

# Indian Olympiad Qualifier in Chemistry (IOQC) 2021-2022

conducted jointly by

Homi Bhabha Centre for Science Education (HBCSE-TIFR)

and

Association of Chemistry Teachers (ACT)

## Part II: Indian National Chemistry Olympiad (INChO)

Homi Bhabha Centre for Science Education (HBCSE-TIFR)

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Total 89 marks

Time- 2 hours

Roll No. --

- Write your Roll No. at the space provided above.
- This question booklet consists of 12 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 invigilator. 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 =  $1000 \text{ kg m}^{-3}$   
 $= 0.08205 \text{ L atm K}^{-1} \text{ mol}^{-1}$

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

Enthalpy of combustion of ethanol =  $-1371 \text{ kJ mol}^{-1}$

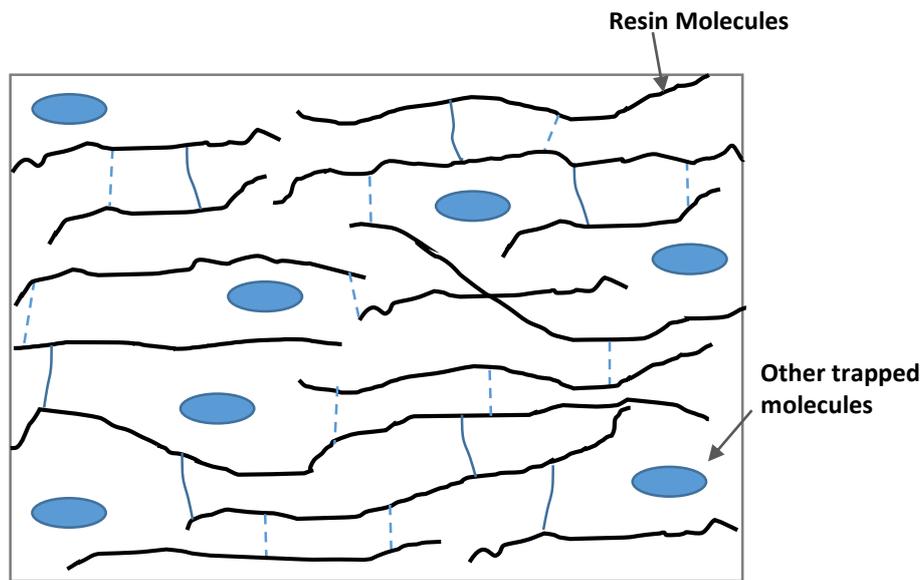
Saturation vapour pressure of ethanol at 298 K = 0.08 atm

For air,  $\gamma = C_p/C_v = 1.4$

**A journey into epoxy resins**

Epoxy resins are a versatile group of chemicals used in many industrial applications, particularly due to their strong adhesive qualities, and stability under conditions such as high temperature, high humidity, and corrosive environments.

Several resin based materials are in use, whose molecular level structure can be represented as shown in figure 1. It has high molar mass molecules (shown by bold lines) which may be monomeric, polymeric, or mixed condensation products of two or more compounds. The molecules are held together with various crosslinking chains (shown by grey solid lines) and/or non-bonding interactions such as charged interaction, van-der Waals forces (shown by dashed lines). Depending on the packing of resin molecules, there may be pore spaces between the molecules. Further there may be additional molecules or ions which may be trapped in this structure during the material production process.



*Figure 1: Model of a resin material*

Properties of resinous materials depend on the nature of interactions between resin molecules (cross-links and non-bonding interactions), and their interactions with the trapped molecules. Sometimes interactions among the trapped molecules also may significantly affect the material properties.

One commonly known example of a commercial epoxy resin is supplied in a syringe/ tube containing a plunger and two compartments as shown in the figure 2. When the liquids present in these syringes are mixed, they condense together to produce resin.

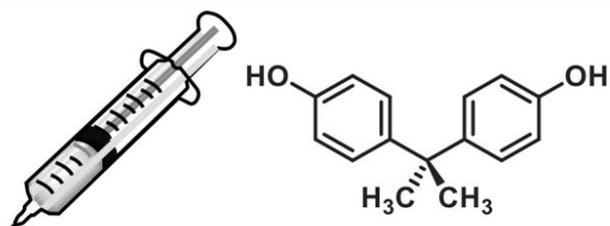
Often, one syringe compartment contains epichlorohydrin (2 molar equivalent) and the other compartment is filled with Bisphenol A (1 molar equivalent) and NaOH (less than 2 molar equivalent).



