

Indian Olympiad Qualifier in Chemistry (IOQC) 2020-2021

conducted jointly by

Homi Bhabha Centre for Science Education (HBCSE-TIFR)

and

Indian Association of Physics Teachers (IAPT)

Part II: Indian National Chemistry Olympiad (INChO)

Homi Bhabha Centre for Science Education (HBCSE-TIFR)

Date: February 6, 2021

Time: 15:45 – 17:45 hrs

Roll No. -

- Write your Roll No. at the space provided above.
- This question booklet consists of 14 printed sheets including periodic table. Check that the booklet has all the pages. If not, report to the invigilator immediately.
- You must show the main steps in the calculations and state the necessary assumptions wherever applicable.
- Answers written in pencil will be penalized.
- Use of non-programmable scientific calculator is allowed.
- A copy of the Periodic Table of the Elements is provided at the end.
- Do not leave the examination room until you are directed to do so.
- The answer sheet must be returned to the invilator. You can carry this question paper with you.

Fundamental Constants

Avogadro number $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ 1 atm = 101325 Pa

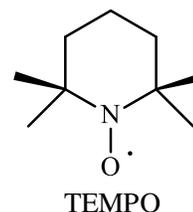
Molar gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ Density of water = 1000 kg m⁻³

$= 0.08205 \text{ L atm K}^{-1} \text{ mol}^{-1}$ 1 Faraday = 96500 C

pH = $-\log [\text{H}^+]$ pK_a = $-\log K_a$

Persistent radical – TEMPO

Radicals are commonly known to be highly unstable due to their reactivity. However, in 1960, the synthesis and isolation of a stable radical, 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) changed this notion. Stable radicals are also called persistent radicals. TEMPO, a persistent radical is a red solid compound which has applications in organic synthesis and chemical analysis.



Part A: The redox equilibria of TEMPO

1.1 Draw the resonance structure of TEMPO (including the lone pairs) other than the one shown above.

The redox reactions of TEMPO are known to be affected by the pH of the medium.

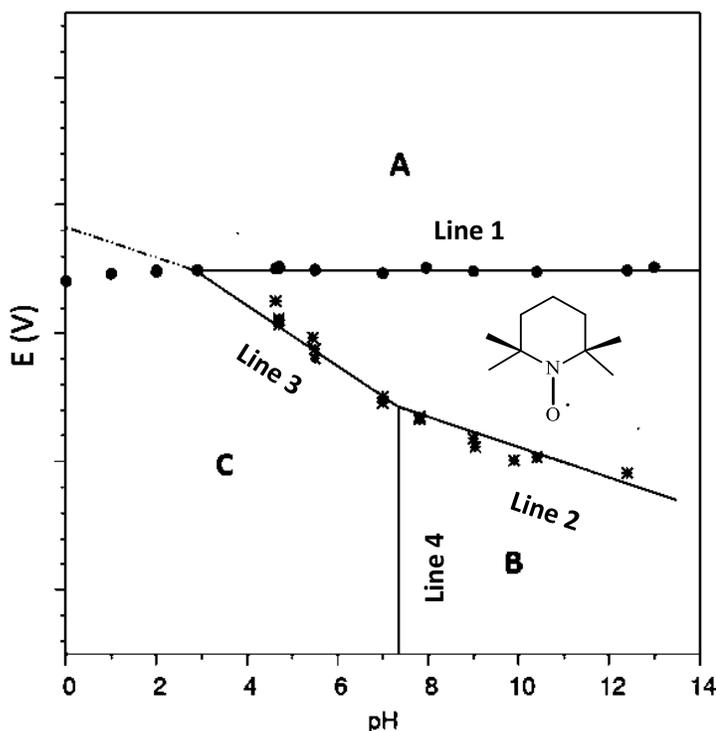
TEMPO undergoes one electron oxidation to yield species **A**. TEMPO also undergoes reduction (accompanied by protonation) to give **B**. $E^\circ_{(\text{A} \rightarrow \text{TEMPO})} = 0.745 \text{ V}$ (w.r.t. NHE) and $E^\circ_{(\text{TEMPO} \rightarrow \text{B})} = 0.610 \text{ V}$ (w.r.t. NHE).

1.2 Draw the structures of **A** and **B**.

1.3 Write the half-cell reaction and Nernst equation for the conversion of TEMPO to **B** (refer 1.2). Derive the relation between the reduction potential (E) of TEMPO and pH.

The stability of different redox species at specific potential and pH can be represented on a 2 dimensional plot as shown here for the TEMPO system. Such a plot is known as Pourbaix diagram. In this diagram, the regions between the lines represent conditions at which one particular species is thermodynamically more stable than all other species.

The lines represent equilibrium between two species (in this case at equal concentrations) under standard condition ($T = 298.15 \text{ K}$). A horizontal line (line 1) separates species related by electron transfer process only. The slant lines (line 2 and 3) separate species related by both electron and proton transfers.



1.4 Draw the structure of **C** and write the equilibrium process between the species (with the structures) separated by line 4 at $\text{pH} = 7.4$.

1.5 Derive the expression for the ratio $\frac{\text{slope (line 3)}}{\text{slope (line 2)}}$ starting from the corresponding Nernst equations and determine its value using the parameters involved.

