi)$  is single valued demands that

$$\Psi(\phi) = \Psi(\phi + 2\pi)$$

$$e^{i\lambda\phi} = e^{i\lambda(\phi+2\pi)}$$

$$e^{i2\pi\lambda} = 1$$

i.e.  $\lambda = m$ , where  $m = 0, \pm 1, \pm 2, \pm 3, \dots$

This shows that angular momentum projection ( $L_z$ ) cannot be an arbitrary real number but can have only discrete values:  $m\hbar$ , where  $m$  is a positive or negative integer (including zero).

## 6. Atomic and molecular orbitals

### A. Atomic orbitals

**a.**

$$\text{i.} \quad \psi_{1s}^N = N e^{-\frac{r}{a_0}}$$

$$1 = \int |\psi_{1s}^N|^2 dv = 4\pi a_0^3 N^2$$

$$= 4\pi N^2 \times \frac{a_0^3}{4} = \pi a_0^3 N^2 \quad (\text{N chosen to be real})$$

$$\therefore N = [\pi a_0^3]^{-\frac{1}{2}}$$

$$\psi_{1s}^N = [\pi a_0^3]^{-\frac{1}{2}} e^{-\frac{r}{a_0}}$$

**ii.** Probability of finding an electron between  $r$  and  $r + dr$

$$= 4\pi r^2 \times [\pi a_0^3]^{-1} e^{-\frac{2r}{a_0}} dr$$

This is a maximum at  $r = r_{\max}$ , given by

$$\frac{d}{dr} \left( r^2 e^{-\frac{2r}{a_0}} \right)_{r=r_{\max}} = 0$$

This gives

$$r_{\max} = a_0$$

The 1s electron is most likely to be found in the neighborhood of  $r = a_0$ .

b.  $\Psi_{2s} = 0$  at  $r = 2a_0$

Nodal surface is a sphere of radius  $2a_0$

$$\Psi_{2p_z} = 0 \quad \text{at } \theta = \frac{\pi}{2}$$

Nodal surface is the xy plane.

$$\Psi_{3d_{z^2}} = 0 \quad \text{at } 3\cos^2\theta - 1 = 0, \quad \text{i.e., } \theta = \cos^{-1}\left(\pm \frac{1}{\sqrt{3}}\right)$$

Nodal surfaces are cones with these values of half-angle, one above the xy plane and the other below it.

(Note: all three wave functions vanish as  $r \rightarrow \infty$ . At  $r = 0$ ,  $\psi_{1s}$  does not vanish, but the other two wave functions vanish.)

c. Each electron in  $n = 1$  shell of helium atom has energy  $-Z_{\text{eff}}^2 \times 13.6 \text{ eV}$

$$\text{Helium ground state energy} = -Z_{\text{eff}}^2 \times 27.2 \text{ eV}$$

$$\text{Energy of He}^+ \text{ ground state} = -4 \times 13.6 = -54.4 \text{ eV}$$

$$\text{Ionization energy} = (-54.4 + Z_{\text{eff}}^2 \times 27.2) \text{ eV} = 24.46 \text{ eV}$$

$$\text{This gives } Z_{\text{eff}} = 1.70$$

## B. Molecular orbitals

a.  $\psi_1$  and  $\psi_2$  are bonding orbitals

$$\tilde{\psi}_1 \text{ and } \tilde{\psi}_2 \text{ are antibonding orbitals}$$

### Bonding orbital

No nodal surface between the nuclei. Electronic energy has a minimum at a certain internuclear distance. Qualitative reason: electron has considerable probability of being between the nuclei and thus has attractive potential energy due to both the nuclei.

**Antibonding orbital**

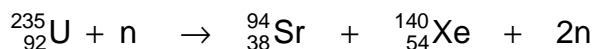
Nodal surface between the nuclei. Electronic energy decreases monotonically with internuclear distance. Hence bound state is not possible.

- b.  $R_e = 1.32 \times 10^{-10} \text{ m}$   
 $D = -1.36 - (-15.36) = 1.76 \text{ eV}$
- c. It will dissociate to a hydrogen atom in 2s state and a bare hydrogen nucleus (proton).
- d. The two electrons occupy the same molecular orbital with the lowest energy. By Pauli's principle, their spins must be antiparallel. Hence the total electronic spin is zero.
- e. In the first excited state of  $\text{H}_2$ , one electron is in  $\psi_1$  (bonding orbital) and the other in  $\psi_2$  (antibonding orbital). It will dissociate into two hydrogen atoms.
- f. Using the aufbau principle, in the ground state two electrons of  $\text{He}_2$  are in  $\psi_1$  (bonding orbital) and two in  $\psi_2$  (antibonding orbital). The bond order is  $\frac{1}{2} (2 - 2) = 0$

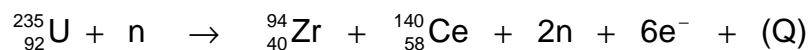
Therefore, bound  $\text{He}_2$  is unstable and difficult to detect. However, if one or more electrons are elevated from the antibonding orbital to (higher energy) bonding orbitals, the bond order becomes greater than zero. This is why it is possible to observe  $\text{He}_2$  in excited states.

**7. Fission**

a.



b. The net nuclear reaction is



The energy released is

$$Q = [m_{\text{N}}({}^{235}\text{U}) - m_{\text{N}}({}^{94}\text{Zr}) - m_{\text{N}}({}^{140}\text{Ce}) - m_{\text{n}} - 6m_{\text{e}}] c^2$$



where the small energy of the initial thermal neutron has been ignored. ( $m_N$  denotes the nuclear mass.) Now

$$m_N(^{235}\text{U}) = m(^{235}\text{U}) - 92m_e$$

ignoring the small electronic binding energies compared to rest mass energies. Similarly for other nuclear masses.

$$Q = [m(^{235}\text{U}) - m(^{94}\text{Zr}) - m(^{140}\text{Ce}) - m_n] c^2$$

Using the given data,

$$Q = 213.3 \text{ MeV}$$

c.  $1 \text{ MWd} = 10^6 \text{ Js}^{-1} \times 24 \times 3600 \text{ s} = 8.64 \times 10^{10} \text{ J}$

$$\text{No. of atoms of } ^{235}\text{U} \text{ fissioned} = \frac{8.64 \times 10^{10}}{213.3 \times 1.60 \times 10^{-13}} = 2.53 \times 10^{21}$$

$$\text{Mass of } ^{235}\text{U} \text{ fissioned} = \frac{2.53 \times 10^{21} \times 235}{6.02 \times 10^{23}} = 0.99 \text{ g}$$

$$\text{Mass of } ^{235}\text{U} \text{ in 1 kg uranium removed from the reactor} = 7.2 - 0.99 = 6.2 \text{ g}$$

Abundance of  $^{235}\text{U}$  is 0.62 %

## 8. Radioactive decay

a.  $1 \mu\text{Ci} = 3.7 \times 10^4 \text{ disintegrations per second (dps)}$ .

$$\text{Initial } \beta \text{-activity} = 3.7 \times 10^6 \text{ dps}$$

$$\left. \frac{-dN_1}{dt} \right|_{t=0} = N_1^0 \lambda_1 = 3.7 \times 10^6 \text{ dps}$$

where  $N_1^0$  is the number of atoms of  $^{210}\text{Bi}$  at  $t = 0$  and  $\lambda_1$  is its decay constant.

$$\frac{0.693}{5.01 \times 24 \times 3600} N_1^0 = 3.7 \times 10^6$$

$$N_1^0 = 2.31 \times 10^{12}$$

$$\text{Initial mass of } ^{210}\text{Bi} = 2.31 \times 10^{12} \times \frac{210}{6.02 \times 10^{23}} \text{ g}$$

$$= 8.06 \times 10^{-10} \text{ g}$$

b. Number of atoms of  $^{210}\text{Bi}$  at time  $t$  is given by

$$N_1 = N_1^0 e^{-\lambda_1 t}$$

The number of atoms of  $^{210}\text{Po}$ ,  $N_2$ , is given by equation

$$\frac{dN_2}{dt} = \lambda_1 N_1 - \lambda_2 N_2$$

where  $\lambda_2$  is the decay constant of  $^{210}\text{Po}$ .

$$\frac{dN_2}{dt} = \lambda_1 N_1^0 e^{-\lambda_1 t} - \lambda_2 N_2$$

Using the integrating factor  $e^{\lambda_2 t}$

$$e^{\lambda_2 t} \frac{dN_2}{dt} + \lambda_2 N_2 e^{\lambda_2 t} = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}$$

$$\frac{d}{dt}(N_2 e^{\lambda_2 t}) = \lambda_1 N_1^0 e^{(\lambda_2 - \lambda_1)t}$$

Integrating

$$N_2 e^{\lambda_2 t} = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 e^{(\lambda_2 - \lambda_1)t} + C$$

To calculate  $C$ , use the condition that at  $t = 0$ ,  $N_2 = 0$

$$C = -\frac{\lambda_1 N_1^0}{\lambda_2 - \lambda_1}$$

This gives

$$N_2 = \frac{\lambda_1}{\lambda_2 - \lambda_1} N_1^0 (e^{-\lambda_1 t} - e^{-\lambda_2 t})$$

The time  $t = T$  when  $N_2$  is maximum is given by the condition

$$\left. \frac{dN_2}{dt} \right|_{t=T} = 0$$

which gives

$$T = \frac{\ln \frac{\lambda_1}{\lambda_2}}{\lambda_1 - \lambda_2} = 24.9 \text{ d}$$

At  $t = T$ ,  $N_2$  can be calculated from above.

$$N_2 = 2.04 \times 10^{12}$$

Mass of  $^{210}\text{Po}$  at  $t = T$ ,

$$= 7.11 \times 10^{-10} \text{ g}$$

c.  $\alpha$ -disintegration rate of  $^{210}\text{Po}$  at  $t = T$

$$= 1.18 \times 10^5 \text{ dps}$$

At  $t = T$

$\beta$  - disintegration rate of  $^{210}\text{Bi}$

$$= \alpha\text{-disintegration rate of } ^{210}\text{Po} = 1.18 \times 10^5 \text{ dps}$$

## 9. Redox reactions

a.

i. Over-all reaction



$$\begin{aligned} \Delta G^\circ &= -nFE^\circ = -2FE^\circ \\ &= -2 \times 96485 \times 0.617 \text{ V} \\ &= -119 \text{ KJ} \end{aligned}$$

ii. 
$$E^{\circ} = \frac{0.0592}{n} \log K$$

$$\log K = \frac{(2 \times 0.617)}{0.0592} \cong 20.84$$

$$K = 6.92 \times 10^{20}$$

b. Before the equivalence point, E of the cell is given by following equation

$$\begin{aligned} E_{\text{cell}} &= \text{ox } E_{\text{S.C.E}}^{\circ} + \text{red } E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} \\ &= -0.242 + 0.154 - \frac{0.0592}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} \end{aligned}$$

i. The addition of 5.00 mL of  $\text{Fe}^{3+}$  converts 5.00/20.00 of the  $\text{Sn}^{2+}$  to  $\text{Sn}^{4+}$ ; thus

$$\frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]} = \frac{15.0/20.0}{5.0/20.0} = 3.00$$

$$E_{\text{cell}} = -0.102 \text{ V.}$$

ii. At the equivalence point, add the two expressions corresponding to  $\text{Sn}^{4+}/\text{Sn}^{2+}$  and  $\text{Fe}^{3+}/\text{Fe}^{2+}$ .

$$2 E_{\text{cell}} = 2 \text{ ox } E_{\text{S.C.E}}^{\circ} + 2 \text{ red } E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Sn}^{2+}]}{[\text{Sn}^{4+}]}$$

$$1 E_{\text{cell}} = \text{ox } E_{\text{S.C.E}}^{\circ} + \text{red } E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

to get

$$3 E_{\text{cell}} = 3 \text{ ox } E_{\text{S.C.E}}^{\circ} + 2 \text{ red } E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} + \text{red } E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Sn}^{2+}][\text{Fe}^{2+}]}{[\text{Sn}^{4+}][\text{Fe}^{3+}]}$$

At the equivalence point,  $[\text{Fe}^{3+}] = 2 [\text{Sn}^{2+}]$  and  $[\text{Fe}^{2+}] = 2 [\text{Sn}^{4+}]$

Thus,

$$E_{\text{cell}} = E_{\text{S.C.E.}}^{\circ} + \frac{2 E_{\text{red Sn}^{4+}/\text{Sn}^{2+}}^{\circ} + E_{\text{red Fe}^{2+}/\text{Fe}^{3+}}^{\circ}}{3}$$

$$= -0.242 + \frac{(2)(0.154) + 0.771}{3} = +0.118 \text{ V}$$

Beyond the equivalence point, E of the cell is given by following equation

$$E_{\text{cell}} = E_{\text{S.C.E.}}^{\circ} + E_{\text{red Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]}$$

When 30 mL of  $\text{Fe}^{3+}$  is added, 10 mL of  $\text{Fe}^{3+}$  is in excess. i.e.

