## Indian National Chemistry Olympiad 2024 <br> Theory (3 hours)

Total 96 marks
Time- 3 hours

| Question No | 1 | 2 | 3 | 4 | 5 | Total |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Marks | 15 | 23 | 23 | 21 | 14 | 96 |
| Marks Obtained |  |  |  |  |  |  |
| Signature of <br> Examiner |  |  |  |  |  |  |

Date: February 03, 2024 Do not write anything above this line

## Instructions for students

Roll No.

$\square$

## Exam Center

- Write your Roll No. in the space provided above.
- This question booklet consists of $\mathbf{2 5}$ printed pages including periodic table. Check that the booklet has all the pages. If not, report to the invigilator immediately.
- Do not write any part of your answer outside the designated rectangular frame. Any writing outside the frame will not be evaluated.
- Use only black or blue pen to write the answers in the booklet. Answers written in pencil will not be graded.
- You must show the main steps in the calculations and state the necessary assumptions made while solving the tasks.
- For multiple choice questions, mark $\mathbf{X}$ in the correct box.
- Page 22 can be used for answering any question requiring additional space for solution. Mark the appropriate question number.
- Page 23 and 24 can be used for rough work.
- A copy of the Periodic Table of the Elements is provided at the end.
- Do not leave the examination room until directed to do so.
- This answer booklet must be returned to the invigilator.


## Signature of student

## Signature of invigilator

## Useful Constants and Formulae

Avogadro number

$$
\begin{aligned}
& \mathrm{N}_{\mathrm{A}}=6.022 \times 10^{23} \mathrm{~mol}^{-1} \\
& \mathrm{R}=8.314 \mathrm{~J} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}
\end{aligned}
$$

Molar gas constant
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$

$$
\mathrm{pK}_{\mathrm{a}}=-\log \mathrm{K}_{\mathrm{a}}
$$

$\frac{d e^{a x}}{d x}=a e^{a x}$

$$
1 \mathrm{~atm}=101325 \mathrm{~Pa}
$$

Density of water $=1000 \mathrm{~kg} \mathrm{~m}^{-3}$

$$
=0.08205 \mathrm{~L} \mathrm{~atm} \mathrm{~K}^{-1} \mathrm{~mol}^{-1}
$$

$$
\begin{aligned}
& e^{x}=1+\frac{x}{1!}+\frac{x^{2}}{2!}+\frac{x^{3}}{3!}+\cdots,-\infty<x<\infty \\
& \frac{d f(y)}{d x}=\frac{d f(y)}{d y} \times \frac{d y}{d x}
\end{aligned}
$$

For an ideal gas, in an adiabatic process, $T V^{\gamma-1}=$ constant; $P V^{\gamma}=$ constant

[^0]
## The Fifth Taste

In 1908, Professor Kikunae Ikeda, a Japanese chemistry professor, was intrigued by the distinct yet indescribable taste of mushrooms, and kombu seaweed. He isolated a white substance $\mathbf{X}$ from these sources and proved that compound $\mathbf{X}$ was responsible for the unique taste of mushrooms and kombu seaweed. It is a taste, different from sweet, sour, bitter, and salty. He named it umami, now identified as the fifth taste.

Compound $\mathbf{X}$, molecular mass $169.11 \mathrm{~g} \mathrm{~mol}^{-1}$, is an odourless, crystalline compound soluble in water (solubility $740 \mathrm{~g} \mathrm{~L}^{-1}$ ) and practically insoluble in ethanol or ether. It melts at $232^{\circ} \mathrm{C}$ and has specific rotation $[\alpha]_{\mathrm{D}}=+24^{\circ} . \mathbf{X}$ can be synthesized from acrylonitrile using the Oxo process, which is an industrial process for the hydroformylation of alkenes. This process involves the net addition of a formyl group ( -CHO ) and a hydrogen atom $(-\mathrm{H})$ across a carbon-carbon double bond as shown:


A commonly used scheme for synthesis of compound $\mathbf{X}$ is outlined here.


B1 is treated with excess of NaOH (aq.) followed by adjusting the pH to 7 to obtain $\mathbf{X}$.
Treatment of $\mathbf{X}$ with excess $\mathrm{HCl}(\mathrm{aq})$ produces $\mathbf{Z}$.
If a solution of pure $\mathbf{Z}$ is titrated with $\mathrm{NaOH}(\mathrm{aq})$, the variation of pH obtained with the amount of NaOH added is shown graphically here.