A disproportionation reaction is one in which two identical **units** of a species react together to give a reduced and an oxidized species. (Reverse of this reaction is called comproportionation reaction). At $\text{pH} < 3$, TEMPO undergoes disproportionation reaction, yielding **A** and **C**.

- 1.6 Write balanced equation for the disproportionation reaction and determine the equilibrium constant for the reaction at standard temperature? Show the main steps of calculations.

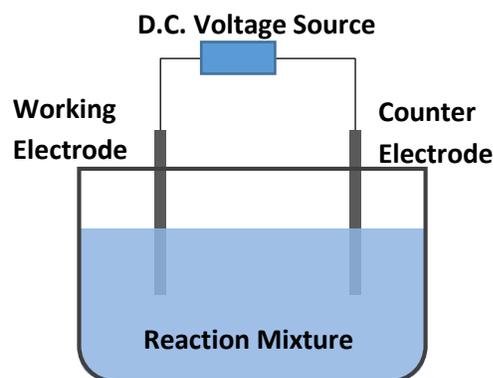
Part B: Using TEMPO in Electrochemical Oxidation

In reaction mixtures, the electrochemical potentials can also be modified by non-reacting species (such as ions) present in the system. Also the typical conditions, such as $[H^+]$ may be very different from standard values of 1 M. In such situations, a formal potential $E^{\circ'}$ is defined for the system as the potential of the system at equilibrium where certain species are at certain (typical) specified concentrations. For the following, net concentration of TEMPO species is taken as 1 mM, and pH as specified in each case.

One of the important applications of **A** is to mediate the electrochemical oxidation of primary and secondary alcohols under mildly basic aqueous conditions. The products of the reaction include aldehydes/ketones in high yields and **B**, which is electrochemically converted back to **A**. A typical setup for this reaction involves –

- a “working electrode” – where the electrochemical regeneration of **A** takes place
- a counter electrode – for completion of the electrochemical circuit

In addition, a reference electrode is used for ensuring the absolute potentials of working and counter electrodes in the cell.



- 1.7 Write the reaction taking place at the counter electrode and identify the anode and the cathode.

Mechanistic studies reveal that the oxidation of alcohol (ROH) proceeds through a nucleophilic attack of the alkoxide ion on **A**.

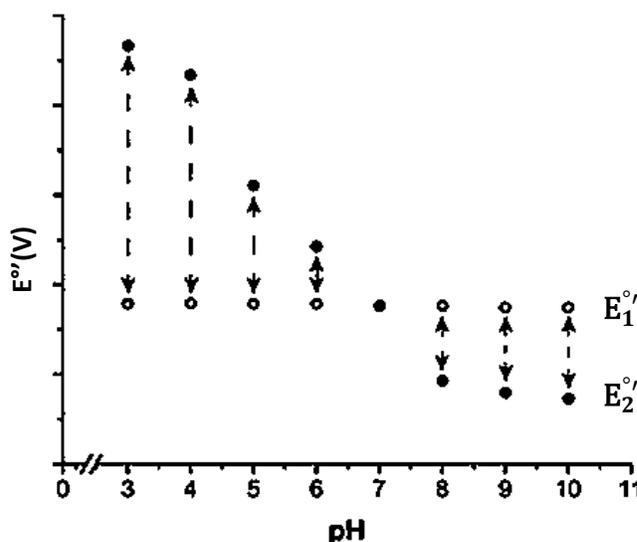
- 1.8 Draw the structure of the most favorable intermediate formed after the nucleophilic attack.

After **A** is converted to **B** by alcohol, the species **A** is regenerated back from **B** in two steps:

Step i) conversion of **B** to TEMPO. If done electrochemically, it requires a formal potential of at least $E_2^{\circ'}$.

Step ii) conversion of TEMPO to **A**. This requires a formal potential of at least $E_1^{\circ'}$.

For TEMPO in the above described cell, $E_1^{\circ'}$ doesn't change with pH, whereas $E_2^{\circ'}$ changes with pH as shown in graph here.

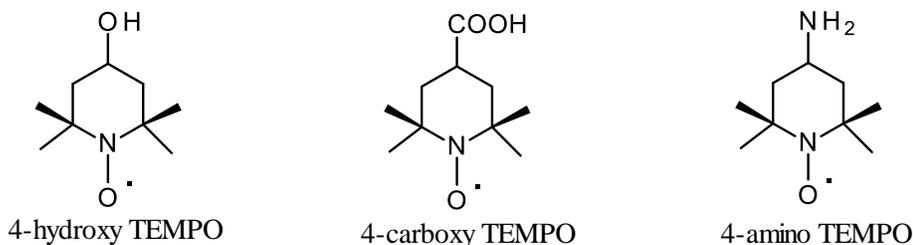


- 1.9 If the working electrode is operated at potential $E_1^{\circ'}$,

- write the balanced equations for the possible pathways by which **B** is converted to TEMPO under the following conditions:
 - $pH < 7$
 - $pH > 7$

b) Based on the above data, which of these conditions (i or ii) is expected to give higher conversion of alcohols to aldehydes/ketones per mol of **A** produced at the working electrode?

Introduction of functional groups to TEMPO can help in tuning its electrochemical properties. The effect of substituents on corresponding $E_1^{\circ'}$ values was studied for TEMPO analogs.