$$\frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = \frac{20.0}{10.0} = 2.00$$

$$E_{\text{cell}} = 0.511 \text{ V}$$

**c.**

$$\text{i. } \Delta G^{\circ} = -RT \ln K_{\text{sp}}$$

$$= 68.27 \text{ KJ}$$

$$\Delta G^{\circ} = -nFE^{\circ}, \quad n=1$$

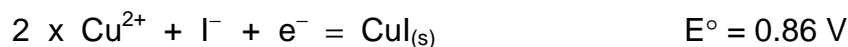
$$E^{\circ} = -0.707 \text{ V}$$



The overall reaction for reduction of  $\text{Cu}^{2+}$  by  $\text{I}^{-}$  is



The  $E^{\circ}$  value for the reduction of  $\text{Cu}^{2+}$  by  $\text{I}^{-}$  can now be calculated



The over-all reaction is



The positive value of effective  $E^{\circ}$  indicates that the reduction reaction is spontaneous. This has come about since in this reaction,  $\text{I}^{-}$  is not only a reducing agent, but is also a precipitating agent. Precipitation of  $\text{Cu}^{+}$  as  $\text{CuI}$  is the key step of the reaction, as it practically removes the product  $\text{Cu}^{+}$  from the solution, driving the reaction in the forward direction.

iii.  $\Delta G^{\circ} = -nFE^{\circ}$

Here  $n = 1$ ,  $E^{\circ} = 0.325 \text{ V}$

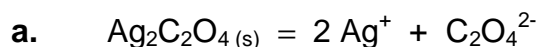
$$\Delta G^{\circ} = -31.3 \text{ kJ}$$

$$\Delta G^{\circ} = -RT \ln K$$

$$\log K = 5.47$$

$$K = 2.9 \times 10^5$$

## 10. Solubility of sparingly soluble salts



The solubility product  $K_{sp}$  is given by

$$K_{sp} = [\text{Ag}^{+}]^2 [\text{C}_2\text{O}_4^{2-}]$$

If  $S$  is the solubility of  $\text{Ag}_2\text{C}_2\text{O}_4$

$$[\text{Ag}^{+}] = 2S \quad (1)$$

The total oxalate concentration, denoted by  $C_{ox}$ , is

$$C_{ox} = S = [\text{C}_2\text{O}_4^{2-}] + [\text{HC}_2\text{O}_4^{-}] + [\text{H}_2\text{C}_2\text{O}_4] \quad (2)$$

The dissociation reactions are:



Eqs. (2), (3) and (4) give

$$C_{\text{ox}} = S = [\text{C}_2\text{O}_4^{2-}] + \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}^+]}{K_2} + \frac{[\text{C}_2\text{O}_4^{2-}][\text{H}^+]^2}{K_1K_2}$$

$$\therefore [\text{C}_2\text{O}_4^{2-}] = \alpha C_{\text{ox}} = \alpha S$$

$$\text{where } \alpha = \frac{K_1K_2}{[\text{H}^+]^2 + K_1[\text{H}^+] + K_1K_2} \quad (5)$$

At pH = 7,  $[\text{H}^+] = 10^{-7}$  and  $\alpha \cong 1$

$$K_{\text{sp}} = 4S^3 = 3.5 \times 10^{-11}$$

At pH = 5.0,  $[\text{H}^+] = 10^{-5}$

From the values of  $K_1$ ,  $K_2$  and  $[\text{H}^+]$ , we get

$$\alpha = 0.861 \quad (6)$$

$$K_{\text{sp}} = [2S]^2 [\alpha S]$$

$$\therefore S = \left( \frac{K_{\text{sp}}}{4\alpha} \right)^{\frac{1}{3}} = 2.17 \times 10^{-4}$$

**b.**  $[\text{NH}_3] = 0.002$

At pH = 10.8,  $[\text{H}^+] = 1.585 \times 10^{-11}$

Eq. (5) implies

$$\alpha = 1$$

$$\text{i.e. } C_{\text{ox}} = S = [\text{C}_2\text{O}_4^{2-}] \quad (7)$$

The total silver ion in the solution is given by

$$C_{\text{Ag}} = 2S = [\text{Ag}^+] + [\text{AgNH}_3^+] + [\text{Ag}(\text{NH}_3)_2^+] \quad (8)$$

The complex formation reactions are



From eqs. (8), (9) and (10)

$$C_{\text{Ag}} = 2S = [\text{Ag}^+]\{1 + K_3[\text{NH}_3] + K_3K_4[\text{NH}_3]^2\}$$

$$\therefore [\text{Ag}^+] = \beta \times C_{\text{Ag}} = \beta \times 2S$$

$$\text{where } \beta = \frac{1}{1 + K_3[\text{NH}_3] + K_3K_4[\text{NH}_3]^2}$$

Using the values of  $K_3$ ,  $K_4$  and  $[\text{NH}_3]$ ,

$$\beta = 2.31 \times 10^{-4}$$

$$\begin{aligned} K_{\text{sp}} &= [\text{Ag}^+]^2 [\text{C}_2\text{O}_4^{2-}] \\ &= [\beta \times 2S]^2 [S] \end{aligned}$$

$$\therefore S = \left(\frac{K_{\text{sp}}}{4\beta^2}\right)^{\frac{1}{3}}$$

$$= 5.47 \times 10^{-2}$$

## 11. Spectrophotometry

- a. Denote the molar absorptivity of  $\text{MnO}_4^-$  at 440 nm and 545 nm by  $\epsilon_1$  and  $\epsilon_2$  and that of  $\text{Cr}_2\text{O}_7^-$  by  $\epsilon_3$  and  $\epsilon_4$  :

$$\epsilon_1 = 95 \text{ Lmol}^{-1}\text{cm}^{-1}, \quad \epsilon_2 = 2350 \text{ Lmol}^{-1}\text{cm}^{-1}$$

$$\epsilon_3 = 370 \text{ Lmol}^{-1}\text{cm}^{-1}, \quad \epsilon_4 = 11 \text{ Lmol}^{-1}\text{cm}^{-1}$$

The absorbance  $A$  is related to % transmittance  $T$  by

$$A = 2 - \log T$$

From the values given for the sample solution

$$A_{440} = 2 - \log 35.5 = 0.45$$

$$A_{545} = 2 - \log 16.6 = 0.78$$



Now if one denotes the molar concentrations of  $\text{MnO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  in the steel sample solution by  $C_1$  and  $C_2$  respectively, we have

$$A_{440} = \epsilon_1 \times C_1 \times 1 + \epsilon_3 \times C_2 \times 1$$

$$A_{545} = \epsilon_2 \times C_1 \times 1 + \epsilon_4 \times C_2 \times 1$$

Using the given data, we get

$$C_1 = 0.0003266 \text{ M}$$

$$C_2 = 0.001132 \text{ M}$$

Amount of Mn in 100 mL solution

$$= 0.0003266 \text{ mol L}^{-1} \times 54.94 \text{ g mol}^{-1} \times 0.1 \text{ L}$$

$$= 0.001794 \text{ g}$$

$$\% \text{ Mn in steel sample} = \frac{0.001794 \times 100}{1.374} = 0.13\%$$

Amount of Cr present in 100 mL solution

$$= 0.001132 \text{ mol L}^{-1} \times 2 \times 52.00 \text{ g mol}^{-1} \times 0.1 \text{ L}$$

$$= 0.0118 \text{ g}$$

$$\% \text{ Cr in steel sample} = \frac{0.0118 \times 100}{1.374} = 0.86\%$$

- b.** In solution 1, since all the ligand is consumed in the formation of the complex,

$$[\text{CoL}_3^{2+}] = \frac{2 \times 10^{-5}}{3} = 0.667 \times 10^{-5}$$

Absorptivity of the complex  $\text{CoL}_3^{2+}$  is

$$\epsilon = \frac{0.203}{0.667 \times 10^{-5} \text{ mol L}^{-1} \times 1.0 \text{ cm}} = 3.045 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$$

If the concentration of the complex  $\text{CoL}_3^{2+}$  in solution 2 is C,

$$C = \frac{0.68}{3.045 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1} \times 1.0 \text{ cm}}$$

$$= 2.233 \times 10^{-5} \text{ M}$$

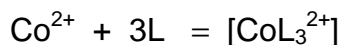
$$[\text{Co}^{2+}] = [\text{Co}^{2+}]_{\text{total}} - [\text{CoL}_3^{2+}]$$

$$= 3 \times 10^{-5} - 2.233 \times 10^{-5} = 0.767 \times 10^{-5}$$

$$\text{Similarly, } [\text{L}] = [\text{L}]_{\text{total}} - 3[\text{CoL}_3^{2+}]$$

$$= 7 \times 10^{-5} - 3 \times 2.233 \times 10^{-5} = 0.300 \times 10^{-5}$$

The complex formation reaction is

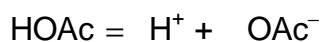
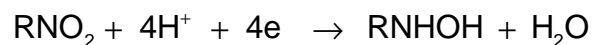


The stability constant K is given by

$$K = \frac{[\text{CoL}_3^{2+}]}{[\text{Co}^{2+}][\text{L}]^3}$$

$$= 1.08 \times 10^{17}$$

## 12. Reactions in buffer medium



$$K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]}$$

i.e

$$\text{p}K_a = \text{pH} + \log \frac{[\text{HOAc}]}{[\text{OAc}^-]}$$

$$4.76 = 5.0 + \log \frac{[\text{HOAc}]}{[\text{OAc}^-]}$$

$$\frac{[\text{HOAc}]}{[\text{OAc}^-]} = 0.5715$$

$$[\text{HOAc}] + [\text{OAc}^-] = 0.500$$

$$[\text{OAc}^-] = 0.3182$$

$$[\text{HOAc}] = 0.5 - 0.3182 = 0.1818$$

mmoles of acetate ( $\text{OAc}^-$ ) present initially in 300 mL

$$= 0.3182 \times 300 = 95.45$$

mmoles of acetic acid ( $\text{HOAc}$ ) present initially in 300 mL

$$= 0.1818 \times 300 = 54.55$$

mmoles of  $\text{RNO}_2$  reduced

$$= 300 \times 0.0100 = 3$$

From the stoichiometry of the equation, 3 mmoles of  $\text{RNO}_2$  will consume 12 moles of  $\text{H}^+$  for reduction. The  $\text{H}^+$  is obtained from dissociation of  $\text{HOAc}$ .

On complete electrolytic reduction of  $\text{RNO}_2$ ,

$$\text{mmoles of HOAc} = 54.55 - 12.00 = 42.55$$

$$\text{mmoles of OAc}^- = 95.45 + 12.00 = 107.45$$

$$4.76 = \text{pH} + \log \frac{42.55}{107.45}$$

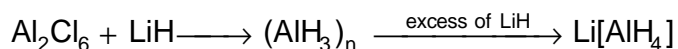
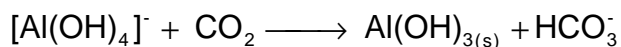
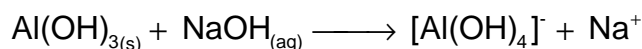
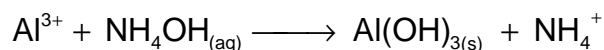
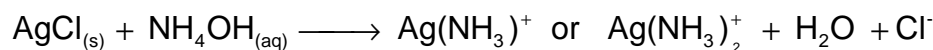
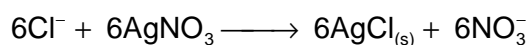
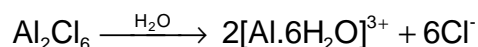
$$\text{pH} = 5.16$$

### 13. Identification of an inorganic compound

- a. The white gelatinous precipitate in group (III) obtained by qualitative analysis of solution **B** indicates the presence of  $\text{Al}^{3+}$  ions. The white precipitate with  $\text{AgNO}_3$  indicates the presence of  $\text{Cl}^-$  ions.

From the above data the compound **A** must be a dimer of aluminium chloride  $\text{Al}_2\text{Cl}_6$ .

- b. The reactions are as follows



### 14. Ionic and metallic structures

- a.
- i. The lattice of NaCl consist of interpenetrating *fcc* lattices of  $\text{Na}^+$  and  $\text{Cl}^-$
  - ii. The co-ordination number of sodium is six since, it is surrounded by six nearest chloride ions.
  - iii. For NaCl, the number of  $\text{Na}^+$  ions is: twelve at the edge centres shared equally by four unit cells thereby effectively contributing  $12 \times 1/4 =$

$3\text{Na}^+$  ions per unit cell and one at body center. Thus, a total of  $3 + 1 = 4$   $\text{Na}^+$  ions per unit cell.

Number of  $\text{Cl}^-$  ions is: six at the center of the faces shared equally by two unit cells, thereby effectively contributing  $6 \times 1/2 = 3$   $\text{Cl}^-$  ions per unit cell and eight at the corners of the unit cell shared equally by eight unit cells thereby effectively contributing  $8 \times 1/8 = 1$   $\text{Cl}^-$  ion per unit cell. Thus, a total of  $3 + 1 = 4$   $\text{Cl}^-$  ions per unit cell.