*Figure 2: Commercial tube of an epoxy resin*

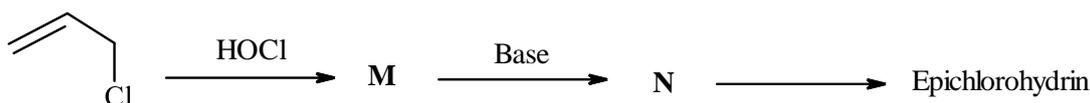


Epichlorohydrin



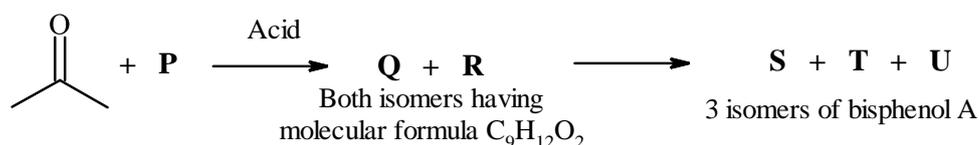
Bisphenol A

- 1.1. Epichlorohydrin is synthesized using a reaction of allyl chloride and hypochlorous acid as shown below. Draw the structures of **M** and **N** in the synthetic pathway.



- 1.2. Bisphenol A is often produced as a mixture of its isomers **S**, **T** and **U** via a reaction between acetone and compound **P** in presence of a mineral acid.

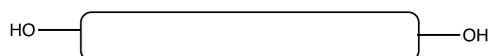
- i) Draw the structures of **P** to **U** in reaction sequence shown below.



In this process, one of the isomers precipitates out easily as crystals, while the other two remain in solution and are separated by other means. This isomer also is found to have the highest melting point, indicating very strong intermolecular bonding, and is the only isomer having no optical activity.

- ii) Identify this isomer (**S**, **T** or **U**).

In the following questions, if you are drawing a polymer, draw all end groups to receive full credit. For easier notation, phenyl groups can be represented as “Ph” and bisphenol A core unit **if unchanged** in the reaction can be represented as following:



When the two liquids in the two tubes (shown in Figure 2) are mixed, they react at a rate dependent on the concentration of epichlorohydrin and bisphenol A but not on the concentration of NaOH. Different molecules are obtained depending on the stoichiometric ratios of epichlorohydrin and bisphenol A.

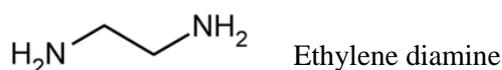
- 1.3. i) Draw the structure of the predominant product **V** obtained when 2 equivalents of epichlorohydrin is treated with 1 equivalent of bisphenol A?
- ii) Draw the structure of the product **W** obtained when bisphenol A is reacted with less than 2 equivalents of epichlorohydrin.
- iii) Identify what kind of interactions are possible between two molecules of **W**.
- ionic bonds
  - van der Waals bonding
  - H- bonds
  - dipole-Dipole interactions

iv) To find the mechanism of the reaction in **1.3 i)** and **ii)**, one can do the isotopic labelling of one of the carbons wherein a particular carbon is replaced with a  $^{13}\text{C}$  (e.g.  $^{13}\text{CH}_3\text{CH}_2\text{Cl}$  or  $\text{CH}_3^{13}\text{CH}_2\text{Cl}$  for chloroethane). In the above reaction, draw structures of all the  $^{13}\text{C}$ -labelled molecules that would be suitable for investigating the reaction mechanism. Position of labelled carbon in a molecule can be identified spectroscopically.

Mechanical properties of resin material such as tensile strength depend significantly on the strength of bonds and their density within the material. Flexibility depends on ease with which resin and trapped molecules may slide over each other or change their molecular conformations without changing the structure and intermolecular bonds within the material.

v) What is the by-product formed in reaction described in **1.3 i)** and **ii)**? If not removed, is it likely to increase or decrease tensile strength of the resin matrix?

Epoxy resins are sometimes treated with co-reactants such as amines, acids, alcohols, thiols, etc., to modify its structural properties. Ethylene diamine is one such co-reactant.



**1.4.** Draw the structure of the product formed in the following reactions carried out in polar aprotic solvent.

**i) V** is reacted with excess ethylene diamine ( $> 4$  equivalents) at high dilution (1 g in 1000 mL).

**ii)** Excess of **V** ( $> 4$  equivalents) is reacted with ethylene diamine at low dilution (1 g in 25 mL). This results in a chemical structure with charged groups.