1.1 Identify structures of $\mathbf{A 1}, \mathbf{A} \mathbf{2}, \mathbf{B} 1, \mathbf{X}$ and $\mathbf{Y}$.

$\mathbf{X}$ obtained by above synthesis is a racemic mixture. The umami taste is due to the L-enantiomer and the D-form is tasteless.
1.2 Draw Fischer projection of the D-enantiomer of $\mathbf{X}$.

1.3 Write the IUPAC name of A2.
1.4 Predict the predominant structure of $\mathbf{X}$ present in solutions of (i) $\mathrm{pH}=3.2$ and (ii) $\mathrm{pH}=0.5$.
pH 3.2 pH 0.5
1.5 When solid $\mathbf{X}$ was heated, another compound $\mathbf{M}$ was obtained having a molecular mass which is less than that of $\mathbf{X}$ by $18 \mathrm{~g} \mathrm{~mol}^{-1}$. Aqueous solution of $\mathbf{M}$ is slightly alkaline which on warming does not give back $\mathbf{X}$. Draw the structure of $\mathbf{M}$.

Later in 1950's, the following two compounds (X1 and X2) were also found to lend umami flavour to food.


X1


X2
1.6 The class(es) of compound(s) to which $\mathbf{X 1}$ and $\mathbf{X 2}$ belong is/are? (Mark $\mathbf{X}$ in correct box(es))


The nitrogen heterocyclic part present in $\mathbf{X 1}$ is

1.7 Draw any one tautomeric structure for the heterocyclic structure in $\mathbf{X} 1$ shown above.
$\square$
Ketones react with alcohols in the presence of an acid to form ketals. When $\mathbf{X 1}$ is heated with equimolar amount of acetone in the presence of an anhydrous acid, $\mathbf{R}$ is obtained.
1.8 Draw the structure of $\mathbf{R}$.

$\mathbf{X 1}$ undergoes stepwise hydrolysis in acidic conditions. When $\mathbf{X 1}$ was mixed with vinegar $(\mathrm{pH}=4)$ in a food preparation, the umami flavor was lost due to first hydrolysis step which produced two species $\mathbf{N}$ and $\mathbf{O}$.
1.9 Draw the structures of $\mathbf{N}$ and $\mathbf{O}$.

$\square$

## A hand-made Freezer

A student made an ice cream freezer as part of a school project. He kept the freezer in an open space where the temperature was $27^{\circ} \mathrm{C}$. Figure on the right shows the schematics of the freezer. Chamber $\mathbf{A}$ is the freezer chamber having an air volume of 100 L , which on five sides was enclosed by wooden panels having very low thermal conductivity. On the sixth side, the chamber is made of copper sheet which is in contact with chamber B, fully made of copper metal. Chamber $\mathbf{B}$ is a cuboidal cylinder having square cross section ( $25 \mathrm{~cm} \times 25 \mathrm{~cm}$ ) through which a piston (made of insulating material) can be moved up and down using a handle above. Compression and expansion of air in chamber $\mathbf{B}$ leads to alternate heating and cooling of this chamber, eventually cooling chamber $\mathbf{A}$.



Cross sectional view (Compressed State)

The chamber $\mathbf{B}$ was so designed that when the piston was at maximum height $h_{1}=39 \mathrm{~cm}$ (maximum air volume $\left.V_{1}\right), 1 \mathrm{~mol}$ of air in it at $27^{\circ} \mathrm{C}$ had pressure of 1 atm . Treat air to be an ideal gas throughout this problem.

| Heat Capacity Values |  |  | Constants related to air |
| :--- | :--- | :--- | :--- |
| Ice cream mix in chamber A | $210 \mathrm{~J} \mathrm{~K}^{-1}$ | Specific heat capacity | $1.005 \times 10^{3} \mathrm{~J} \mathrm{~kg}^{-1} \mathrm{~K}^{-1}$ |
| The copper wall of Chamber A | $1.5 \mathrm{~kJ} \mathrm{~K}^{-1}$ | Density | $1.16 \mathrm{~g} \mathrm{~L}^{-1}$ |
| Each copper wall of Chamber B | $1.5 \mathrm{~kJ} \mathrm{~K}^{-1}$ | $\gamma=\frac{C_{p}}{C_{v}}$ | 1.4 |
| Base plate of Chamber B | $1.0 \mathrm{~kJ} \mathrm{~K}^{-1}$ |  |  |