Hence, the number of formula units of  $\text{NaCl}$  per unit cell =  $4\text{Na}^+ + 4\text{Cl}^-$   
=  $4\text{NaCl}$

- iv. The face diagonal of the cube is equal to  $\sqrt{2}$  times 'a' the lattice constant for  $\text{NaCl}$ . The anions/anions touch each other along the face diagonal. The anion/cations touch each other along the cell edge.

$$\text{Thus, } a = 2 (r_{\text{Na}^+} + r_{\text{Cl}^-}) \quad \dots\dots\dots(1)$$

$$\text{Face diagonal } \sqrt{2} a = 4 r_{\text{Cl}^-} \quad \dots\dots\dots(2)$$

Substituting for 'a' from (1) into (2) we get :

$$\sqrt{2} \times 2 (r_{\text{Na}^+} + r_{\text{Cl}^-}) = 4 r_{\text{Cl}^-} \text{ from which,}$$

the limiting radius ratio  $r_{\text{Na}^+} / r_{\text{Cl}^-} = \underline{0.414}$

- v. The chloride ion array is expanded to make the octahedral holes large enough to accommodate the sodium ions since, the  $r_{\text{Na}^+} / r_{\text{Cl}^-}$  ratio of 0.564 is larger than the ideal limiting value of 0.414 for octahedral six coordination number.
- vi. As the cation radius is progressively increased, the anions will no longer touch each other and the structure becomes progressively less stable. There is insufficient room for more anions till the cation / anion radius ratio equals 0.732 when, eight anions can just be grouped around the cation resulting in a cubic eight coordination number as in  $\text{CsCl}$ .

- vii. Generally, the *fcc* structure with a six coordination number is stable in the cation/anion radius ratio range 0.414 to 0.732. That is, if  $0.414 < r^+/r^- < 0.732$  then, the resulting ionic structure will generally be NaCl type *fcc*.

b.

- i. Bragg's law states  $\lambda = 2d_{hkl} \sin(\theta)$

$$154 \text{ pm} = 2 \times d_{200} \sin(15.8^\circ)$$

$$d_{200} = \frac{154 \text{ pm}}{2 \times \sin(15.8^\circ)} = \frac{154 \text{ pm}}{2 \times 0.272} = 283 \text{ pm}$$

Thus, the separation between the (200) planes of NaCl is 283 pm.

- ii. Length of the unit cell edge,  $a = d_{100} = 2 \times d_{200}$

$$a = 2 \times 283 \text{ pm} = \underline{566 \text{ pm}}$$

- iii. Since it is an *fcc* lattice,

$$\text{cell edge, } a = 2(r_{\text{Na}^+} + r_{\text{Cl}^-})$$

$$\text{radius of sodium ion } r_{\text{Na}^+} = \frac{a - 2 r_{\text{Cl}^-}}{2} = \frac{566 - 362}{2} = \underline{102 \text{ pm}}$$

c.

- i. The difference in an *hcp* and a *ccp* arrangement is as follows:

The two 'A' layers in a *hcp* arrangement are oriented in the same direction making the packing of successive layers ABAB.. and the pattern repeats after the second layer whereas, they are oriented in the opposite direction in a *ccp* arrangement resulting in a ABCABC... packing pattern which repeats after the third layer.

The unit cell in a *ccp* arrangement is based on a cubic lattice whereas in a *hcp* arrangement it is based on a hexagonal lattice.

- ii. Packing fraction =  $\frac{\text{Volume occupied by 4 atoms}}{\text{Volume of unit cell}}$

Let 'a' be the length of the unit cell edge

Since it is an *fcc* lattice, face diagonal =  $\sqrt{2}a = 4r$  .....(1)

Volume of the unit cell =  $a^3$

$$\text{Packing fraction} = \frac{4 \times 4 \pi r^3}{3 \times a^3} \dots\dots\dots(2)$$

Substituting for 'a' from (1) into (2), we get

$$\text{Packing fraction} = \frac{4 \times 4 \times 22 \times (\sqrt{2})^3 \times r^3}{3 \times 7 \times (4r)^3} = 0.74$$

Thus, packing fraction in a *ccp* arrangement = 0.74

- iii. The coordination number(12) and the packing fraction (0.74) remain the same in a *hcp* as in a *ccp* arrangement.

d.

- i. For an *fcc*, face diagonal =  $\sqrt{2}a = 4r_{\text{Ni}}$

where a = lattice constant

$r_{\text{Ni}}$  = radius of the nickel atom

$$r_{\text{Ni}} = \frac{\sqrt{2} \times a}{4} = \frac{\sqrt{2} \times 352.4 \text{ pm}}{4} = \underline{124.6 \text{ pm}}$$

- ii. Volume of unit cell =  $a^3 = (3.524 \text{ \AA})^3 = 43.76 \text{ \AA}^3$

- iii. Density of Nickel,  $\rho_{\text{Ni}} = \frac{Z \times M / N}{V}$

No. of Ni atoms,  $Z = 4$  for an *fcc* lattice

Avogadro constant

$$N = \frac{Z \times M}{\rho_{\text{Ni}} V} = \frac{4 \times 58.69 \text{ g mol}^{-1}}{8.902 \text{ g cm}^{-3} \times 43.76 \times 10^{-24} \text{ cm}^3}$$

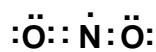
$$N = \underline{6.02 \times 10^{23} \text{ mol}^{-1}}$$

## 15. Compounds of nitrogen

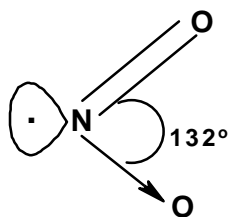
a.

- i.  $\text{NO}_2$  : No. of electrons in the valence shell around nitrogen  
 $= 5 + 0 + 2 = 7$

The Lewis structure for  $\text{NO}_2$  is as shown below.

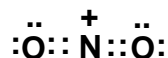


According to VSEPR, the molecule ideally should have linear geometry. However, this molecule has one single unpaired electron present on nitrogen. Due to the repulsion between the unpaired electron and the other two bonded pairs of electrons, the observed bond angle is less than  $180^\circ$  ( $132^\circ$ ). Thus, the shape of the molecule is angular as shown below.

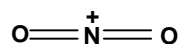


- ii.  $\text{NO}_2^+$ : No. of electrons in the valence shell around nitrogen  
 $= (5 + 2 + 2 - 1) = 8$

The Lewis structure is as shown below



Thus, there are no non-bonded electrons present on nitrogen. The two  $\sigma$  - bonds will prefer to stay at  $180^\circ$  to minimize repulsion between bonded electron pairs giving a linear geometry ( $180^\circ$ ). The  $\pi$ -bonds do not influence the shape.





$\text{NO}_2^-$ : No. of electron in the valence shell around nitrogen  
 $= 5 + 2 + 1 = 8$

The Lewis structure is as shown below

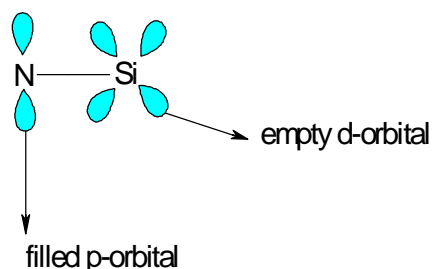


In case of  $\text{NO}_2^-$ , there is a lone pair of electrons present on nitrogen. Due to strong repulsion between the lone pair of electrons and the bonded pairs of electrons the angle between the two bond pairs shrinks from the ideal  $120^\circ$  to  $115^\circ$ .

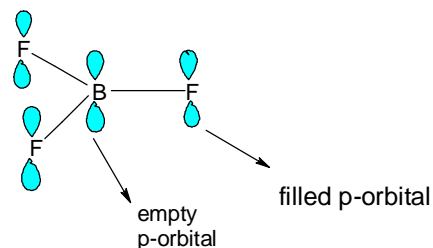
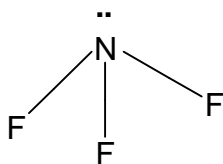
- b. In case of trimethylamine, the shape of the molecule is pyramidal with a lone pair present on nitrogen. Due to the lone pair Me-N-Me angle is reduced from  $109^\circ 4'$  to  $108^\circ$ .



However, in case of trisilylamine, d orbital of silicon and p orbital of nitrogen overlaps giving double bond character to the N-Si bond. Thus, delocalisation of the lone electron pair of nitrogen takes place and the resultant molecule is planar with  $120^\circ$  bond angle.



- c. Both N and B are trivalent. However,  $\text{NF}_3$  is pyramidal in shape. In case of  $\text{BF}_3$ , the B-F bond gets double bond character due to the overlapping of p orbitals present on boron and fluorine. The observed bond energy is, therefore, much greater in  $\text{BF}_3$



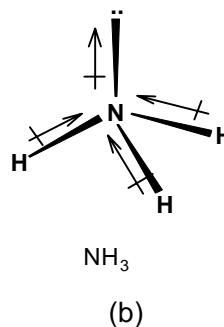
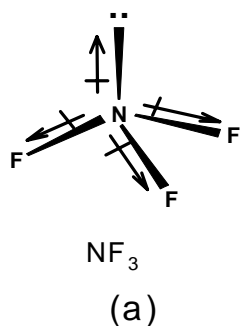
d.

- i. The difference in boiling points of  $\text{NF}_3$  and  $\text{NH}_3$  is due to hydrogen bonding which is present in ammonia.

High electronegativity of fluorine decreases the basicity of nitrogen in  $\text{NF}_3$ . Thus,  $\text{NF}_3$  does not act as a Lewis base.

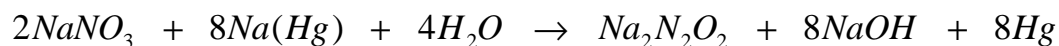
- ii. In  $\text{NF}_3$ , the unshared pair of electrons contributes to a dipole moment in the direction opposite to that of the net dipole moment of the

N-F bonds. See figure (a).



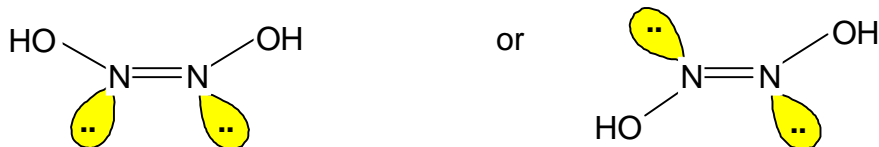
In  $\text{NH}_3$ , the net dipole moment of the N-H bonds and the dipole moment due to the unshared pair of electrons are in the same direction. See figure (b).

e.

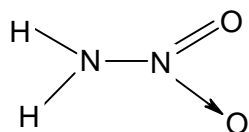


$\text{Na}_2\text{N}_2\text{O}_2$  is the salt of  $\text{H}_2\text{N}_2\text{O}_2$  (Hyponitrous acid).

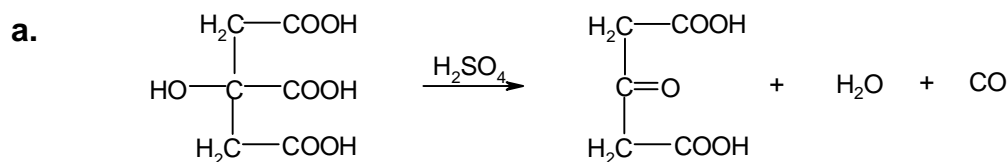
Structure :



Isomer is:  $\text{H}_2\text{N}-\text{NO}_2$  (Nitramide)



## 16. Structure elucidation with stereochemistry



3-oxo-1,3-pentanedioic acid

$\alpha$  - Hydroxy carboxylic acids undergo similar reaction.

- b. Molecular weight of **A** = 236  
 20 mL 0.05 M KOH  $\equiv$  118 mg **A**  
 1000 mL 1 M KOH  $\equiv$  118 g **A**

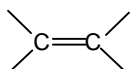
$\therefore$  The acid is dibasic

Molecular weight of **A** = 236

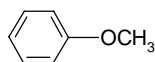
80 mg Br<sub>2</sub>  $\equiv$  118 mg **A**

160 gm Br<sub>2</sub>  $\equiv$  236 g **A**

**A** contains one double bond



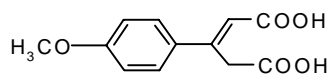
It has anisole ring in the molecule



It is formed from HOOC-CH<sub>2</sub>-CO-CH<sub>2</sub>-COOH

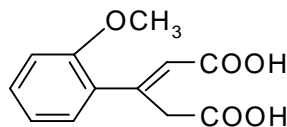
It has molecular formula **C<sub>12</sub>H<sub>12</sub>O<sub>5</sub>**

Due to steric hindrance the attachment of the aliphatic portion on the anisole ring will be para with respect to -OCH<sub>3</sub>. Hence the structure will be

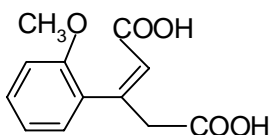


As **A** forms anhydride the two COOH groups should be on the same side of the double bond.

- c. Isomers of **A**



( E ) 3-( 2-methoxyphenyl )-2-pentenedioic acid



( Z ) 3-( 2-methoxyphenyl )-2-pentenedioic acid



hindrance of **OCH<sub>3</sub>** group favours the attack at the *para* position. Steric hindrance of the **OH** group is comparatively less. Thus, the attack is possible at the *ortho* or *para* positions. However, addition at *ortho* position is favoured as it leads to cyclization of the intermediate acid to stable **B**.