**iii)** Treatment described in **1.4 ii)** makes the resin (mark X for the correct option(s)).

- a) more flexible
- b) more electrically conducting
- c) gain in tensile strength

**1.5.** Epoxy resins act as adhesives for which of the following surfaces (mark X for all the correct ones).

**i)** surfaces made out of polyethylene, polystyrene.

**ii)** surfaces that have thiol ( $-\text{SH}$ ) groups.

**iii)** cellulose surface on wood.

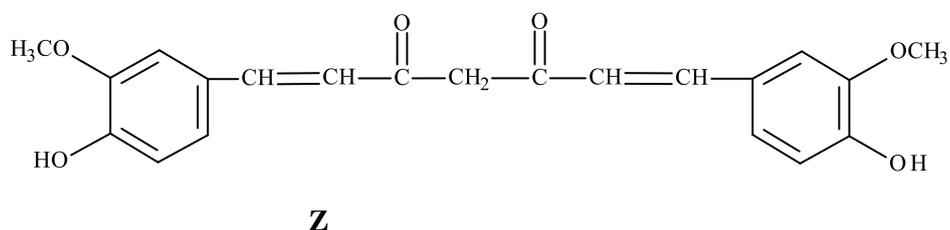
**iv)** polyester fabric.

## Problem 2

19 marks

### An edible compound and a colouring agent

A compound **Z** found in several natural edible plants has been an exciting area for researchers for centuries. It was first isolated from a plant in 1815 in Germany. A hundred years later, it was synthesized in laboratory and was identified to have the following structure.



But it took a few more decades to understand its 3-D structural form existing in solutions and solids. In 1953, a scientist Srinivas in Chennai tried extracting **Z** again from the same plant source using benzene as a solvent. To check if the extract contained only **Z** or also other components, he added it into a chromatography column.

A chromatography column is a cylindrical tube filled with a stationary phase of a solid such as powdered silica. The mixture to be separated is added from the top followed by a solvent, which acts as the mobile phase. As the mobile phase flows down the silica in the tube, it carries components of mixture with it. Due to different affinities of components with stationary and mobile phases, these get separated into bands.

Using benzene as a mobile phase, Srinivas found 6 bands separating out as shown in Figure 1, of which three bands **1**, **2** and **4** were significant. One of these three bands was of **Z**, while the two other bands were of compounds **Y** and **X** with molar masses, 338 and 308, respectively, and similar molecular framework as **Z**.

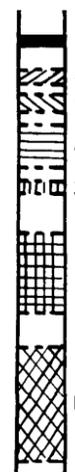


Figure 1: Chromatogram of benzene extract on silica

On reaction with acidic  $\text{FeCl}_3(\text{aq})$ , all three compounds gave very dark red colours, which according to Srinivas were more intense than what should be obtained due to phenolic groups in the structure shown above. He predicted that there should be other group(s) within molecules of **X**, **Y**, and **Z** which also bonds with  $\text{Fe}^{3+}$  ions. Several geometrical isomers are possible for **X**, **Y** and **Z**. Srinivas predicted that only one isomer is predominantly observed experimentally each for **Z**, **Y**, and **X** (which is also stabilized by several inter-atomic interactions in the molecules). All of his above predictions were found true by later experiments.

- 2.1 Based on Srinivas' inferences, draw the most stable geometrical isomer of **Z**, **Y** and **X**. Each structure should indicate all possible inter atomic interactions, if any.
- 2.2 Identify which of the bands **1**, **2** and **4** are **X**, **Y**, and **Z**.
- 2.3 Solubility of **Z** in aqueous solutions increases with pH, accompanied by change in its colour. Draw the form in which **Z** would exist in strongly alkaline solutions (pH ~ 14).

*In this problem, if structure is asked for ionic compounds, both ions should be shown.*

Until 20th century, boron was not known to be a part of plant tissues because analytical methods to determine it below milligram levels were not available. In the beginning of 20th century, reaction of boric acid with **Z** producing coloured compounds paved way for detailed analysis of boron in plant samples.

One of the challenges in using boric acid-**Z** reaction for quantitative analysis was reducing the time required for reaction to complete. Certain experiments indicated that initial addition of oxalic acid to the mixture of boric acid and **Z** finished the colour development in shorter time (in less than one hour). Mechanistic investigations showed that boric acid reacted with sufficient oxalic acid to produce a species **P**, which had much higher pKa than oxalic acid. **P** on reaction with **Z** gave visible colour due to formation of **Q** in solutions even with low boron concentrations of  $\sim 1 \mu\text{M}$ .

- 2.4 Draw the structures of **P** and **Q**.