The student starts the cooling cycle with piston at the topmost position and all components in thermal equilibrium with the surrounding. Consider the cycle of 4 steps as shown in the following diagram:


Step I. The piston was pushed down extremely fast to $h_{2}$, such that the volume of chamber $\mathbf{B}$ reduced to $V_{2}\left(V_{2}\right.$ $=V_{1} / 5$ ).

Assume that air compression in chamber $\mathbf{B}$ was completely reversible and adiabatic.
2.1 Determine the temperature $T_{2}$ and pressure $P_{2}$ of air inside chamber $\mathbf{B}$ at the end of Step I.


Step II. The piston was kept at the compressed height, $h_{2}$ till chamber $\mathbf{B}$ again reached thermal equilibrium with the outside surrounding air.

Assume that there was no heat exchange of chamber $\mathbf{B}$ with chamber $\mathbf{A}$ during this step.
2.2 Determine the pressure $P_{3}$ of air in chamber $\mathbf{B}$ at the end of Step II.
$\square$
2.3 For air in chamber $\mathbf{B}$ to go from state $\left(T_{1}, P_{1}, V_{1}\right)$ to state ( $T_{3}, P_{3}, V_{3}$ ), number of possible thermodynamic paths are (Mark $\mathbf{X}$ for the correct option(s))
i) one only (given above)

ii) two (one given above and second involving isothermal compression)

iii) infinite (speed of piston compression can be altered in many ways)


Step III. The piston was pulled up extremely fast to reach volume $V_{4}=V_{1}$.
Assume that air in chamber B underwent completely reversible and adiabatic expansion in this step.
2.4 Determine the temperature $T_{4}$ and pressure $P_{4}$ of air inside chamber B at the end of Step III.


Step IV. The piston was kept in this position $\left(V_{5}=V_{4}=V_{1}\right)$ for sufficient time till chamber A attained thermal equilibrium with chamber $\mathbf{B}$.

Heat exchange of air in chamber $\mathbf{B}$ with surrounding air (outside the chamber) vs with chamber $\mathbf{A}$ depends on the respective contact surface area of heat exchange.

Assume that heat transfer between chamber A and $\mathbf{B}$ is proportional to the surface area of contact, and heat transfer with surrounding is proportional to the remaining surface area of chamber B. [This is approximately true because chamber A had same starting temperature as the surrounding air].
2.5 Determine the fraction of heat exchange ( $x$ ) of chamber $\mathbf{B}$ with chamber A in Step IV, where
$x=\frac{\text { Heat transferred from chamber } \mathbf{A} \text { (including walls between the two chambers) to air in chamber } \mathbf{B}}{\text { Total heat gained by air in chamber } \mathbf{B}}$
$\square$
If you were unable to calculate $T_{4}$ and $P_{4}$ in 2.4, then take $T_{4}=220 \mathrm{~K}$ and $P_{4}=0.75 \mathrm{~atm}$ for further questions.
2.6 Determine the temperature $T_{5}$ which chamber $\mathbf{A}$ and $\mathbf{B}$ attain at the end of Step IV. Assume that the chamber $\mathbf{B}$ gains $\boldsymbol{x}$ fraction heat from chamber $\mathbf{A}$, and rest from the surrounding.

The student repeated this cycle multiple times to get the desired freezing temperature of chamber $\mathbf{A}$.
2.7 The student discovered that the temperature drop of chamber A at the end of Step IV was much smaller than the temperature drop in chamber B after Step III. The factor(s) responsible for the observation is/are: (Mark X for the correct option(s))
i) heat gain by chamber $\mathbf{B}$ from surrounding air

ii) heat absorbed by copper walls

iii) higher air volume of chamber $\mathbf{A}$ than $\mathbf{B}$
iv) heat produced during the compression Step I

$\square$
2.8 As this cycle is repeated and if the assumptions remain the same, which of the following parameter values will remain the same over cycles, which will decrease with cycles and which will increase with cycles:
$P_{2}, P_{3}, P_{4}, P_{5}, T_{2}, T_{3}, T_{4}, T_{5}$.
Parameters which will remain same:
Parameters which will decrease:


Parameters which will increase:

2.9 If the compression and expansions in a cycle are done slowly, what changes are expected from the above results (Mark the statements as $\mathbf{T} / \mathbf{F}$ ):
i) Work done in compression step would be lower.
ii) Temperature drop of chamber A per cycle would be lower.
iii) Work done in expansion step by the gas in chamber $\mathbf{B}$ would be lower.
iv) Heat dissipated from chamber $\mathbf{B}$ to surrounding during Step II would remain the same. $\square$

## Acetic acid

Acetic acid is a colorless liquid with a pungent odour. The worldwide production of acetic acid, which has wide applications in food and other industries, is expected to reach 18 million tons in few years with an average growth of $5 \%$ per year. Traditionally, acetic acid is produced by fermentation of apple, grape, honey, cane, coconut, dates etc. The maximum concentration of acetic acid in vinegar that can be obtained by fermentation process is $10 \% \mathrm{v} / \mathrm{v}$. This route is highly energy intensive and uneconomical for pure acetic acid production.

## Part-I: General Methods of Preparation

3.1 It is difficult to separate pure acetic acid from an aqueous solution of acetic acid by distillation alone. Four true statements about acetic acid and water are given below. The statement(s) consistent with difficulty in effective separation of acetic acid from water by distillation is/are (Mark $\mathbf{X}$ for the correct option(s))
i) Boiling points of water and acetic acid are close.
ii) Acetic acid and water do not form an azeotrope.

ii) Acetic acid and water do not form an azeorope.

iii) Acetic acid molecule forms hydrogen bonding with water.

iv) Acetic acid molecules form a cyclic dimer in the vapour phase.

3.2 One of the laboratory methods for preparation of acetic acid is by hydrolysis of acetonitrile (methyl cyanide). Identify the correct statement(s) about the method by marking $\mathbf{X}$ against it.
i) Acid or base catalysis is needed for this hydrolysis reaction.
ii) Acid or base is not needed for this hydrolysis reaction.

iii) Acetamide can be obtained if acetonitrile is heated with excess of alkali.

iv) Ammonia or its salt is formed as a byproduct.


## Part-II: Commercial method for acetic acid production

A commercial process for acetic acid production is methanol carbonylation at high temperature ( $180-220^{\circ} \mathrm{C}$ ) and high pressure ( $30-40 \mathrm{~atm}$ ) in the presence of a transition metal coordinate complex catalyst. One such catalyst is $\left[\mathrm{Rh}(\mathrm{CO})_{2} \mathrm{I}_{2}\right]^{-1}$.

The net reaction is: $\mathrm{CH}_{3} \mathrm{OH}+\mathrm{CO} \rightarrow \mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H} \quad$ Reaction - 1
An interesting feature of this reaction is that it requires a small amount of $\mathrm{CH}_{3} \mathrm{I}$ to start the reaction. Also, under given reaction conditions, the rate of formation of acetic acid is essentially first order with respect to both catalyst and $\mathrm{CH}_{3} \mathrm{I}$ and zero order with respect to CO and methanol.
$3.3\left[\mathrm{Rh}(\mathrm{CO})_{2} \mathrm{I}_{2}\right]^{-1}$ shows stereoisomerism. Draw the structures of stereoisomers.


Transition metal ions in coordination complexes which act as catalysts often are able to increase or decrease their coordination number as well as can undergo oxidation and reduction.

The overall carbonylation of methanol to acetic acid takes place in several steps. Three new Rh-containing complexes, $\mathbf{C 1}, \mathbf{C} 2, \mathbf{C} 3$ and one Rh -free compound $\mathbf{V}$ are identified to be formed in the reaction system sequentially once the reaction starts. The step $\mathbf{C 1} \rightarrow \mathbf{C} 2$ involves a rearrangement wherein two adjacent ligands combine to form a new ligand in the coordination sphere.

$$
\mathbf{C 1} \xrightarrow{\text { rearrangement }} \mathbf{C 2} \xrightarrow{\mathrm{CO}} \mathbf{C 3} \longrightarrow \mathbf{V}+\left[\mathrm{Rh}(\mathrm{CO})_{2} \mathrm{I}_{2}\right]^{-1}
$$