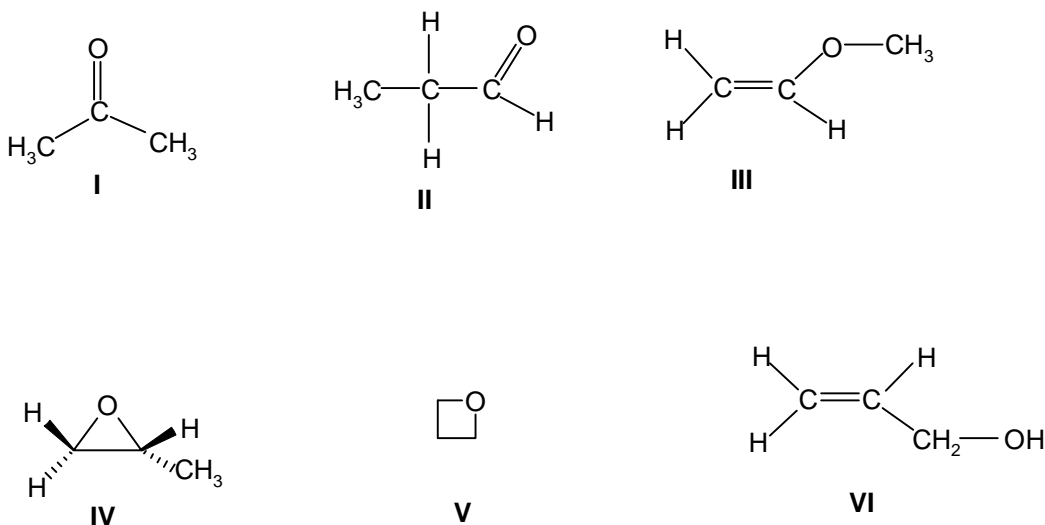
- h.** Phenol has only one **OH** group on the phenyl ring whereas resorcinol has two **OH** groups on the phenyl ring at the *m*-positions. Hence, position 4 is considerably more activated (i.e, electron rich) in the case of resorcinol.



Therefore, under identical reaction conditions, the yield of compound **C** is much higher than that of **B**.

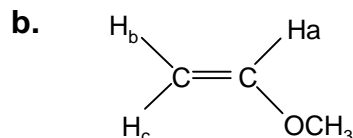
## 17. Organic spectroscopy and structure determination

- a.** The given Molecular formula is **C<sub>3</sub>H<sub>6</sub>O**. Therefore, the possible structures are:



The NMR spectrum of compound **A** shows a single peak which indicates that all the protons in **A** are equivalent. This holds true only for structure I. The IUPAC name of this compound is 2-propanone.

The NMR spectrum of compound **B** shows four sets of peaks, which indicate the presence of four non-equivalent protons. This holds true for structures III and IV. However, for structure IV, no singlet peak (see peak at  $\delta = 3$ ) will be observed. So, compound **B** must have structure III. The IUPAC name is 1-methoxyethene.



Three doublets of doublets centred at 6.5 ppm, 3.9 ppm, 3.5 ppm are seen in the spectrum. The assignments in the spectrum are

$H_a$	:	6.5 ppm
$H_b$	:	3.5 ppm
$H_c$	:	3.9 ppm

Due to the presence of electron donating **OCH<sub>3</sub>**, the trans proton  $H_b$  has higher electron density and thus more shielded than  $H_c$ . Thus,  $H_b$  appears upfield as compared to  $H_c$ . There is also a singlet line at  $\delta=3$ . This corresponds to the **H** in **OCH<sub>3</sub>**.

**c.** Coupling constants

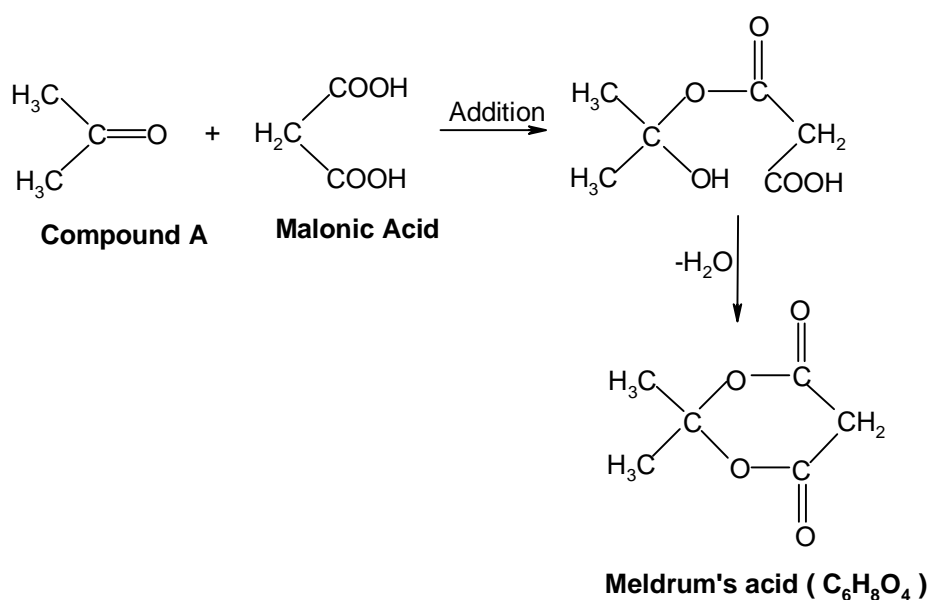
$H_a$	:	12, 16 Hz	$J (H_a, H_b) = 12 \text{ Hz}$
			$J (H_a, H_c) = 16 \text{ Hz}$
$H_b$	:	8, 12 Hz	$J (H_a, H_b) = 12 \text{ Hz}$
			$J (H_b, H_c) = 8 \text{ Hz}$
$H_c$	:	8, 16 Hz	$J (H_b, H_c) = 8 \text{ Hz}$
			$J (H_c, H_a) = 16 \text{ Hz}$

**Note:**  $J = (\text{difference in two lines in ppm}) \times (\text{Instrument frequency})$

Geminal coupling < *cis*-vicinal coupling < *trans*-vicinal coupling

d.

Peak positions in Hz (for 400 MHz instrument)	Peak positions in Hz (for 600 MHz instrument)
2614	3921
2602	3903
2598	3897
2586	3879

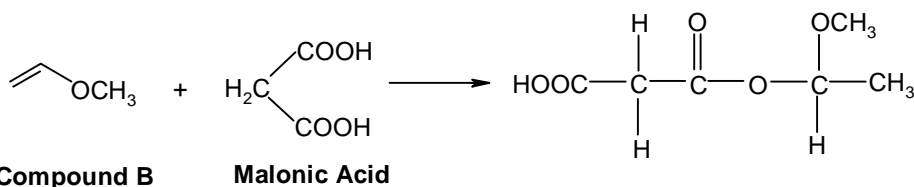
e. Compound **A** will react with malonic acid in the following manner

The structure of Meldrum's acid is consistent with the <sup>1</sup>H-NMR and IR data.

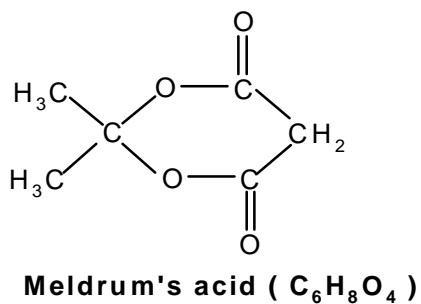
The peak in the IR spectrum at 1700 –1800 cm<sup>-1</sup> is because of the C=O stretching. The presence of peaks only between 0 – 7 δ in the <sup>1</sup>H-NMR spectrum indicates that the compound doesn't have any acidic group like COOH or OH.

If compound B reacts, the only possibility is that it will add across the double bond giving a product with molecular formula equal to **C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>**. This molecular formula does not match with the one stated in the problem.

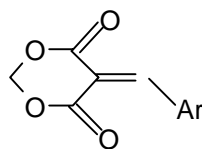




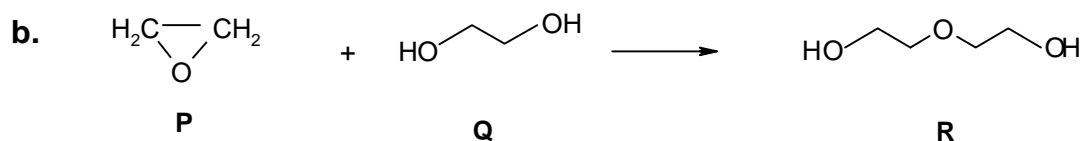
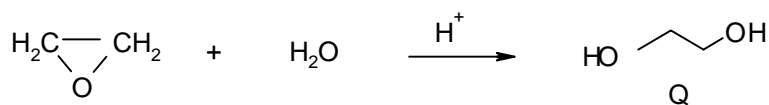
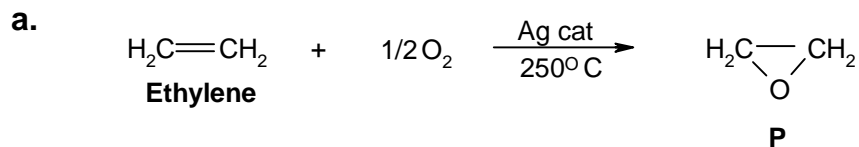
- f. The increased acidity is due to active  $-\text{CH}_2$  group of Meldrum's acid flanked by two  $-\text{CO}$  groups. The carbanion formed at  $-\text{CH}_2$  will be stabilised by these  $-\text{CO}$  groups, which are coplanar.

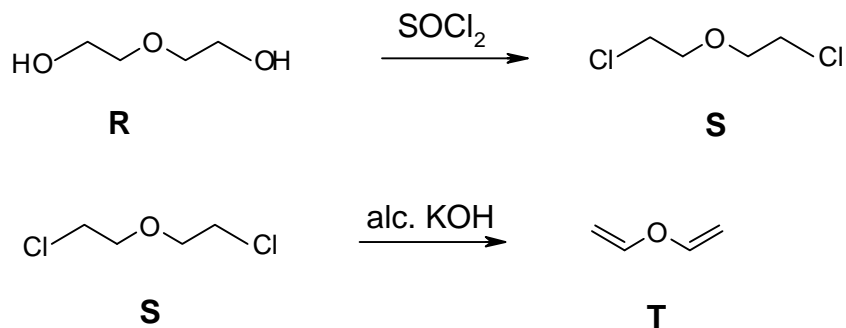


- g. The condensation product of Meldrum's acid with an aromatic aldehyde has the structure

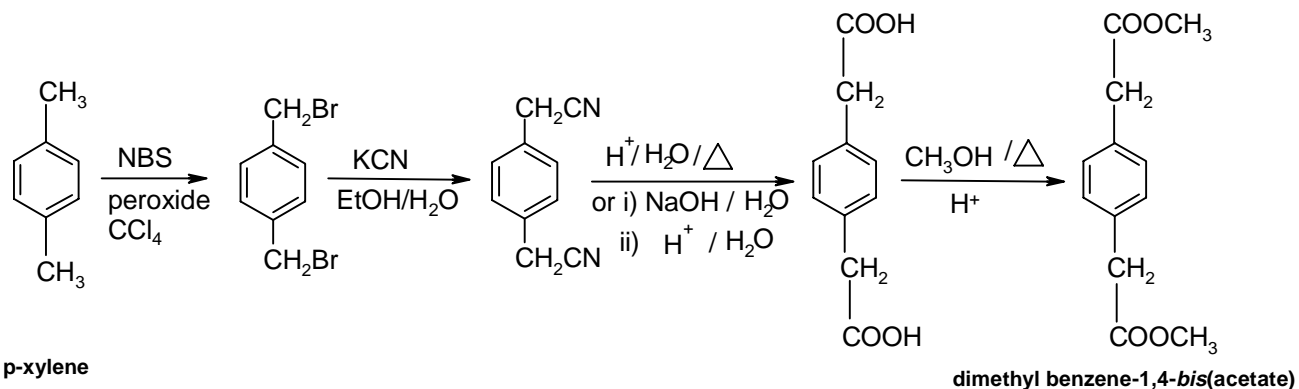


## 18. Polymer synthesis

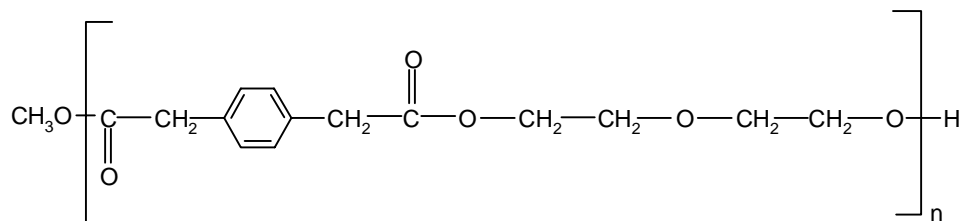




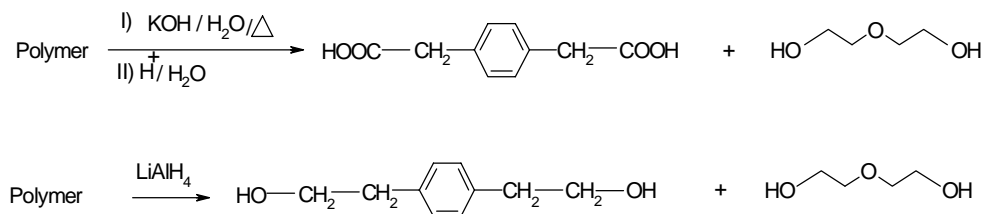
c.