While **Z** was synthesized in laboratory in 1910's, but the yield was low due to formation of many side products. A modified and efficient synthesis method was developed in 1960 by Pabon and his team in the Netherlands. In this method, 0.2 mole of acetylacetone (pentan-2,4-dione) was stirred with 10 g (excess) of boric anhydride ( $\text{B}_2\text{O}_3$ ), and a thick paste was formed containing a new ionic compound **R**. **R** was mixed with butylamine and this mixture further reacted with compound **S** (used as a flavouring agent in food) in the presence of N,N-dimethylformamide (a polar, aprotic solvent) and trimethyl borate (a dehydrating agent) to form another ionic

compound **T**, which had much higher molar mass than **Q**. Acidic hydrolysis of **T** in dilute HCl yielded compound '**Z**' and an inorganic acid.

2.5. Draw the structures of **R**, **S**, and **T**.

2.6. What are the other by-products obtained in this reaction?

Boric anhydride was added to suppress formation of some unwanted compounds.

2.7. Draw structure of two of the side products which would have formed if boric anhydride was not used in the above reaction (which was observed in the synthesis in 1910's).

### Problem 3

31 marks

#### Chemical Oxygen Generation and Oxygen safety

Producing gaseous O<sub>2</sub> from a material through chemical reactions is called chemical oxygen generation. Such materials, known as chemical oxygen generators (COGs), are useful for O<sub>2</sub> storage and delivery at places where pressurized oxygen cylinders/tanks can pose risks. This problem looks at COGs such as chlorates, peroxides, and superoxides which are used for obtaining breathable O<sub>2</sub> under special needs.

#### Oxygen Candles

Oxygen candles containing chlorate salts are used to produce oxygen gas in an emergency in aircrafts, space stations, etc. An oxygen candle, typically, contains NaClO<sub>3</sub>, BaO<sub>2</sub>, and iron powder. An ignition causes oxidation of iron powder generating heat. At a high temperature (~ 500°C), NaClO<sub>3</sub> decomposes spontaneously producing breathable oxygen.

In aircrafts, it is instructed to pull down the mask oxygen first before wearing it in emergency. That pulling releases the firing pin and causes the ignition. Once the reaction starts, it continues exothermically.

3.1 The reaction producing breathable oxygen must also produce non-toxic by-products. Identify the missing product(s) in the given equation and balance the equation.



Often, chlorate decomposition is associated with a side reaction, which produces a toxic gas **A**. Separation of **A** from the gas mixture is a must. One of the roles of BaO<sub>2</sub> in oxygen candle is to remove **A**. Successful reaction between BaO<sub>2</sub> and gaseous **A** results in a barium salt **B**, and another gas, **C**.

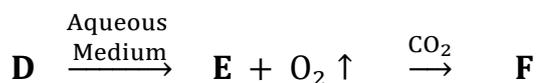
3.2 Identify **A**, **B** and **C**, and balance the chemical equation below.



#### Superoxides

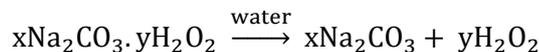
Metal superoxides (containing O<sub>2</sub><sup>-</sup> ions) are used as effective COGs in mining industry to tackle breathing problem. An aqueous yellow solution of a metal superoxide, **D**, produces oxygen gas (33.8% of its mass) and compound **E**, as shown in the following scheme. Interestingly, the exhaled CO<sub>2</sub> from breathing can be consumed by **E** producing **F**, without hampering the O<sub>2</sub> generation process.