Two additional reactions happen in the system producing $\mathbf{Y}$ and $\mathbf{Z}$ (both are Rh-free compounds) as given below.

$$
\begin{array}{ll}
\mathbf{V}+\mathbf{Y} \rightarrow \mathbf{Z}+\mathrm{CH}_{3} \mathrm{COOH} & \text { Reaction }-2 \\
\mathbf{Z}+\mathrm{CH}_{3} \mathrm{OH} \rightarrow \mathrm{CH}_{3} \mathbf{I}+\mathbf{Y} & \text { Reaction }-3
\end{array}
$$

3.4 Identify $\mathbf{C} \mathbf{1}, \mathbf{C} 2, \mathbf{C} 3, \mathbf{V}, \mathbf{Y}$ and $\mathbf{Z}$, along with stereochemical structures for the complexes.
C1
C2
C3
3.5 Write the balanced chemical equation with stereochemical structure(s) for the rate determining step in this production method.
$\square$

Part-III: Side reactions in commercial acetic acid production
The percent conversion in the process presented in Part II is about $85 \%$ with respect to CO and $99 \%$ with respect to $\mathrm{CH}_{3} \mathrm{OH}$. The loss of CO is due to several side reactions which happen in the system as given below.
i) One of the reactions which happens in the presence of the $\left[\mathrm{Rh}(\mathrm{CO})_{2} \mathrm{I}_{2}\right]^{-1}$ catalyst is -

$$
\mathbf{C O}+\mathbf{Y} \rightarrow \mathbf{M}+\mathbf{N} \quad \text { Reaction }-4
$$

( $\mathbf{M}$ has lower molar mass than that of $\mathbf{N}$.)
ii) The rhodium catalyst system can generate acetaldehyde by reaction 5 given below. Acetaldehyde is then reduced by one of the products formed in the reaction process, to give an intermediate which subsequently yields propionic acid by the same carbonylation process.

$$
\mathbf{C 2}+\mathrm{HI} \rightarrow\left[\mathrm{RhI}_{4}(\mathrm{CO})\right]^{-1}+\mathrm{CH}_{3} \mathrm{CHO} \quad \text { Reaction }-5
$$

iii) Acetaldehyde undergoes aldol condensation in the presence of an acid and the product is converted to carboxylic acid $\mathbf{S}$ as shown below.

3.6 Draw structures of $\mathbf{M}, \mathbf{N}, \mathbf{P}, \mathbf{Q}, \mathbf{R}$ and $\mathbf{S}$.
3.7 For the following group of compounds formed in the reaction with methanol as indicated above, identify for each group, which carbon chain lengths are possible and which are not possible (Indicate number of C atoms as $\mathrm{n}, 2 \mathrm{n}, 2 \mathrm{n}-1,2 \mathrm{n}+1,2 \mathrm{n}+2,3 \mathrm{n}+1,4 \mathrm{n}+1$, etc. where $\mathrm{n}=1,2,3, \ldots$.

|  | Possible | Not Possible |
| :--- | :--- | :--- |
|  |  |  |
| i) Aldehydes |  |  |
| ii) Carboxylic acids |  |  |

3.8 Suppose the acetic acid process was performed with unlabelled methanol but with ${ }^{13} \mathrm{C}$-labeled ${ }^{13} \mathrm{CO}$. Draw the structures of the following products with ${ }^{13} \mathrm{C}$ labelled carbon-
i) propionic acid (by-product)

ii) $\mathbf{S}$ (by-product)

3.9 Determine the $\Delta H^{\circ}$ formation of acetic acid at $25^{\circ} \mathrm{C}$.

| $\Delta \boldsymbol{H}^{\circ}{ }_{\mathrm{f}}$ values |  |  |  |
| :--- | :--- | :--- | :--- |
| $\mathrm{CH}_{3} \mathrm{OH}(\mathrm{l})$ | $-239.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$ | $\mathrm{CH}_{3} \mathrm{CO}_{2} \mathrm{H}(\mathrm{l})$ | $-386.1 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |
| $\mathrm{CO}(\mathrm{g})$ | $-110.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$ | $\mathrm{CH}_{3} \mathrm{I}(\mathrm{l})$ | $-13.6 \mathrm{~kJ} \mathrm{~mol}^{-1}$ |

3.10 The important advantages of Rh- catalyzed method over fermentation method of acetic acid production is (are) (Mark $\mathbf{X}$ against the correct option(s))-
i) Higher percent conversion of methanol to product. $\square$
ii) Acetic acid is produced at much higher concentration than vinegar. $\square$
iii) Uses reactants which are not toxic. $\square$

## Inter-atomic Forces and Static Friction

Frictional force between two surfaces in contact originates from inter-atomic forces between the contact atoms of the surfaces.