d. Three signals (three singlets for -CH<sub>3</sub>, -CH<sub>2</sub> and aromatic protons)

e. Structure of polymer

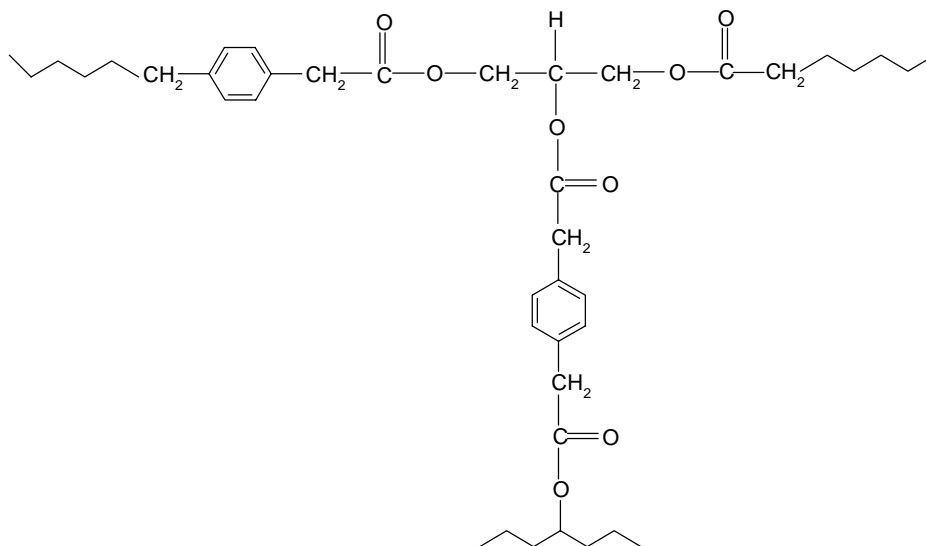
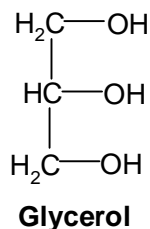


f.



g. With Glycerol (being a triol), cross-links between the polymer chains involving

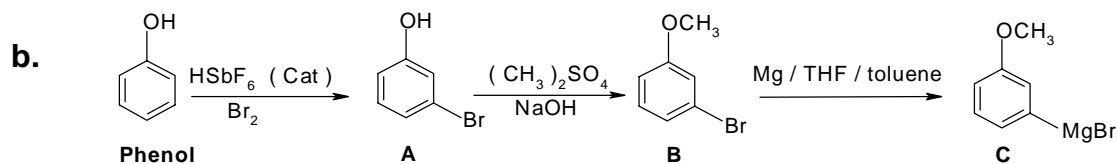
the secondary hydroxyl group will form giving a three-dimensional network polymer is possible.



The polymer is unsuitable for drawing fibers because of its cross-linked, resin-like property.

## 19. Organic synthesis involving regioselection

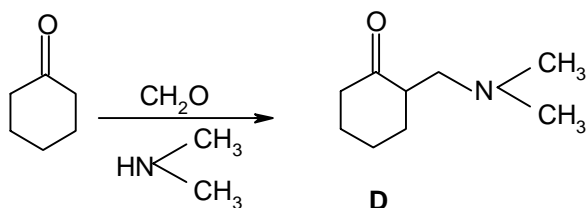
- a. The product obtained in the presence of catalyst  $\text{HSbF}_6$  is *m*-bromophenol. From the mass spectra given in the problem, direct bromination of phenol gives *o/p*-bromo derivatives as OH group present in phenol is *o/p*-directing.



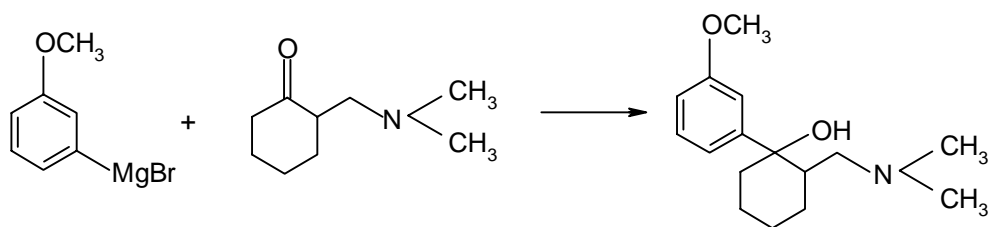
Compound **B** may undergo nucleophilic reaction at the carbon bearing bromine. Compound **C** contains a carbanion and hence functions as a

nucleophile and will attack an electrophile. Thus, reactivity of **B** is reversed on its conversion to **C** (umpolung).

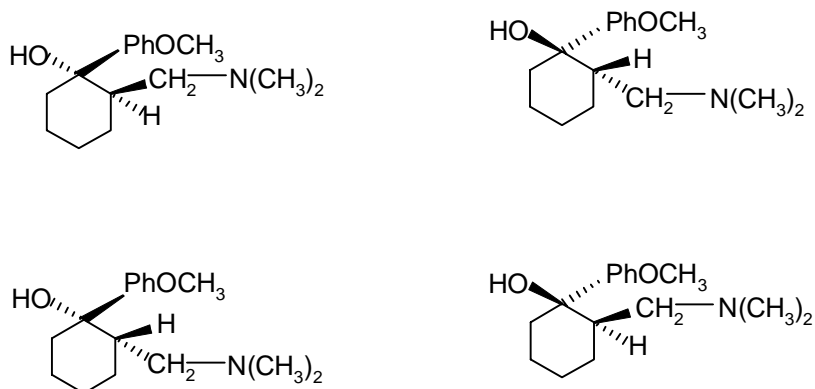
c.



Cyclohexanone

**C****D****Tramadol**

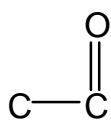
d.



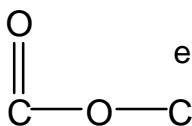
Tramadol has two asymmetric carbon atoms. It has two pairs of enantiomers .

## 20. Carbon acids

a. The molecular formula of the keto ester is  $\text{C}_5\text{H}_8\text{O}_3$ . Since **X** and **Y** are keto esters, they must have the following units-



keto group



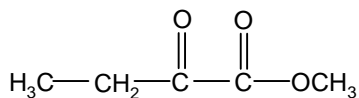
ester group

This accounts for  $\text{C}_4\text{O}_3$ . The remaining part comprises of  $\text{CH}_8$ . Thus, only two types of ester groups are possible, methyl or ethyl.

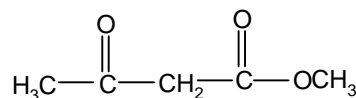
For a methyl ester: **CH<sub>3</sub>** will be a part of the ester moiety. This leaves CH<sub>5</sub> to be attached.

For an ethyl ester: **CH<sub>2</sub>CH<sub>3</sub>** will be a part of the ester group. Therefore H<sub>3</sub> unit needs to be accounted for.

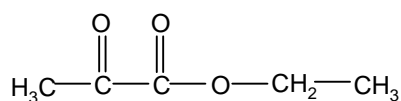
Therefore, possible structures of the keto esters are:



**Structure I**

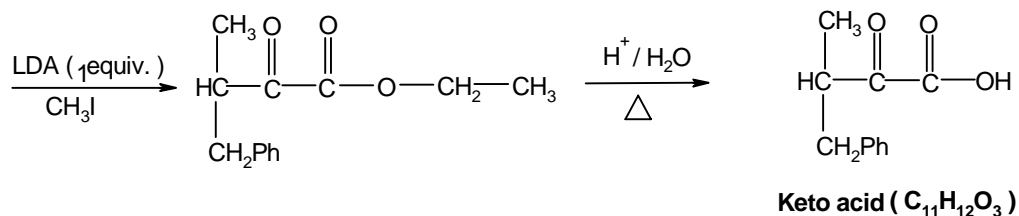
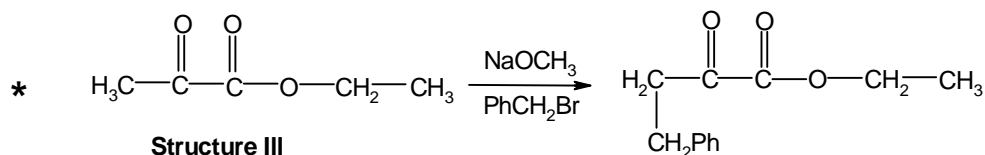
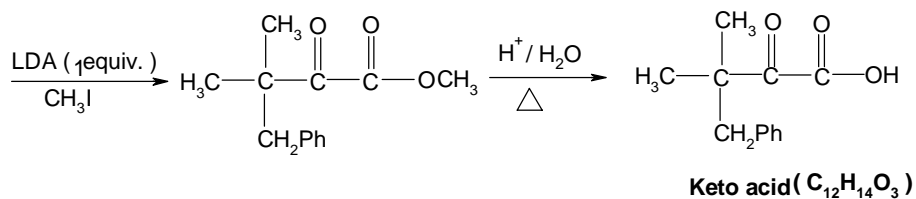
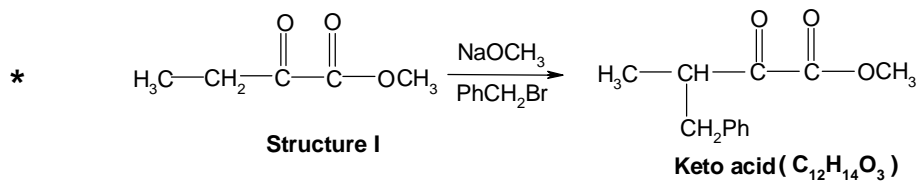


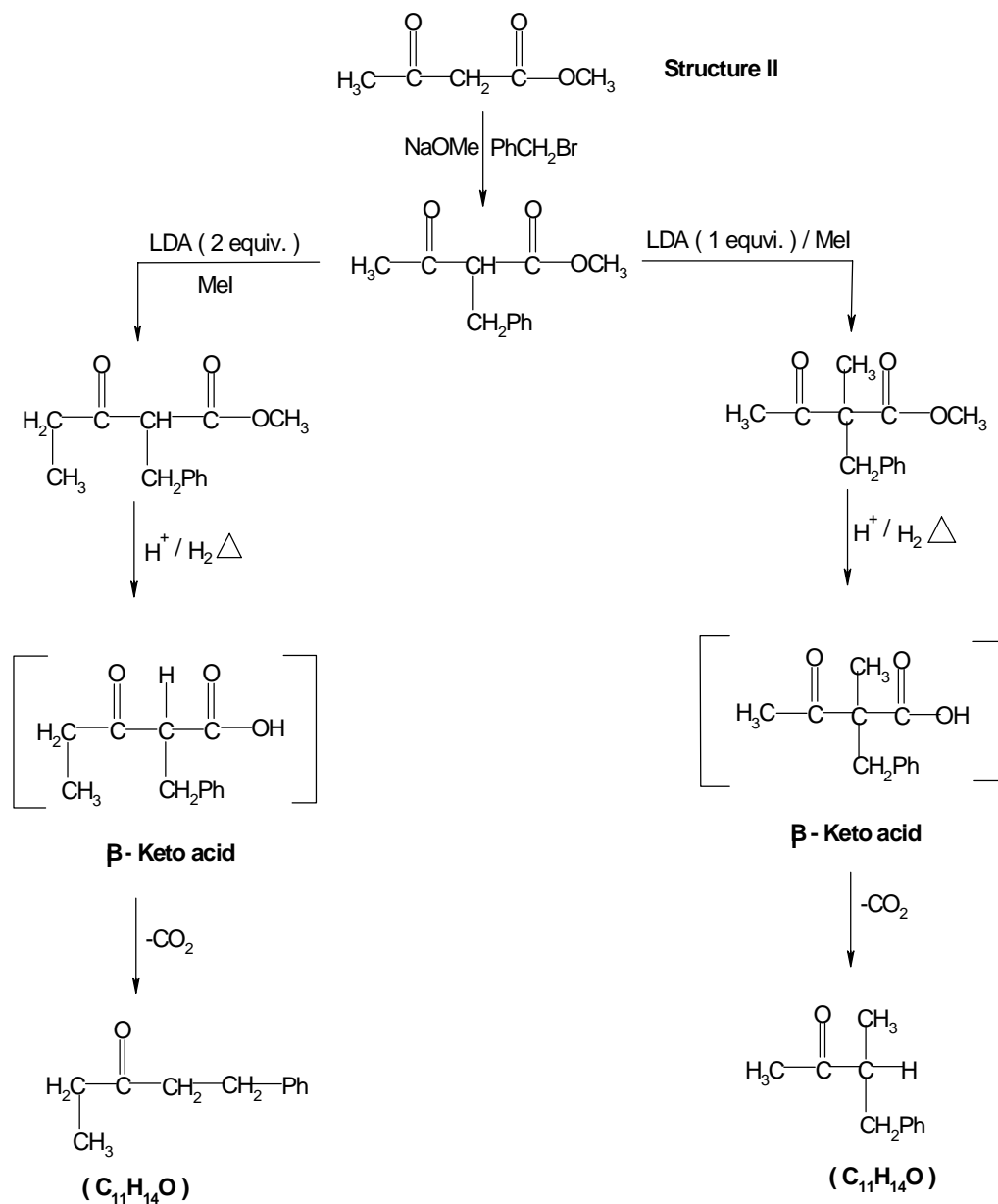
**Structure II**



**Structure III**

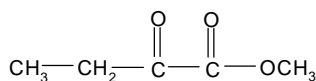
**b. Reaction sequence for keto esters**





- ◆ Structure I gives a keto acid with molecular formula **C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>** which matches with the formula of the keto acid obtained from Y. ∴ Structure I is Y.
- ◆ Structure II gives a neutral compound with molecular formula **C<sub>11</sub>H<sub>14</sub>O** that matches with the molecular formula of the neutral acid stated for X. ∴ Structure II is X.
- ◆ Structure III gives a keto acid with molecular formula **C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>** that also does not match with any given molecular formula.