3.3. Identify **D**, **E**, and **F**. Shows steps and calculations wherever required.

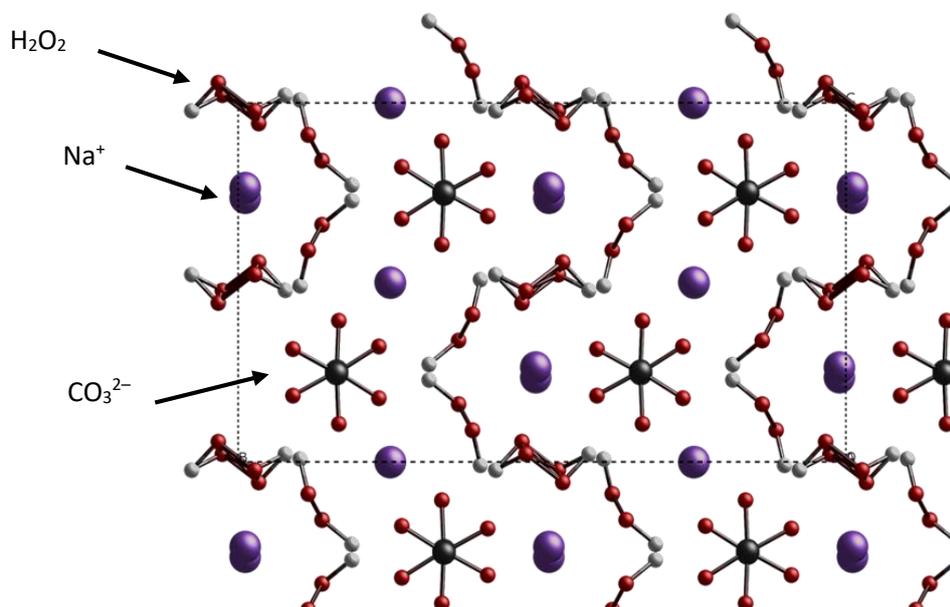


#### Peroxides:

H<sub>2</sub>O<sub>2</sub> is a very good COGs, but its storage and transport are difficult due to its unstable nature. A solid adduct of H<sub>2</sub>O<sub>2</sub> with sodium carbonate: Sodium percarbonate with formula xNa<sub>2</sub>CO<sub>3</sub> • yH<sub>2</sub>O<sub>2</sub> (x and y are the respective stoichiometries), releases H<sub>2</sub>O<sub>2</sub> in presence of water.



The unit cell of crystal structure of this adduct is given below. In this arrangement, each carbonate oxygen makes one H-bond with one –OH of neighboring peroxide. (Note: two  $\text{CO}_3^{2-}$  units stacked on each other are rotated with respect of each other, which in 2-Dimensional view give a false impression of a hexagonal species)



**3.4.** Find  $x$  and  $y$ . Show calculation/steps required to arrive at the answer.

Another such solid peroxide material is  $\text{G} \cdot \text{H}_2\text{O}_2$ . Upon exposing to water it produces 17% of its mass of  $\text{O}_2$ .

**3.5.** Find the molecular weight of  $\text{G}$ . Show steps of calculation.

In a research lab of a cosmetic company, one new intern was instructed to prepare this adduct. When he was carrying the white solid  $\text{G}$  to his bench, it was accidentally spilled into a hot sodium hydroxide solution. Immediately, gas bubbles started coming out of the solution. A moist red litmus paper held over the evolving bubbles turned blue. To confirm what gas might be evolving, he took a sky blue coloured salt,  $\text{H}$ , and dissolved it in water. A filter paper wet with this sky blue solution held above the evolving bubbles turned deep blue.

**3.6.** Identify  $\text{G}$  and  $\text{H}$ . Write chemical equations for the reactions responsible for the colour change of filter paper wet with  $\text{H}$  from sky blue to deep blue.

### Risk associated with the use of $\text{O}_2$ :

Oxygen gas is not flammable by itself but it supports combustion. Alcohols are volatile and flammable in air—in presence of 21% (v/v)  $\text{O}_2$ , these can catch fire at room temperature if there is a spark, flame or heat source in vicinity. At higher  $\text{O}_2$  concentrations, a substance may catch fire even at lower temperatures. Therefore, in spaces (particularly closed rooms) with higher concentrations of oxygen (~23%), risks of fire outbreaks are much higher. Intensive Care Units (ICUs) in hospitals are spaces where both of the above risks need to be carefully managed.

Consider an ICU room of size  $12 \text{ m} \times 7 \text{ m} \times 2.6 \text{ m}$  with 12 beds. On a day, the ICU had 11 patients on ventilator support. Unfortunately, nobody noticed that the exhaust of the ICU was damaged; due to which the room air was getting replaced only over a period of 6 hours (instead of 30 minutes). Leaks from ventilator tubes had increased oxygen concentration in the room air to 23.4% (mole fraction).

Additionally, a sanitizer containing 70% w/v ethanol was being used in the ICU. Per day, typically 60 mL of sanitizer was used per patient, and 200 mL sanitizer was used four times for sanitizing the floor after mopping, all of which eventually evaporated and become a part of the room air.

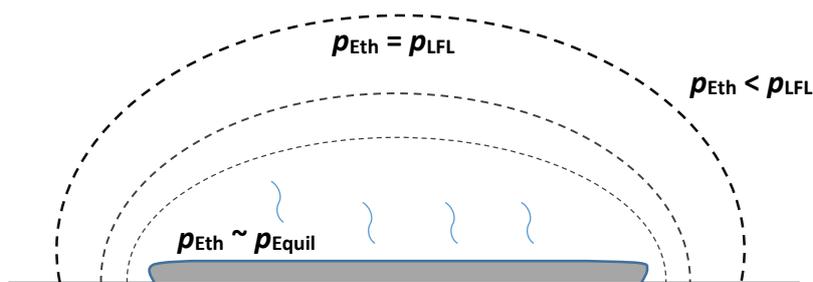
Assume for ambient air in ICU-

- i) all component gases to be ideal.
- ii) density =  $1225 \text{ g m}^{-3}$ , specific heat  $\sim 1.01 \text{ J g}^{-1} \text{ K}^{-1}$
- iii) average temperature = 298 K.
- iv) specific heat per unit mass of the gases considered in this problem is same as that of air.