This problem first explores variation in inter-atomic interaction with distance between two atoms (Part I) and uses this idea to understand atomic origins of friction (Part II).

## Part I: Electrostatic interaction between two atoms

Philip Morse, an American scientist gave a simple functional form for inter-atomic (electrostatic) potential (energy) between two atoms in terms of inter-nuclear distance, $r$ as:

$$
V_{\text {Morse }}(r)=D\left[1-e^{-\alpha\left(r-r_{e}\right)}\right]^{2}-D
$$

where $D, r_{e}$ and $\alpha$ are constants independent of the mass of the nuclei. [Note that the Morse potential does not go to the expected limit of $V=\infty$ at $r=0$.]

The corresponding force $F(r)$ between two atoms along $r$ direction can be defined as:

$$
F(r)=-\frac{\partial V_{\text {Morse }}}{\partial r}
$$

4.1 Derive an expression for $F(r)$ in terms of $D, r_{e}$ and $\alpha$.


Potential is considered attractive when $F(r)$ is negative, and repulsive when $F(r)$ is positive.
4.2 Derive expressions for the following quantities in terms of $D, r_{e}$ and $\alpha$ :
(a) the inter-nuclear distance $r_{\min }$ where $V_{\text {Morse }}(r)$ is minimum, and
(b) the energy difference $\epsilon=V_{\text {Morse }}(\infty)-V_{\text {Morse }}\left(r_{\text {min }}\right)$.

If we ignore quantum mechanical effects, $r_{\text {min }}$ represents the equilibrium bond length between the two atoms and $\epsilon$, their bond dissociation energy.
4.3 A $V_{\text {morse }}$ vs. $r$ plot is given below. Assuming $\alpha r_{e}=1$, indicate on the plot:
(i) the potential values at $r=0, r=r_{\text {min }}$ and $r=\infty$.
(ii) ranges of $r$ where potential is repulsive and attractive respectively.

4.4 Among the four plots shown below, the plot of force $F(r)$ as a function of $r$ is likely to be (Mark $\mathbf{X}$ for the correct graph):




## Part II: The nature of static frictional force

Static friction is the 'resisting' force experienced by an object $\mathbf{A}$ of mass M at rest on a surface $\mathbf{B}$, when an external horizontal force is applied on this object. First proposed by Leonardo da Vinci and then formally theorized by French engineer Guillaume Amontons 200 years later in 1669, frictional force was largely found to be proportional to the normal force:

$$
F=\mu M g
$$

where $\mu$ is the static friction coefficient and $g$ is the acceleration due to gravity.


A zoomed in picture of two surfaces in contact is shown above (right). We assume surface $\mathbf{B}$ is atomically flat as shown. Contact surface of $\mathbf{A}$ is rough (as most surfaces are rough). There will be multiple ( $n$ ) atoms of $\mathbf{A}$ that will come in close contact with $\mathbf{B}$. Consider an atom $\mathbf{P}$ on surface $\mathbf{A}$, that is in contact with surface $\mathbf{B}$. We assume $\mathbf{A}$ to be a rigid body and forces acting from $\mathbf{B}$ on $n$ contact atoms (like $\mathbf{P}$ ) to be equal, and for all other A atoms to be zero.
4.5 What is the net normal force felt by each contact atom like $\mathbf{P}$ ?


If an external force $F_{\text {ext }}$ applied on $\mathbf{A}$ along $x$-direction is just more than the static frictional force, then $\mathbf{A}$ may microscopically move a small distance $\delta x$ in the $x-z$ plane. This movement would not be noticeable at bulk scale. A being a rigid body, $F_{\text {ext }}$ is experienced equally by all atoms of $\mathbf{A}$.