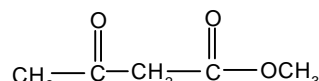
Hence the two keto esters are :



**Compound Y**

(Structure I)

$\alpha$ -keto ester

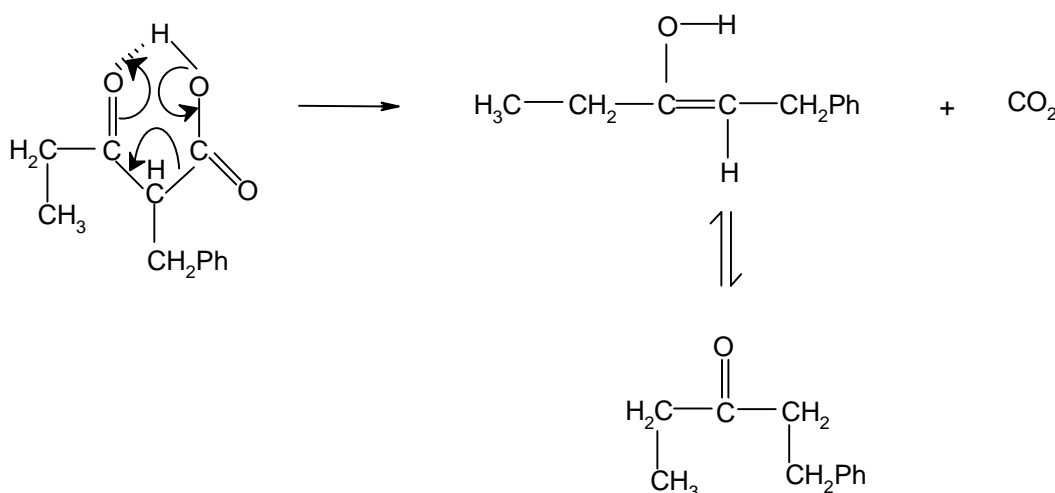


**Compound X**

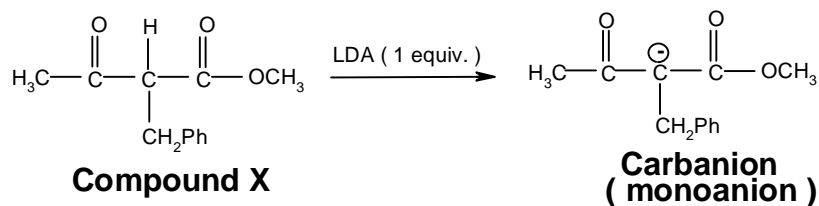
(Structure II)

$\beta$ -keto ester

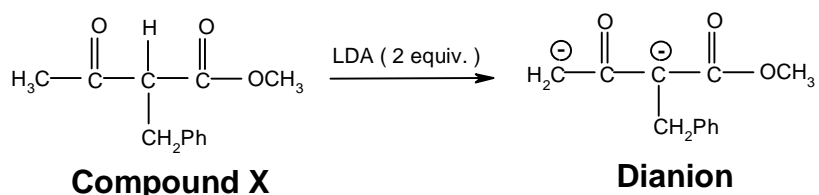
- c. The  $\beta$ -keto ester gives on hydrolysis a  $\beta$ -keto acid. This acid readily undergoes decarboxylation involving a 6-membered transition state, giving a neutral product (Ketone).



- d. i. When 1 equivalent of LDA is used compound X produces a carbanion (monoanion) as shown below.



- ii. Use of 2 equivalents of LDA leads to the formation of a dianion.



## 21. Amino acids and enzymes

- a. The protonated amino group has an electron withdrawing effect. This enhances the release of proton from the neighboring  $-\text{COOH}$ , by stabilizing the conjugate base  $-\text{COO}^-$ . This effect is greater when the  $-\text{COO}^-$  is physically closer to  $-\text{NH}_3^+$ . As  $-\text{NH}_3^+$  group is present on the  $\alpha$ -carbon, the effect is greater on  $\alpha$ - $\text{COOH}$  than on the  $\gamma$ - $\text{COOH}$ . So the  $\text{pK}_a$  value of  $\alpha$ - $\text{COOH}$  is lower than that of  $\gamma$ - $\text{COOH}$ .
- b. The ratio of ionized to unionized  $\gamma$ - $\text{COOH}$  group is obtained by using Henderson-Hasselbalch equation,

$$\text{pH} = \text{pK}_a + \log \frac{[\text{COO}^-]}{[\text{COOH}]}$$

The  $\text{pH} = 6.3$  and  $\text{pK}_a$  of  $\gamma$ - $\text{COOH}$  group is 4.3. Substituting these values in the above equation we get,

$$6.3 = 4.3 + \log \frac{[\text{COO}^-]}{[\text{COOH}]}$$

$$\therefore [\text{COOH}] = \frac{100}{101} = 0.99\% \text{ at pH } 6.3$$

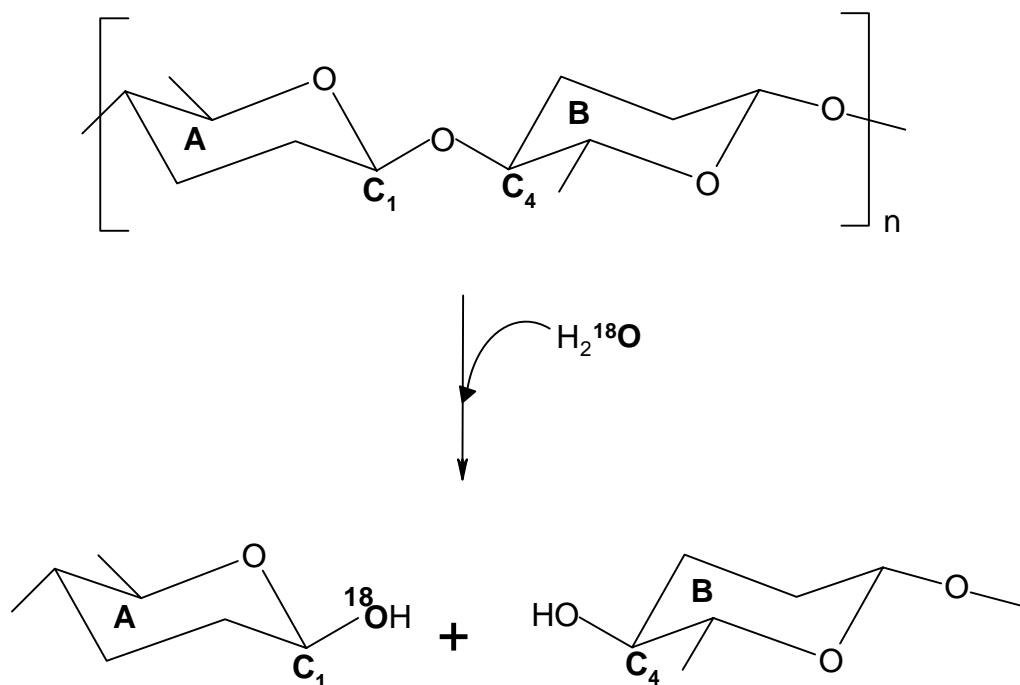
- c. Glutamic acid has two  $\text{pK}_a$  values lower than 7.0 and one  $\text{pK}_a$  value higher than 7.0. Thus, the isoelectric point ( $\text{pI}$ ) for glutamic acid will lie between the two acidic  $\text{pK}_a$  values.

$$\text{pI} = (2.2 + 4.3) / 2 = 3.25$$

At  $\text{pH} = 3.25$ , net charge on glutamic acid will be zero since this  $\text{pH}$  coincides with  $\text{pI}$  of glutamic acid. Hence, glutamic acid will be stationary at  $\text{pH} 3.25$ .

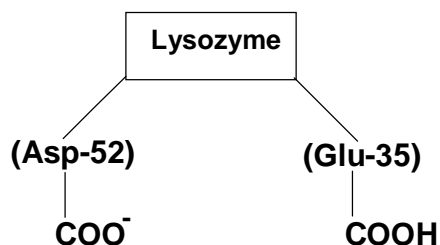


- d. In the hydrolysis of the glycosidic bond, the glycosidic bridge oxygen goes with C<sub>4</sub> of the sugar **B**. On cleavage, <sup>18</sup>O from water will be found on C<sub>1</sub> of sugar **A**.



NOTE: The reaction proceeds with a carbonium ion stabilized on the C<sub>1</sub> of sugar **A**.

- e. Most glycosidases contain two carboxylates at the active site that are catalytically important. Lysozyme is active only when one carboxylate is protonated and the other is deprotonated. A descending limb on the alkaline side of the pH profile is due to ionization of -COOH. An ascending limb on the acidic side is due to protonation of -COO<sup>-</sup>. Thus the enzyme activity drops sharply on either side of the optimum pH. The ideal state of ionization at pH = 5 will be,



NOTE: It is desirable to study the amino acid side chains (R-groups) and their ionization properties. The pKa values of these groups significantly determine the pH dependence of enzyme activity.

f. Answers 2 and 4 are correct. Ionization of  $-\text{COOH}$  leads to generation of a negatively charged species,  $-\text{COO}^-$ . This charged species is poorly stabilized by diminished polarity and enhanced negative charge. Hence ionization of  $-\text{COOH}$  group is suppressed and the pKa is elevated.

g. The ratios of pseudo-first order rate constant (at 1M  $\text{CH}_3\text{COO}^-$ ) in (a) to the first order rate constants in (b) and (c) provide the effective local concentrations.

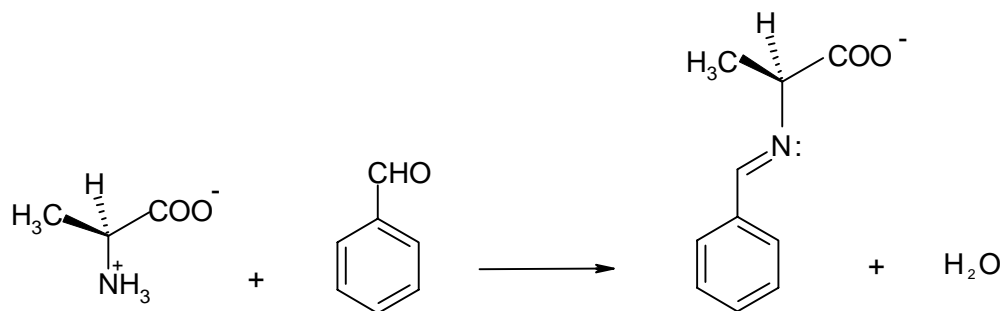
For example, (2)  $(0.4) / (0.002) = 200$   
i.e. the effective concentration = 200 M

(3)  $(20) / (0.002) = 10,000$   
i.e. the effective concentration = 10,000 M

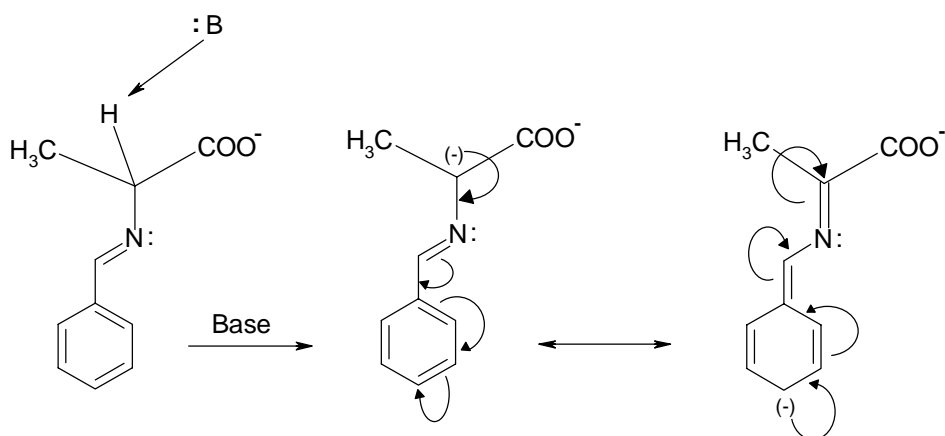
h. In addition to the enhanced local concentration effect, the  $\text{COO}^-$  group in (3) is better oriented to act in catalysis. The double bond restricts the motion of  $\text{COO}^-$  and thus reduces the number of unsuitable orientation of  $-\text{COO}^-$ , thereby enhancing the reaction rate.