1.10 Of the above three, write the analogs which are most likely to show pH-dependent $E_1^{\circ'}$ values in the pH range 2 to 7.

1.11 Arrange the values of $E_1^{\circ'}$ for substituted TEMPO analogs at pH 7 in order.

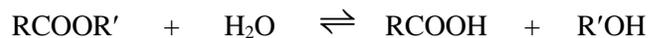
Graphs and diagrams are adapted from (Chem. Rev. 2018, 118, 4834–4885).

Problem 2

14 marks

Esters

Many sweet-smelling compounds contain an ester functional group, R-CO-O-R', where R/R' = alkyl, aryl groups. Hydrolysis of an ester is an exhaustively studied reaction:

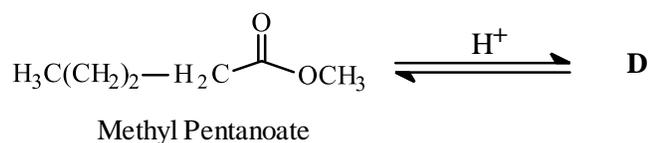


The hydrolysis can be catalyzed by an acid (A) or a base (B). The reaction may be unimolecular (1) or bimolecular (2), and may involve breaking of acyl-O bond (AC) or alkyl-O bond (AL). Thus, there are eight different mechanisms possible as listed in the table below.

Acid catalyzed		Base catalyzed	
Unimolecular	Bimolecular	Unimolecular	Bimolecular
A_{AC1}	A_{AC2}	B_{AC1}	B_{AC2}
A_{AL1}	A_{AL2}	B_{AL1}	B_{AL2}

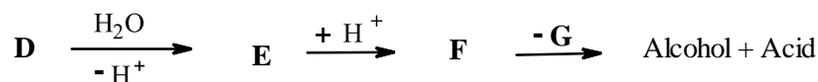
The mechanism in a given reaction depends on the structure of the ester and the reaction conditions.

2.1 Consider the acidic hydrolysis of methylpentanoate in aqueous H_2SO_4 .

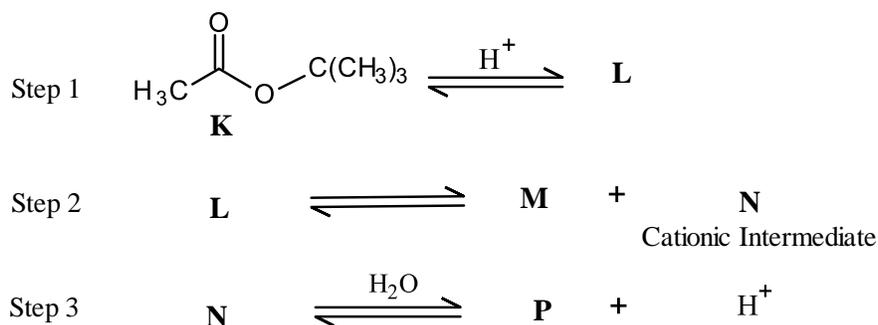


i) Draw the structure of the most favorable conjugate acid (**D**) of methyl pentanoate.

ii) **D** is attacked by a water molecule (nucleophile) and, through a series of reactions, is broken into a carboxylic acid and an alcohol. Identify the species **E** (a neutral molecule), **F** and **G** (both charged species).



2.2 In the hydrolysis of **K** in moderately concentrated aq. H_2SO_4 , the preferred mechanism involves conjugated acid (**L**) of **K**. **L** undergoes decomposition to form a stable product **M** and a cation **N**. **N** on reaction with water forms **P**.

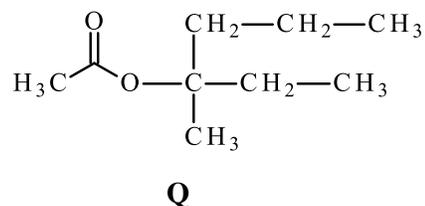


i) Draw the structures of **L**, **M**, **N**, and **P**.

ii) Identify the slowest step in the reaction mechanism.

iii) Using the Table in page 4, label the above reaction mechanism appropriately.

2.3. An optically active sample of ester **Q** is completely hydrolyzed under aqueous acidic conditions.

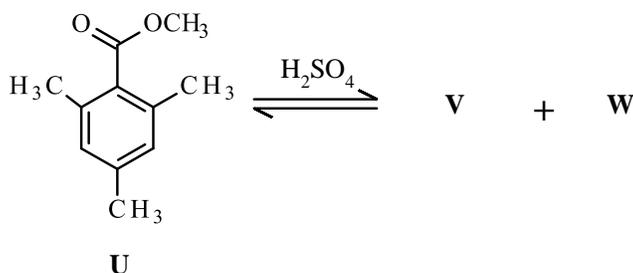


In the hydrolysis using moderately concentrated H_2SO_4 , two additional compounds **R** and **S** (other than the expected alcohol and carboxylic acid) having identical molecular formulae are formed in small amounts.