Consider the atom $\mathbf{P}$ with center at $(0,0, z)$ interacting with two atoms of surface $\mathbf{B}$ with centers at: $(-a, 0,0),(a, 0,0)$ as shown here.


We consider interactions between $\mathbf{P}$ and $\mathbf{B}$ atoms using two models.
i) Hard Sphere Model- Assume atoms of $\mathbf{A}$ and $\mathbf{B}$ as hard spheres which can come a closest distance $r_{A B}$ and do not have any inter-atomic potential (or bond).


In this model, as $F_{\text {ext }}$ moves atom $\mathbf{P}$ from $x=0$ to $x=a$, object $\mathbf{A}$ (being a rigid body) will get lifted by the same height as atom $\mathbf{P}$. The net work ( $W$ ) done by $F_{\text {ext }}$ on $\mathbf{A}$ is

$$
W=F_{e x t} a
$$

This work will change gravitational potential energy of $\mathbf{A}$ by $E_{\text {grav }}$, and kinetic energy of $\mathbf{A}$ by $E_{k i n}$ as per the following equation.

$$
F_{\text {ext }} a=E_{\text {grav }}+E_{k i n}
$$

Since $F_{\text {ext }}$ is just more than the static frictional force, we take the limiting case of $E_{\text {kin }}=0$, when $F_{\text {ext }}=\mu M g$.
4.6 Determine (i) increase in height $\Delta z$ of atom $\mathbf{P}$ as it moves from $x=0$ to $x=a$; and
(ii) $\mu$ in terms of $r_{A B}$ and $a$ showing all steps clearly.

ii) Morse Model- We include Morse interactions (potential energy) between atom $\mathbf{P}$ and $\mathbf{B}$ atoms such that $r_{A B}=r_{e}\left(r_{A B}\right.$ is distance without considering gravitational effects). In this model, due to gravitational force, equilibrium distance $r$ between centers of atoms $\mathbf{P}$ and $\mathbf{B}$ will be lower than $r_{A B}$. Further, in this model,


The difference in equilibrium position $\delta r=r-r_{e}$ due to the gravitational force is much smaller compared to $r_{e}$. Thus, we can take

$$
\begin{aligned}
& e^{-\alpha\left(r-r_{e}\right)} \approx 1-\alpha\left(r-r_{e}\right) \\
& \text { i.e. } V_{\text {Morse }}(r) \approx D \alpha^{2}\left(r-r_{e}\right)^{2}, \text { and } \\
& \frac{z(0)}{r(0)} \approx \frac{z_{e q}}{r_{e}}
\end{aligned}
$$

where $z_{e q}$ is the value of $z$ without gravitational effects.
As atom $\mathbf{P}$ moves from $x=0$ to $x=a$, its Morse interaction with atom at $(-a, 0,0)$ becomes very weak that we can consider that bond to be broken. Thus for movement of $n$ equivalent contact atoms of the surface $\mathbf{A}$, the minimum energy $E_{\text {Morse }}$ to break one of the two bonds with contact atoms of $\mathbf{B}$ for $n$ atoms would be $n \epsilon$.
4.7 Derive an expression for equilibrium value of $z$ at (i) $x=0$ and (ii) $x=a$ with Morse Model. At $x=a$, assume atom $\mathbf{P}$ interacts only with $(a, 0,0)$ atom. Use the approximations $r-r_{e} \ll r_{e}$ to get the simplified expression.


For many surfaces, static frictional force is related to $M$ as $F_{\text {static }}=\mu M g+K$, which can be explained by the Morse model.
4.8 Taking the limiting case of $E_{k i n}=0$, derive $\mu$ and $K$ in terms of $D, \alpha, r_{e}, a$, and $n$ showing all steps clearly. [Note that $\mu$ will also have a small component which is dependent on $M$ ]
$\square$
4.9 For the Morse model, estimate the value of $\mu$, given $M=1 \mathrm{~kg}, g=10 \mathrm{~m} \mathrm{~s}^{-2}, n=10^{10}, D=6.4 \times$ $10^{-19} \mathrm{~J}, \alpha=10^{10} \mathrm{~m}^{-1}, r_{e}=2.5 \AA, a=1.5 \AA$.