**3.7** If the ethanol vapour in the room at any given time undergoes combustion instantaneously, determine the maximum rise in the room air temperature. [Hint: Ethanol concentration in room air at any time would be about 6/24 of the total ethanol evaporated in room in the whole day.]

However, at low vapour concentrations of ethanol in room air discussed above, it will not catch fire. At a temperature of 25 °C, lower flammability limit (LFL) of ethanol is 3.0%. [LFL: minimum concentration in v/v at which the vapour can catch fire in ambient air].

Accidentally, 500 mL of sanitizer from a bottle spilled on the floor. During evaporation, the partial pressure of ethanol close to the liquid surface is close to its equilibrium vapour pressure and decreases with distance from the surface (as shown below). In 15 min, the vapour spreads, and a zone of volume  $1.5 \text{ m}^3$  has ethanol concentration above its LFL.



**3.8** Determine the average mole fraction of oxygen in this zone of  $1.5 \text{ m}^3$ , assuming: i) average ethanol vapour concentration in this zone is mean of the minimum and maximum values in the zone; and ii) average pressure in this space remains 1 atm, and other gases in air (oxygen, nitrogen) as a homogenous mixture which diffuse out of this zone uniformly as ethanol vapour keeps adding.

In this zone if there is an electrical spark in any electronic equipment, the ethanol can catch fire and get burned within fraction of a second.

**3.9** Assume that this zone acts as an adiabatic closed system which expands to twice its volume within 0.5 s of burning. For this system, estimate the following quantities at the end of 0.5 sec. [Note that the pressure increases because of heat released as well as increase in number of molecules in the zone.]

- i) average temperature of the gaseous mixture
- ii) average mole fraction of oxygen left in this zone (which may support burning of other materials in this zone, and sustain fire)

**3.10** In the room, increased oxygen level increased fire risk because it (Write True/False as applicable):

- i) increases rate of combustion reaction.
- ii) increases peak temperature of air (as cooling due to diffusion or air circulation is slower).
- iii) increases heat released per unit mass of ethanol.
- iv) increases peak pressure in air mixture during combustion (making it more explosive).
- v) allows for longer combustion if fuel is available.

**3.11** Better air circulation in closed rooms helps in reducing fire hazards by preventing (Mark X against the correct option(s))

- i) fuel vapour buildup in any space.
- ii) oxygen level from dropping below a certain level.
- iii) oxygen level from increasing above a certain level.
- iv) fast temperature rise in any small air space.

## Problem 4

19 marks

### Polyoxometallates

One of the interesting aspect of chemistry is reactions among colorless substances to produce colored substances. One such reaction is when colorless substances, namely, phosphate salts, molybdate salts, mineral acids and reducing agents (such as ascorbic acid) are mixed in appropriate proportion, it produces a deep blue substance known as molybdenum blue (MB). This reaction is known since 18<sup>th</sup> century and has been used in estimation of phosphates in water samples. However, its molecular level understanding was developed in 21<sup>st</sup> century.

This problem explores two aspects of MB reaction: the chemical structure of the coloured species, and some reactions which can interfere with this reaction in natural water samples.

#### Part A- Structure

The coloured specie in the above MB reaction is a unique polymeric cluster of molybdenum oxides, whose properties are explored here.

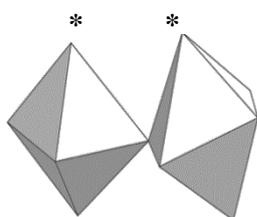
Oxides of Group VI transition metals in highest oxidation state (general formula  $\text{MO}_3$ , where  $\text{M} = \text{Cr}/\text{Mo}/\text{W}$ ) are known to be acidic, and dissolve in strong aqueous alkalis to form  $[\text{MO}_4]^{2-}$  ions.

**4.1** The  $[\text{MO}_4]^{2-}$  ions of Mo and W are not reduced easily but that of Cr is easily reduced. The likely reason(s) for the above is/are (Mark X against the correct option(s))-

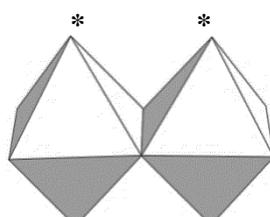
- i) Due to higher electronegativity, oxygen can oxidize the metals to the highest oxidation state
- ii) Higher oxidation states of members down in the group in transition series are more stable.
- iii) Mo and W show the effect of lanthanide contraction.
- iv) Effect of nuclear charge on d orbitals decreases down the group making them more available for bonding.