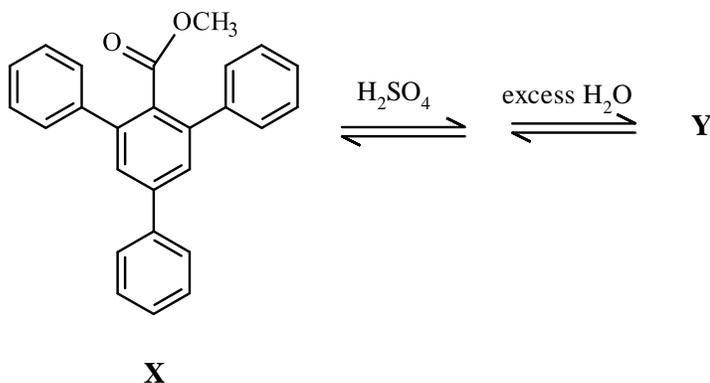
i) Draw the structures of **R** and **S**.

ii) When the hydrolysis is carried out in aqueous ethanol containing H_2SO_4 , another compound **T** which is not an acid/alcohol/ester is also formed. Identify **T**.

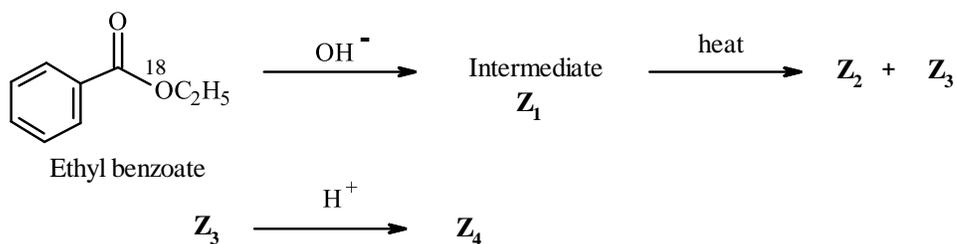
2.4. Hydrolysis of **U** is difficult under normal reaction conditions, most likely due to bulky methyl groups near the carbonyl group. The ester is hydrolyzed by dissolving in concentrated H_2SO_4 , and then pouring the reaction mixture into a large excess of cold water. Draw the structure of cationic intermediate **V** and neutral compound **W** formed in concentrated acid before pouring into water.



- 2.5. When ester **X** is dissolved in concentrated H_2SO_4 , and the mixture is poured in water, an unusual product **Y** is obtained which is neither an acid nor an alcohol. Draw the structure of **Y**.



- 2.6. An ester can also be hydrolyzed by heating with aqueous NaOH followed by acidification to yield the carboxylic acid. For alkaline hydrolysis of ethyl benzoate labeled with ^{18}O , the rate of hydrolysis depends on the concentrations of both ester and alkali.



- i) Draw the structures of the species/products **Z₁** to **Z₄** along with the label of ^{18}O .
- ii) Using the Table in page 4, label the above reaction mechanism appropriately.

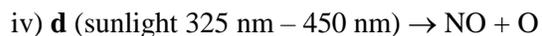
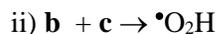
Problem 3

16 marks

Ozone in Troposphere

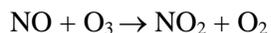
In recent decades, tropospheric ozone is being observed in higher concentrations, particularly in urban atmospheres. At concentrations above 70 ppb (parts per billion by mass), ozone is hazardous for our health and environment. Carbon monoxide, volatile organic compounds, hydroxyl radical and nitrogen oxides (NO_x) are some of the major components of exhaust gases from vehicles. In presence of near-UV solar radiation (325 nm to 450 nm), a series of reactions among these gases produces significant amount of ozone in the troposphere.

- 3.1 In the following steps (i to v) showing one such reaction sequence (all gaseous species), write the species **a**, **b**, **c**, **d**, **e** (Coefficients of given species should not be changed). Write the net reaction from steps i) to v).

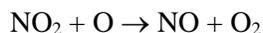


v) The oxygen radical reacts with oxygen molecule to form ozone.

The ozone formed in troposphere is also degraded by the following reaction:



If oxygen radicals are present in air, NO_2 can convert into NO .



The gases CO , NO_x and O_3 are tropospheric air pollutants. Their concentrations at one location may change over time of the day, and also over seasons.

About the above mentioned atmospheric gases, following facts are available with us.

Facts:

(R1) During day time, it is sunlight rather than high temperature that leads to more free radical production as compared to that during night time.

(R2) Colder days have lower convection currents in air and hence, have lower mixing and dilution of gases from different zones in local atmosphere.

(R3) Winter days can have higher relative humidity than summer days inspite of having lower absolute humidity.

(R4) Acidic gases react with atmospheric water and come to ground in rainwater.