## 22. Coenzyme chemistry

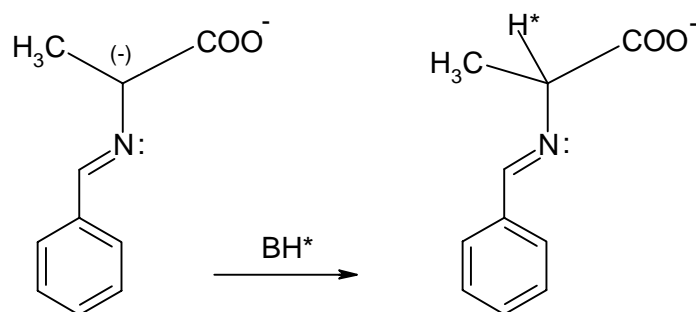
a. Step 1: Schiff base formation



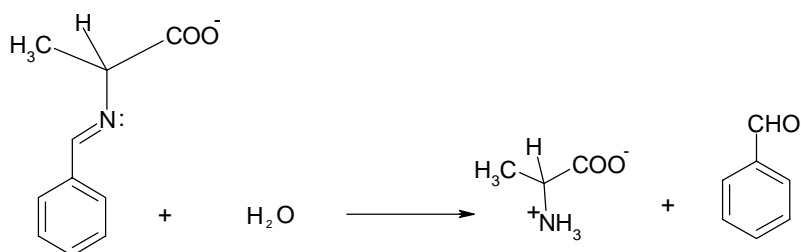
## Step 2: Proton abstraction



## Step 3: Reprotonation



## Step 4: Hydrolysis



- b.** From the information stated in the problem, the following conclusions can be drawn:

Structure 2: Removal of the phosphate group does not hamper the activity. This indicates that the phosphate is not critical for the activity of PLP.

Similarly,

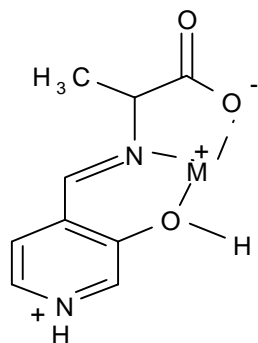
Structure 3:  $\text{CH}_2\text{-OH}$  is not critical.

Structure 4: Phenolic OH is needed in the free form.

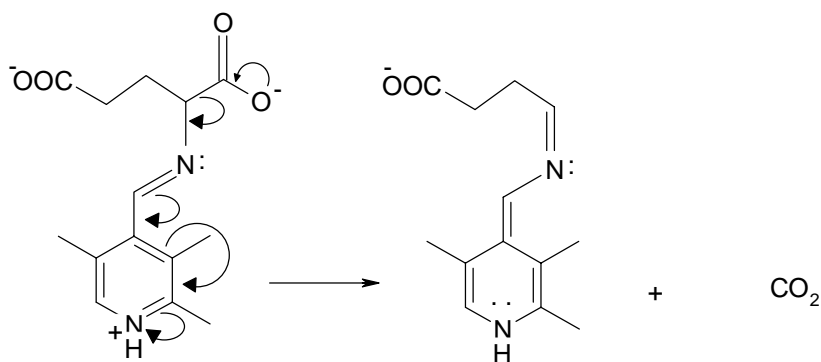
Structure 5:  $\text{NO}_2$ , a well-known electron withdrawing group, causes benzaldehyde to become activated. Hence positively charged nitrogen in structure 3 must be also important for its electron withdrawing effect.

Structure 6: Electron withdrawing effect of  $\text{NO}_2$  is only effective from the *para* position. Introduction of this group at *meta* position leads to an inactive analog.

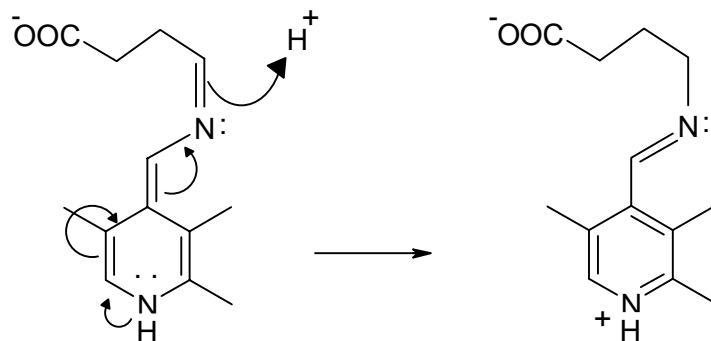
- c. **Role of metal ion:** The metal ion is involved in a chelation, as shown below, and provides an explanation for the critical role of the phenolic OH. The planar structure formed due to chelation assists in the electron flow.



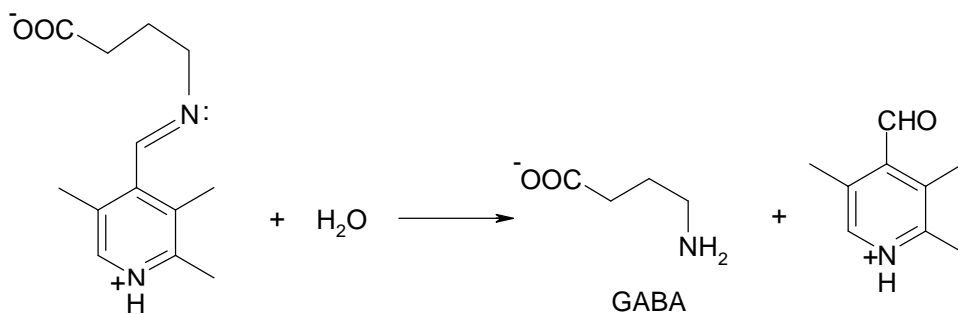
- d. Step 1: Schiff base formation and decarboxylation



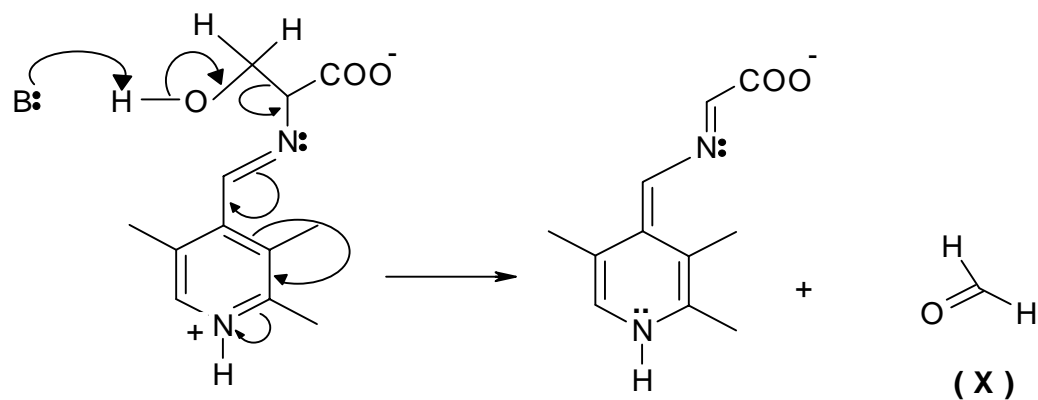
Step 2: Tautomerization



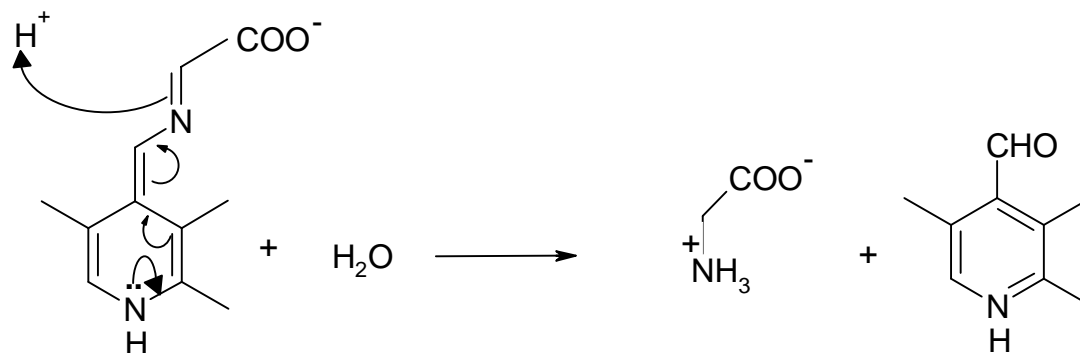
Step 3: Hydrolysis



e. Step 1: Schiff base formation followed by carbon-carbon bond scission.

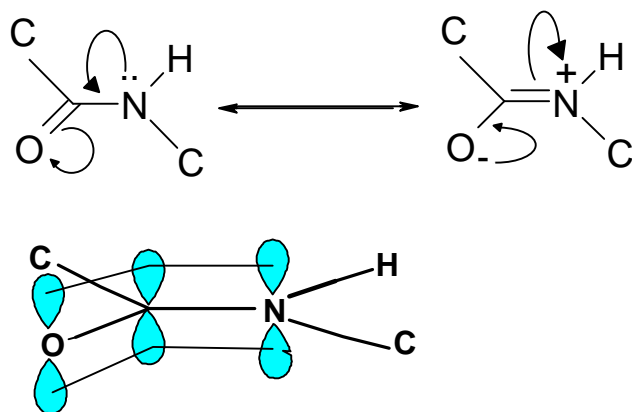


Step 2: Tautomerization followed by hydrolysis

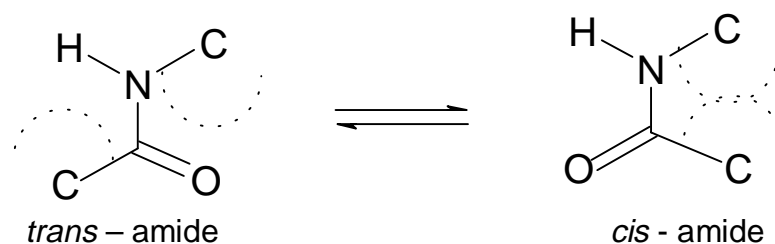


### 23. Protein folding

- a. The planar amide group, that is,  $C_{\alpha}$ , O, H and the next  $C_{\alpha}$  are in a single plane - is stabilized by resonance. The C-N bond of the amide assumes partial double bond character and the overlap between p orbitals of O, C and N is maximized. The  $C_{\alpha}$ 's across this partial double bond can assume *cis* or *trans* arrangement.



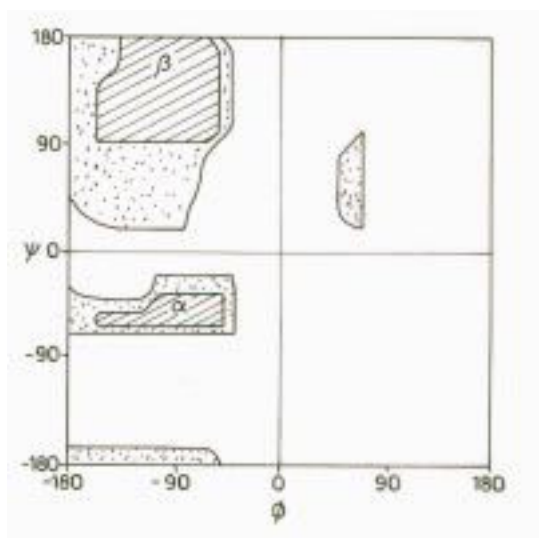
- b. With nineteen of the amino acids, the *trans* arrangement is sterically favoured (i. e. it is comparatively less crowded). In the case of proline, *cis* and *trans* arrangements are almost equally crowded.



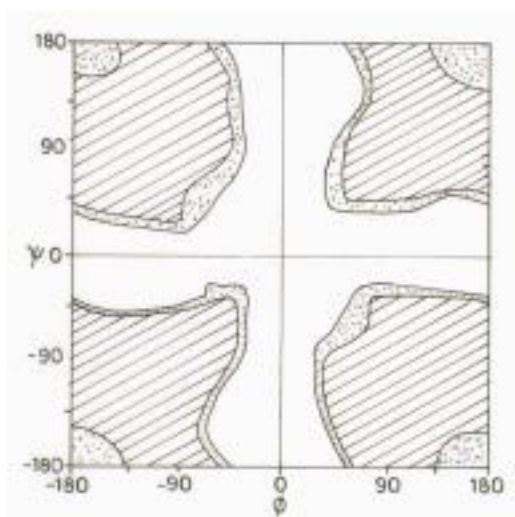


- c. Note about Ramchandran diagram:** In a polypeptide, the amide units are planar (partial double bond character across the N-C bond) but the bonds connecting N and C<sub>α</sub>, and the carbonyl carbon and C<sub>α</sub> are free to rotate. These rotational angles are defined as  $\phi$  and  $\psi$ , respectively. The conformation of the main chain is completely defined by these angles. Only some combinations of these angles are allowed while others are disallowed due to steric hindrance. The allowed range of  $\phi$  and  $\psi$  angles are visualised as a steric contour diagram, shown below, known as the Ramachandran diagram.

For nineteen amino acids, the conformational choice is largely restricted to the so-called  $\alpha$  and  $\beta$  regions on left half of the Ramachandran diagram (Panel A). This is due to the L - chiral nature of amino acids and the steric effects of their R groups. Glycine is an achiral residue with H as the R group. Therefore, much larger conformational regions on both left and right halves of Ramachandran diagram are accessible to this residue (Panel B).