Under acidic conditions,  $[\text{MO}_4]^{2-}$  ions get protonated, which, depending on pH, may then polymerize or precipitate back as  $\text{MO}_3$ . The  $\text{CrO}_4^{2-}$  units rarely polymerise beyond dichromate. However, protonation of  $[\text{MoO}_4]^{2-}$  results in expansion of coordination sphere to octahedral units such as  $[\text{MoO}_3(\text{OH}_2)_3]$  which often polymerize to form clusters.

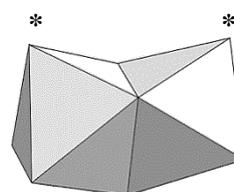
Two octahedral units can combine in three different ways are shown below, where O is at each vertex and metal ion is at the center of each octahedron.



Corner shared



Edge shared



Face shared

4.2 Assuming that the metal - oxygen bond lengths are equal for all these three polyhedra, the true statement(s) from the following is/are – (Mark X against the correct option(s))

- The effective negative charge around each molybdenum ion in edge sharing polyhedra will be less than that in corner sharing polyhedral.
- The distance between two molybdenum ions in edge sharing polyhedra will be less than that in corner sharing polyhedral.
- The O atoms at the apex positions (\*) in face sharing polyhedra are at a maximum distance from each other leading to most stable structure.
- Corner sharing polyhedra will lead to more stable structure than an edge sharing polyhedral.

Under mild acidic conditions (pH = 5-6), molybdate ions readily condense to give heptamolybdate ion containing seven octahedron units, where each octahedron shares 3 edges with its neighbours.

4.3 Write the balanced chemical equation for this transformation.



In presence of  $\text{PO}_4^{3-}$  (and under acidic conditions), molybdates can produce clusters with general formula  $[\text{PMo}_q\text{O}_r]^{n-}$ . The structure of first such cluster (of **Z**, shown in Fig. 1) was discovered by James Keggin using X-ray crystallography, and hence these are called Keggin structures.

4.4 Let us try to build the Keggin structure **Z** ( $[\text{PMo}_{12}\text{O}_r]^{n-}$ ), stepwise by building its sub-units (whose charges are not explicitly shown) in following questions.

- Consider three octahedra condensing to form a polyhedra  $[\text{Mo}_3\text{O}_x]$ , where each  $\text{MoO}_6$  unit shares an edge each with the other two units. Determine x in the given formula.
- Consider four of  $[\text{Mo}_3\text{O}_x]$  joined to each other through corner shared oxygen atoms forming a new condensed polyhedron  $[\text{Mo}_{12}\text{O}_y]$ . Determine y in the given formula.

In structure **Z** (shown below),  $[\text{Mo}_{12}\text{O}_y]$  framework has been formed around a phosphate unit, where P is bonded to four O atoms, one each from the  $[\text{Mo}_3\text{O}_x]$  sub-units.

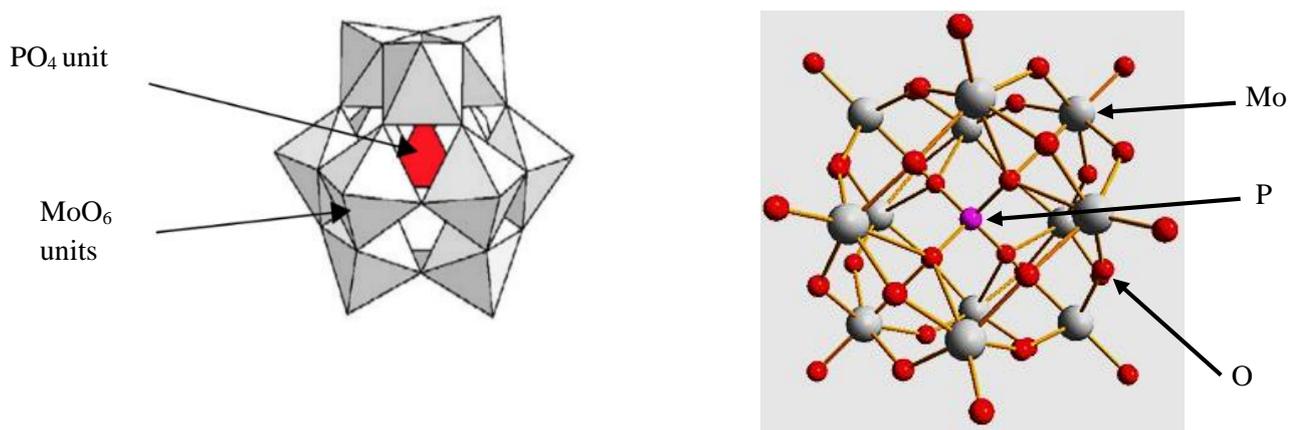


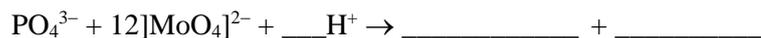
Figure 1: Keggin structure of **Z** in a) polyhedral notation b) ball and stick notation