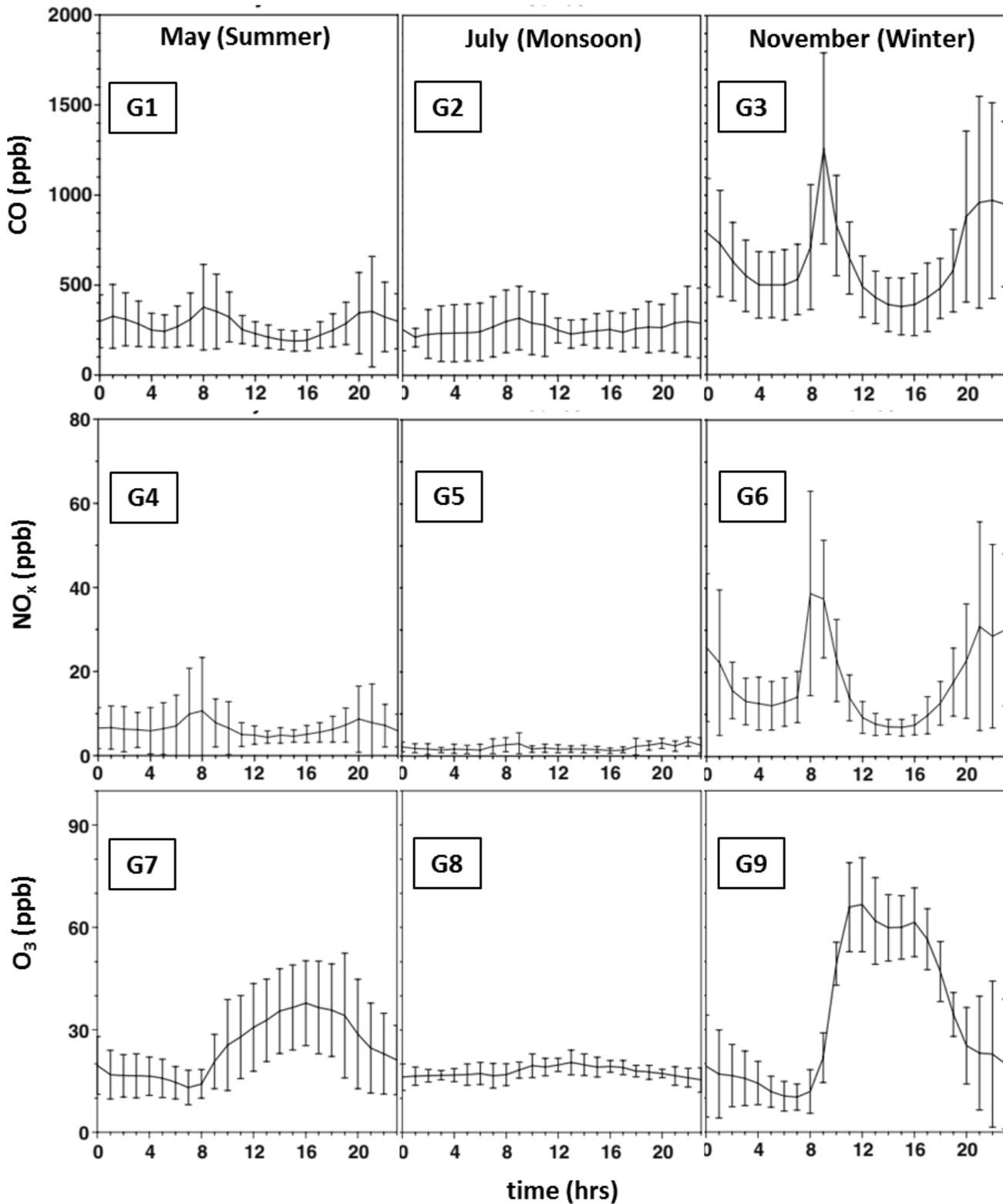
(R5) NO_x facilitate decay of ozone.

(R6) NO_x facilitate production of ozone.

(R7) Slope of concentration vs time graph for a gas indicates difference of production rate and decay rate of that gas.

Continued on next page →

Following figure shows tropospheric concentration of CO, NO_x, and ozone in air recorded in Pune city, in India in a year. Time 0 is midnight. Vertical lines in the plot indicate variations in the concentrations of the gases over the month. The values may be considered typical of the given months in any year.



Based on the information provided above and the tropospheric concentration of CO, NO_x, and ozone in air in Pune city as given in the graphs in page 8, certain statements (S1-S5) are given below which may be **Correct** or **Incorrect** for the Pune site.

S1. Amount of water vapour in the air does not affect ozone concentration.

S2. Ratio of NO₂: NO in the air is higher at 8 p.m. than at 8 a.m.

S3. Higher concentration of CO in the month of November is an evidence of higher production rates of the gases than in the month of May.

S4. Rate of ozone buildup increases with increase in temperature.

S5. Observed lifetime of ozone during day time is much longer than that of NO_x and CO.

3.2 Sort the above statements in two categories (**correct and incorrect**) by writing the codes of statements (S1 — S5) in appropriate category. For each statement code, write the codes for appropriate facts (R1 — R7), and the Graph (G1 — G9) that supports your answer.

A group of students constructed a setup at school laboratory to measure the concentration of ozone in tropospheric air. They used a small pump to bubble an air stream through a 10.0 mL solution containing 0.06 M KI, 0.1 M boric acid and deionized water.

The students measured a concentration of triiodide ion as 2.6 μmol L⁻¹ when 5.0 litre air was bubbled through the solution. Laboratory temperature and pressure were 298 K and 1 atm.

3.3 Write the balanced equation for the chemical reaction leading to production of triiodide. Calculate the concentration of ozone in air in ppb (parts per billion by mass). Assume that the air contains approximately 21% oxygen and 79% nitrogen by mass.