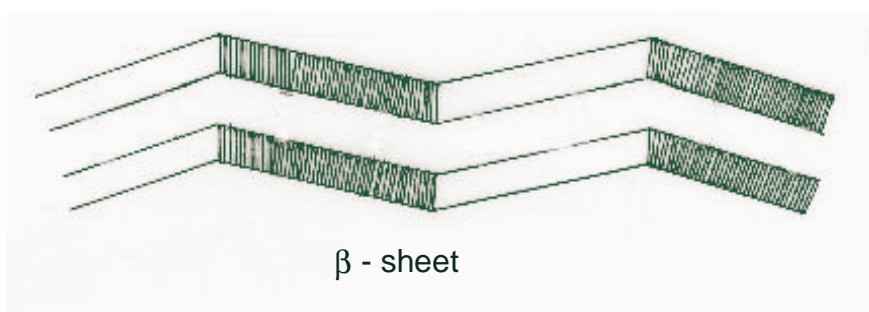


Panel A

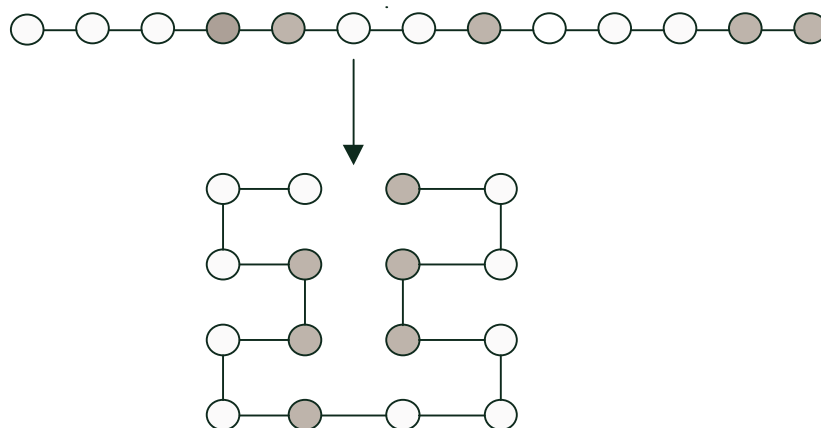


Panel B

- d. Consecutive residues in  $\alpha$  conformation form the  $\alpha$ -helix. Similarly, consecutive residues in  $\beta$  conformation form the  $\beta$ -sheet. Both  $\alpha$ -helix and  $\beta$ -sheet structures feature extensive networks of hydrogen bonds which stabilise them. Thus random combinations of  $\alpha$  and  $\beta$  conformations are rarely found.

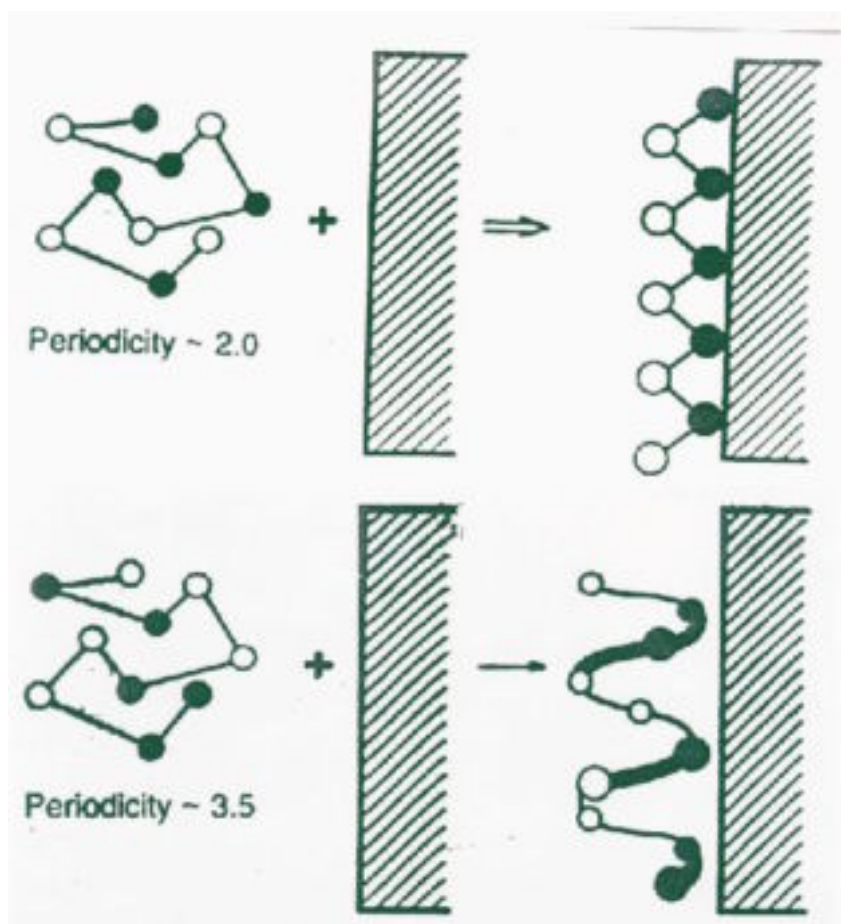


- e. For a polypeptide to fold in an aqueous environment, nearly half the R groups should be nonpolar (water hating) and the other half polar (water loving). Upon folding to form a globular protein, the nonpolar R groups are packed inside (away from water) while the polar groups are positioned on the surface (in contact with water). The phenomenon is similar to the hydrophobic aggregation of a micellar structure in water. If all the R groups are either polar or non-polar, no hydrophobic segregation is possible, and no folding will occur.





- f. Alternating polar/nonpolar periodicity of R groups favors  $\beta$ -sheets. All the non-polar groups will face the apolar surface while the polar groups will be exposed to water. So the net folding will be like a  $\beta$ -sheet. On the other hand, a complex periodic pattern of R group polarities is needed in forming the  $\alpha$ -helix.



Hydrophobic  
periodicity  
(primary  
sequence)

+ Apolar  
surface  
(interface)

$\Rightarrow$

Induced  
(secondary  
structure)

## 24. Protein sequencing

The sequence of amino acids in a protein or polypeptide is expressed starting from the N-terminal amino acid. From Edman degradation method the N-terminal amino acid is Asp. In the N-terminal fragment generated by trypsin or CNBr this amino acid should, therefore, be in position 1. All other peptides generated by CNBr cleavage will

be preceded by Met on their N-terminal side. Likewise, all peptides generated by trypsin should be preceded by Arg or Lys. As we proceed from N-terminal amino acid to C-terminal amino acid, we carefully examine the different amino acids in each position shown in Table1(a) and 1(b)

For the first fragment starting from N-terminal Asp in position 1, we look for residues common in each position to CNBr and trypsin cleaved peptides. This gives

Position	1	2	3	4	5	6	
Residue	Asp	-Pro/Tyr	- Tyr	-Val	-Ile/Leu	-Arg	.....(1)

At position 6 Arg will render the polypeptide susceptible to trypsin. Therefore, 7<sup>th</sup> residue of this CNBr fragment (Table1a) should be same as residue1 in another peptide generated by trypsin and 8<sup>th</sup> residue of this CNBr fragment will be same as residue 2 in Table 1(b). Therefore we get

7	8	
Gly/Phe -	Tyr	.....(2)

Since 8 will be Tyr, Pro will be assigned to position 2 of the polypeptide .....(3)

Residue 9 in the polypeptide should be at position 3 in the Table1(b) and residues 10,11,12,13 and 14 should be at positions 4,5,6,7 and 8 respectively in Table1(b). The same residues should be in positions 1 onwards in Table1(a).

None of the residues in position 3 (Table1b) is same as in position 1 in Table 1(a). However, positions 4 to 8 in Table 1(b) have residues common with positions 1 to 5 in Table 1(a). Further Glu in position 1 (Table 1a) will be preceded by Met (since it is a part of CNBr cleaved peptide). And position 3 in Table 1(b) has Met. Therefore, we get

9	10	11	12	13	14	
Met-	Glu -	Thr -	Ser -	Ilu -	Leu	.....(4)

Position 5 in the polypeptide can now be firmly assigned to Ilu .....(5)

Positions 15 and 16 in the polypeptide will be beyond residue 8 in the trypsin cleaved peptide (not shown here). We now attempt to construct the remaining trypsin or CNBr fragments.

Table 1 (a) shows Arg in position 1. This will be preceded by a Met. Matching of the unassigned residues in position 2 in Table 1(a) with those in position 1 in Table 1(b) and for subsequent positions by the procedure demonstrated earlier that will give.

Met - Arg - Tyr - Pro - His - Asn - Trp - Phe - Lys - Gly - Cys .....(6)

(The last two residues are the unassigned residues in position 1 and 2 in Table 1b) Considering (2), (5) and (6) together it is now possible to firmly assign position 7 on the polypeptide to Gly .....(7)

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

1	2	3	4	5
Asp	- Pro	- Tyr	- Val	- Ile

**b.** The sequence of the first fragment generated by CNBr treatment is

1	2	3	4	5	6	7	8
Asp	- Pro	- Tyr	- Val	- Ile	- Arg	- Gly	- Tyr

To complete the sequence of the polypeptide we need to construct the sequence of another trypsin fragment. Starting from position 4-(Arg) in Table 1(a) we get the sequence,

Arg-Phe-His-Thr-Ala ..... (8)

At this stage, we again examine the unassigned residues. The Arg in (8) will have to be serially preceded by Asn, Gln, Gly and Met (these are the unassigned residues in respective positions in Table 1(a)). We then get the sequence,

Met-Gly-Gln-Asn-Arg-Phe-His-Thr-Ala .....(9)

And following the Ala in (9)

Leu-Ser-Cys-Glu ... ..(10)

From (9) and (10), we get the sequence

Met-Gly-Gln-Asn-Arg-Phe-His-Thr-Ala-Leu-Ser-Cys-Glu .....(11)

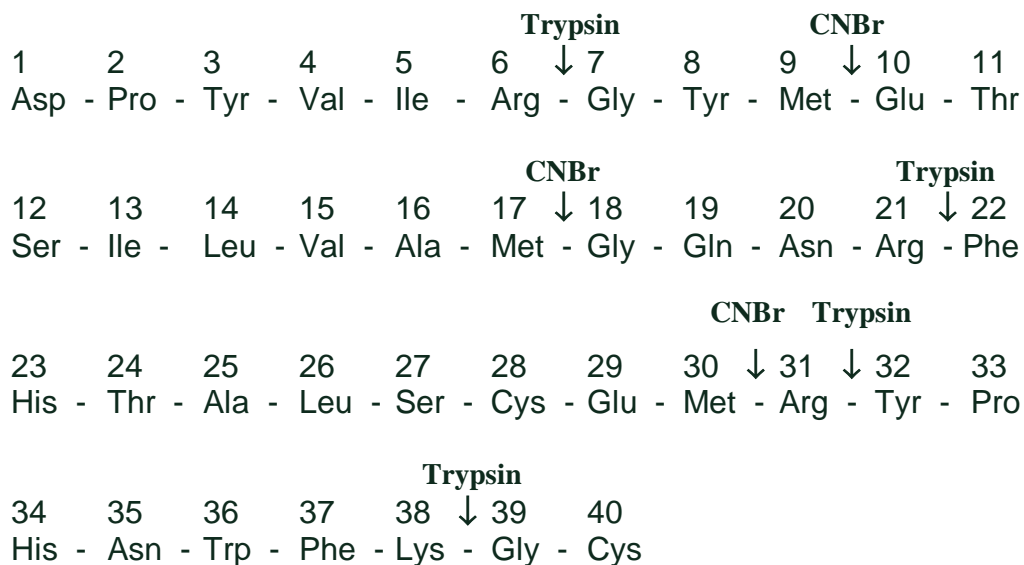
Since the smallest fragment is a dipeptide (Table 1b) and (6) shows that it follows Lys, it follows that this will be at the C-terminal end. Therefore, the partial sequence shown in (6) will follow the partial sequence shown in (11). Thus, we get

Met-Gly-Gln-Asn-Arg-Phe-His-Thr-Ala-Leu-Ser-Cys-Glu-Met-Arg-Tyr-Pro-His-Asn-  
Trp-Phe-Lys-Gly-Cys .....(12)

There is already a Met in position 9 of the polypeptide. The next Met can only come earliest at position 17 since CNBr fragment have at least 8 amino acids. Therefore, the starting residues of (12) can be assigned position 17.

This leaves positions 15 and 16 which will be filled by the unassigned residues Val and Ala in the CNBr fragment at positions 6 and 7 (Table 1a).

c. The final sequence, therefore, will be



Arrows (↓) indicate the CNBr and trypsin-labile sites.

d. There are 6 basic amino acid residues in the polypeptide.  $6/40 = 15\%$

e. An  $\alpha$  helix has 3.6 amino acid residues per turn of  $5.4\text{\AA}$ .

Thus, the length of the polypeptide in  $\alpha$  helical conformation will be :

$$40/3.6 \times 5.4 = 59.4 \text{ \AA}$$

- e. The polypeptide has 40 amino acids. Since each amino acid is coded for by a triplet of nucleotides, the total number of nucleotide pairs in the double stranded DNA of the exon will be

$$40 \times 3 = 120 \text{ base pairs.}$$

The molecular weight of the DNA making the exon

$$= 330 \times 2 \times 120$$

$$= 79200 \text{ Da}$$

- g. If the exon contains 120 base pairs and A and C are in equal numbers, there will be 60 A-T pairs and 60 G-C pairs. Each A-T pair is held by two H-bonds and each G-C pair is held by three H-bonds. Hence the total number of H-bonds holding this double helix is :

$$(60 \times 2) + (60 \times 3) = 300$$