**Z** contains four types of oxygen atoms and the description for the same is as follows-

- $\text{O}_a$  - refers to the oxygen at shared edge of two  $\text{MoO}_6$  octahedra (bridging neighbouring Mo within  $[\text{Mo}_3\text{O}_x]$  units)
- $\text{O}_b$  - refers to the oxygen at shared corner of two  $\text{MoO}_6$  octahedra (of different  $[\text{Mo}_3\text{O}_x]$  units)
- $\text{O}_p$  - refers to the oxygen shared between  $\text{MoO}_6$  octahedra and the  $\text{PO}_4$  unit
- $\text{O}_t$  - refers to the oxygen at terminal position (unshared with other octahedra)

iii) Determine the number of  $\text{O}_a$ ,  $\text{O}_b$  and  $\text{O}_p$  atoms in the above structure.

**4.5** The species **Z** shown above is pale yellow in color (all Mo retaining +6 oxidation state). Complete the chemical equation leading to the formation of **Z**.



Addition of a reducing agent in reaction mixture described in **4.5**, leads to 4e<sup>-</sup> reduction of **Z** producing a deep blue coloured species, **Z<sub>red</sub>**. The reduction is facilitated by protonation of some of the oxygen atoms in **Z**. The electrons involved in reduction are not added to any particular Mo atoms but are delocalized across multiple Mo atoms. The colour of **Z<sub>red</sub>** originates because of electron transfers between a Mo(V) and its neighboring Mo(VI) ions and not due to d-d transitions in Mo.

**4.6** Among the 4 types of oxygen, protonation of one type is favorable, which also can allow fast electron transfer between neighboring Mo ions; thus facilitating reduction of **Z**. This oxygen type is (Mark X against the correct option)

i) O<sub>a</sub>

ii) O<sub>b</sub>

iii) O<sub>t</sub>

iv) O<sub>c</sub>

### Part B - Phosphate determination

Typical phosphate level in polluted waters is ~ 0.1 – 1 mM. In MB test, water sample is mixed with reagents (Na<sub>2</sub>MoO<sub>4</sub>, acid and reductant) and the colour intensity of the blue species **Z<sub>red</sub>** formed is measured (which is proportional to the amount of phosphate present).

**4.7** For estimation of phosphate in a 100 mL polluted water sample, the appropriate amount of 10 mM Na<sub>2</sub>MoO<sub>4</sub> solution which should be added is:

i) 10 mL

ii) 100 mL

iii) 200 mL

iv) 25 mL

v) 75 mL

Natural water samples sometimes have species such as silicates, fluorides and organic acids like oxalic acid which may react with some of the reagents used in MB test, and hence interfere in phosphate estimation in different ways.

Silicates (Si(OH)<sub>4</sub>) present in water can react with molybdates at neutral or alkaline conditions to produce colored Keggin ions **R** (similar to **Z**). Thus, silicate can cause error in phosphate determination if molybdate salt is added before addition of acid.

**4.8.** Write balanced chemical equation for the formation of **R** from silicates under the above condition.

Flouride (F<sup>-</sup>) if also present can react with silicates under acidic condition.

**4.9** Write the possible balanced reaction(s) between silicates and fluorides that can take place in water sample when acid is added.

However, F<sup>-</sup> itself interferes in MB test by binding to Mo(VI). H<sub>3</sub>BO<sub>3</sub> is effective in preventing F<sup>-</sup> interference in MB test.

**4.10** Write the balanced equation for reaction that occurs between F<sup>-</sup> and H<sub>3</sub>BO<sub>3</sub> under acidic conditions.

Oxalic acid interferes in phosphate determination by reacting with molybdates but formic acid does not.

**4.11** Draw the structure of species formed by the reaction between oxalic acid and molybdate.

**4.12** Using excess Na<sub>2</sub>MoO<sub>4</sub> in MB test under acidic condition can minimize the errors induced by (Mark X against the correct option(s)):

i) silicates

ii) fluorides

iii) oxalate