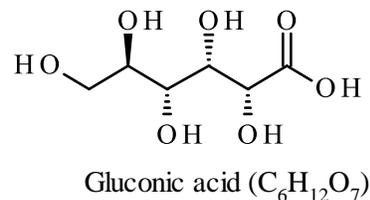
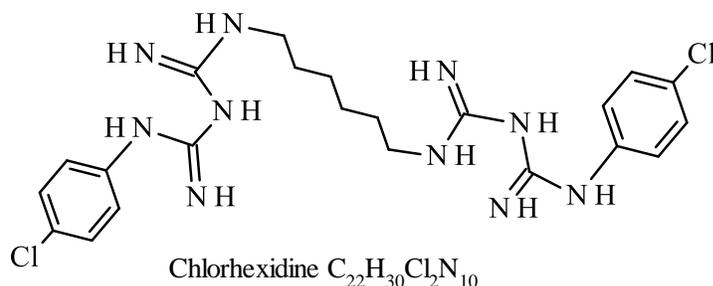
[Adapted from: *Beig, J (2007) Atmospheric Chemistry, 57:239–253*].

Problem 4

22 marks

Chlorhexidine

In the past few decades, chlorhexidine (Ch), has been used as a disinfectant for skin, to sterilize surgical instruments, in mouthwashes, hand sanitizers, etc. Its structure is given below.



Chlorhexidine is sparingly soluble in water. Hence, it is marketed in the form of salts such as chlorhexidine dihydrochloride (ChH₂Cl₂), chlorhexidine diacetate (ChH₂A₂), and chlorhexidine digluconate (ChH₂G₂). The structure of gluconic acid is given above. Chlorhexidine in salt form has high adherence on surfaces applied because of the dicationic form. Typically one part of cation binds with the proteins/or anion groups in pellicle/skin tissue and the other is free to bind with the bacterial cell membrane.

While drawing Ch structure in your answer, you can represent the phenyl ring as Ph and the alkyl chain in the middle as curved line.

Part A: Synthesis

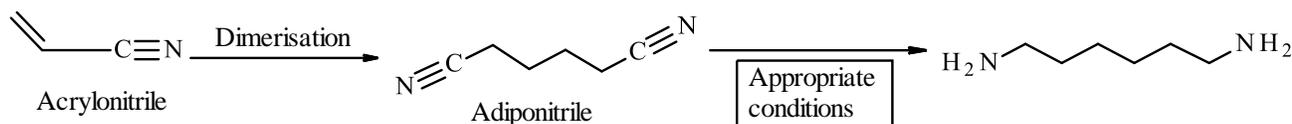
4.1 Draw the most stable dicationic form of chlorhexidine.

Synthesis of chlorhexidine requires 4-chloroaniline and 1,6-hexamethylene diamine as two of the starting materials. 4-Chloroaniline can be obtained from chlorobenzene via intermediate compound 'M'.



4.2 Draw the structure of 'M'.

A brief synthetic route of 1,6-hexamethylenediamine is given below. In this route, acrylonitrile undergoes hydrodimerization to adiponitrile. Adiponitrile can be converted to 1,6-hexamethylene diamine.



4.3 Identify the most ideal condition for converting adiponitrile to 1,6-hexamethylenediamine from the following options. Mark X for the correct option.

- Ni/ H₂ /NH₃ (80 bar)/110°C
- H₂ (1 atm), Pd/ BaSO₄, Quinoline, Methanol
- Na or Li, - 33°C, Liquid NH₃
- (I) Diisobutylaluminium hydride [DIBAL-H /0°C] (II) CH₃OH

4.4 A sodium salt 'N' reacts with 1,6-hexamethylene diamine to generate an intermediate which on treatment with 2 equivalents of 4-chloroaniline gives chlorhexidine. Predict the structure of 'N'.

Part B: Formulations of Chlorhexidine

Given: $K_{sp}(\text{ChH}_2\text{Cl}_2) = 2.1 \times 10^{-9}$; $K_{sp}(\text{ChH}_2\text{A}_2) = 2.0 \times 10^{-4}$; $K_a(\text{acetic acid}) = 1.76 \times 10^{-5}$.

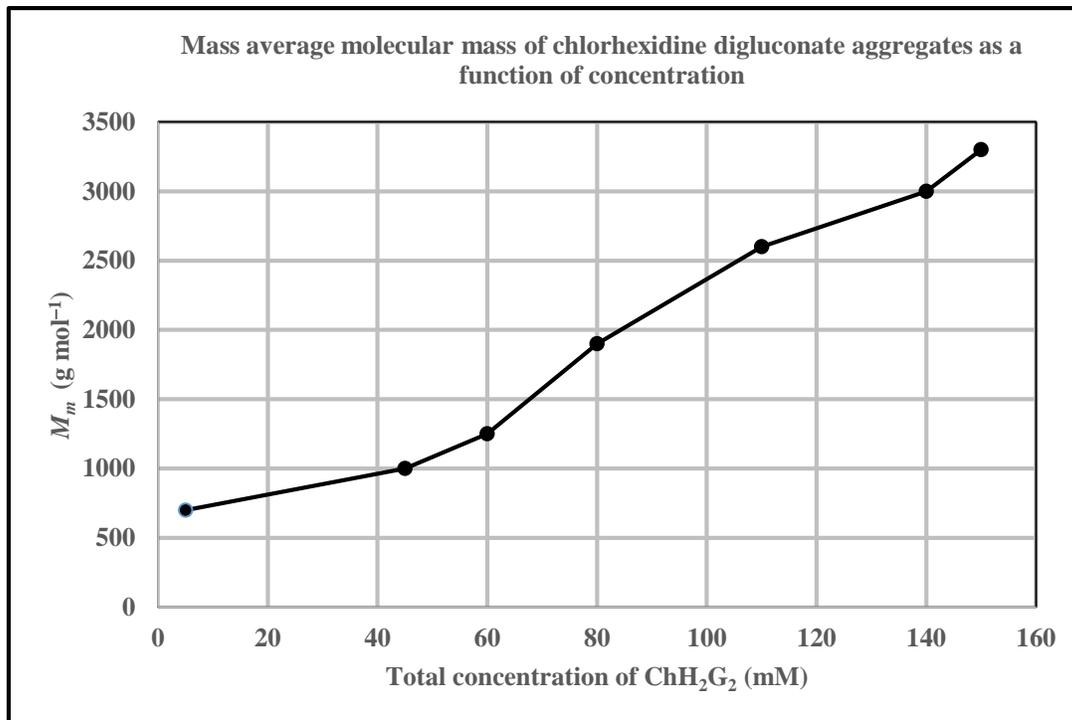
4.5 Calculate the solubility (in mol L⁻¹) of the diacetate salt (ChH₂A₂) in water. Write all equilibria related to the salt in this solution and specify any approximations, if made, in calculations.

Solubility of chlorhexidine gluconate is much higher than the other two salts. However, in solution phase, as the ChH₂G₂ concentration increases above 0.011 M, the extra ChH₂G₂ units start forming aggregates that remain in the aqueous phase. The concentration of active (un-aggregated) units also depends strongly on other species in the solution.

Mass average molecular weight of an aggregate is defined as $M_m = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i}$

where n_i is the number of aggregates having molar mass M_i .

M_m indicates the typical mass of the larger size aggregates (as it has lower weightage of smaller aggregates), and its variation with concentration of ChH_2G_2 in aqueous solution is shown in the graph below.

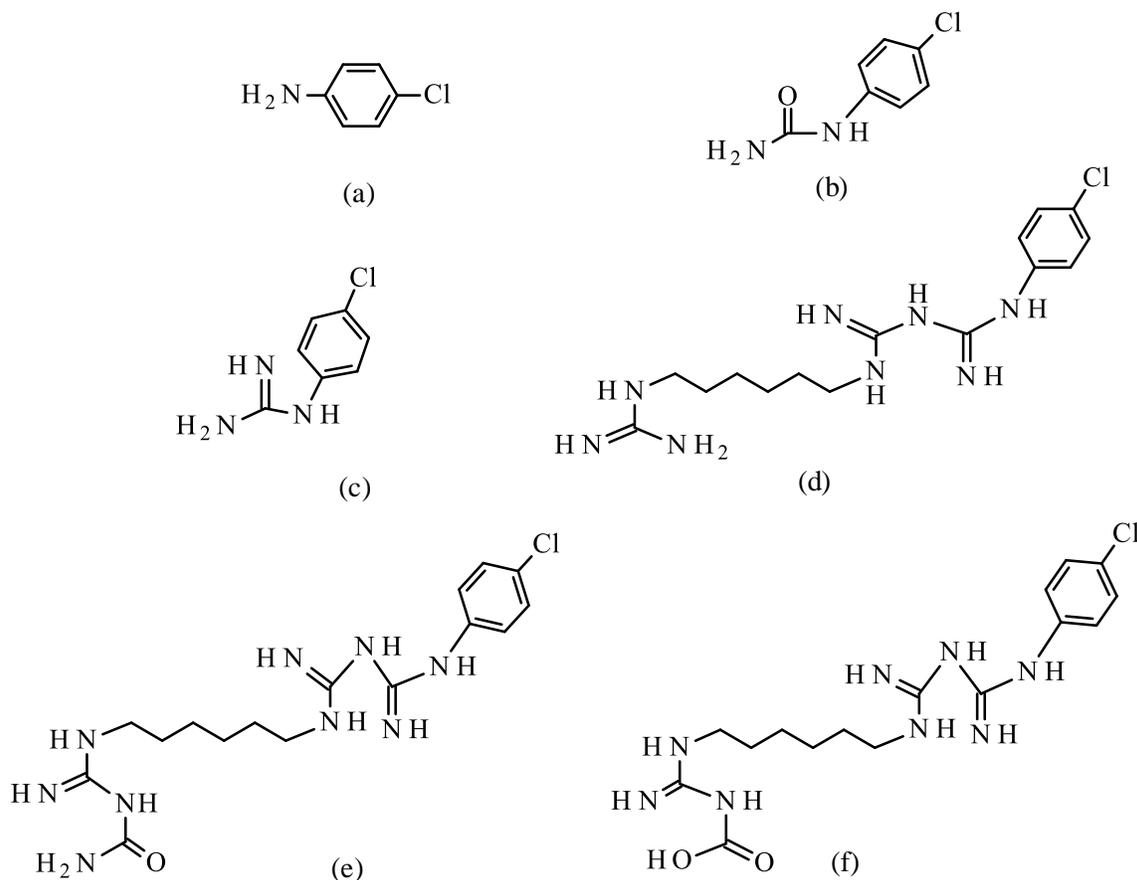


Concentration of commercial ChH_2G_2 solution for disinfection purposes is 20% (w/v). Consider a solution prepared by diluting 500 mL of the commercial solution with water to prepare 1 L diluted solution.

- 4.6** Determine the typical number of ChH_2G_2 units in larger aggregates in the diluted solution.
- 4.7** Given the above data about the three salts, check if preparing the following mixture 5 min before use (assumed sufficient for systems to reach equilibrium) can reduce the effectiveness of the mentioned ChH_2G_2 solution more than what is affected through dilution. Show using appropriate calculations.
- Mixing 1 mL of a 0.12% ChH_2G_2 solution (typical in mouthwashes) with 99 mL of 1% salt (NaCl) water for gargling.
 - Mixing 10 mL of 1% ChH_2G_2 solution (typical in bathroom cleaners) with 90 mL of 1 M vinegar (CH_3COOH) solution for cleaning.

The stability of chlorhexidine is limited as it easily degrades under both acidic and alkaline conditions.

- 4.8** Identify which of the compounds (a-f) are obtained in pairs during the hydrolysis of chlorhexidine under different aqueous conditions.



Commercial ChH_2G_2 solutions often contain a few impurities which may be produced during storage. One such compound is **O** usually also formed as a result of alkaline hydrolysis of **Ch** and has a molar mass of 61 g mol^{-1} .

4.9 Identify **O**.

Another kind of **Ch** formulations being explored involve its complexes with transition metal ions as many transition metal ions also have inhibitory effects on bacteria.

If an alcoholic solution of CuCl_2 is mixed in 1:1 molar ratio with alcoholic solution of ChH_2A_2 , a dark purple complex **P** is obtained which doesn't ionize in water. Similar mixing of alcoholic solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ with alcoholic solution of ChH_2A_2 in 1:1 molar ratio produces a pink-violet complex **Q**, which ionizes in aqueous solutions. The atoms of **Cu** in **P** and **Q** have the same oxidation state. Both **P** and **Q** are 1:1 complexes of **Cu** and **Ch** but have **Cu** in different coordination numbers.

4.10 Draw the structures of **P** and **Q**.

When alcoholic ChH_2A_2 is mixed in 1:2 molar ratio with alcoholic CuCl_2 , a blue complex **R** with **Cu**:**Ch** ratio of 2:1 is obtained. A solution of **R** has very low electrical conductivity, indicating low ionization. **R** had higher activity against certain bacteria as compared to ChH_2A_2 .

4.11 Draw the structure of **R**.

Helium in Rocks

All radioactive nuclei naturally present in Earth seem to have been created by sequential radioactive decay of three primary isotopes: ^{238}U , ^{235}U and ^{232}Th . All three were present in the proto-star: the cloud that eventually condensed to form our sun, the Earth, and the planets. Members of these three series continue to decay till they produce the stable nuclides ^{206}Pb , ^{207}Pb and ^{208}Pb , respectively.

For example, ^{238}U undergoes 14 decay steps (each involving α - or β -particle emission) eventually forming ^{206}Pb .



Note that ^{235}U and ^{232}Th are not formed in the decay process of ^{238}U . In other words, the three decay series don't have any common radioisotopes.

With the current age of the Earth, the nuclides in these series have reached a stage, in which the production and decay rates of each of the intermediate nucleotides of a series are approximately equal. Therefore, in each series, the last member can be considered as the direct decay product of the first member following approximately a first order kinetics, with following half-lives ($t_{1/2}$):

$$t_{1/2} (^{238}\text{U} \rightarrow ^{206}\text{Pb}) = 4.47 \times 10^9 \text{ years,}$$

$$t_{1/2} (^{235}\text{U} \rightarrow ^{207}\text{Pb}) = 0.707 \times 10^9 \text{ years,}$$

$$\text{and } t_{1/2} (^{232}\text{Th} \rightarrow ^{208}\text{Pb}) = 1.4 \times 10^{10} \text{ years.}$$

Emission of an α -particle from a radioactive nucleus is accompanied by production of an ^4He nuclei whereas β -particle emission reduces the neutron count in the parent nucleus by one and increases the proton count by one with no additional nuclei produced.

- 5.1** Determine the number of helium nuclei produced by conversion of one ^{238}U nuclei to ^{206}Pb .
- 5.2** For a soil sample with equal amount of Uranium and Thorium, calculate the ratios of the production rates of ^4He from the three nuclei (^{238}U , ^{235}U and ^{232}Th). [Given: In natural Uranium, mass ratio $^{238}\text{U}/^{235}\text{U} = 138:1$] Show the main steps of calculation.

In rocks, helium gas is constantly produced due to radioactive decay of nuclides originating from U and Th present in them. In absence of any escape channel to the atmosphere, these gases accumulate in the pores in the rocks. If these pores are filled with water, then helium gets dissolved in the water.

A porous rock saturated with water was found to yield $3.5 \times 10^{-4} \text{ cm}^3 \text{ He}$ per cm^3 of water at STP. The rock contains 1 ppm (parts per million by mass) uranium, with U to Th mass ratio $\sim 1:4$. Mass of water per unit volume of rock and density of the rock were $2 \times 10^{-3} \text{ g cm}^{-3}$ and 2.9 g cm^{-3} , respectively.

- 5.3** Calculate the residence time of water in the rock, assuming that this time is much smaller than the half-life of the three parent radioactive nuclei, & hence their amounts change by less than 0.1% during this period.