## Analysis of a solid mixture containing iron and iron oxides

Triplicate samples (each with mass 4.72 g ) of a homogeneous mixture containing iron ( Fe ) and oxides of Fe (II) and Fe (III) were received in a lab for analysis. The samples had to be analyzed first to determine the exact moles of each component present in the mixture. To determine the same, two methods (A and B) described below were used by the lab expert

A: 4.72 g of the sample was taken in a flask and hydrogen gas was filled in the flask. The flask was sealed and heated. At the end of reaction. 3.92 g iron and 0.90 g of water were obtained.

B: An excess of aqueous $\mathrm{CuSO}_{4}$ solution was added to the second sample of mass 4.72 g . At the end of the reaction, 4.96 g of a solid mixture was obtained.

| $\mathbf{E}^{0}$ values of reducing half-cell equations |  |
| :--- | :--- |
| $2 \mathrm{H}^{+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{H}_{2}(\mathrm{~g})$ | 0.00 V |
| $\mathrm{Fe}^{2+}(\mathrm{aq})+2 \mathrm{e}^{-} \rightarrow \mathrm{Fe}(\mathrm{s})$ | -0.44 V |
| $\mathrm{Fe}^{3+}(\mathrm{aq})+3 \mathrm{e}^{-} \rightarrow \mathrm{Fe}(\mathrm{s})$ | -0.04 V |

5.1 i) Write balanced chemical equations for the reactions involved in methods A and B.

Method A:

Method B:
ii) Calculate the moles of Fe (metal), Fe (II) and Fe (III) oxides present in the sample using method A and
B. Show all steps in the calculations.
$\square$
$\square$
For another analysis, the third sample weighing 4.72 g was dissolved completely in $7.3 \%$ ( $\mathrm{w} / \mathrm{w}$ ) aqueous HCl .
5.2 i) Write balanced chemical equations for all reactions involved in the dissolution of the sample in HCl .

ii) Determine the minimum volume of $7.3 \%(\mathrm{w} / \mathrm{w})$ aqueous $\mathrm{HCl}\left(\rho=1.03 \mathrm{~g} \mathrm{~cm}^{-3}\right)$ required in milliliters $(\mathrm{mL})$ for complete dissolution of the sample. Show all steps in the calculations.

iii) Calculate the volume of gas released in the above reaction at 1 atm and $25^{\circ} \mathrm{C}$.
IUPAC Periodic Table of the Elements

| $\stackrel{\infty}{\sim}$（1） |  | （1） |  |  | ®乐产 |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| $\uparrow$ |  |  |  |  |  |  |
| $\bigcirc$ |  | －¢ |  |  | ¢ $\mathrm{O}_{\text {O }}^{\text {亳 }}$ |  |
| $\stackrel{\square}{6}$ |  |  |  | 的の悥䃄 |  |  |
| $\pm$ |  |  |  |  |  |  |
| $\stackrel{\sim}{\sim}$ |  |  |  |  |  | ¢ ${ }_{\text {¢ }}^{\text {¢ }}$ |
|  |  | $\simeq$ | ${ }_{¢}^{\text {¢ }}$ N |  | ® 오 訇骨 | －${ }^{\text {c }}$ |
|  |  | F |  |  |  |  |
|  |  | $\bigcirc$ |  |  |  |  |
|  |  | の | へ ${ }^{\circ} \mathrm{O}$ |  |  |  |
|  |  | $\infty$ |  |  |  |  |
|  |  | $\wedge$ |  |  |  | － |
|  |  | － |  |  |  | － |
|  |  |  |  |  |  | 号吕言 |
|  | $\qquad$ | ＋ |  |  |  | － |
|  |  | $\cdots$ |  |  |  | \％ |
| $\sim$ |  |  |  |  |  | \％¢ ¢ ¢ |
|  |  |  |  |  |  |  |


|  |  |
| :---: | :---: |
| 88 ［ | \％ 2 |
| 8， | － |
| 84！ | 级 |
| ＝욘 | ｜ |
| 8 | 『¢ |
| 82］： | ： |
| $8{ }^{\text {8 }}$ | \％ |
| \％ | 戓 |
| ${ }^{\circ}$ | ） |
| ＝ | 8\％ |
| $8{ }^{2}$ | 831 |
| 8 | 5il |
| \％ | \％ 8 ！ |
| 5 |  |

For notes and updates to this table，see www．iupac．org．This version is dated 1 December 2018. Copyright © 2018 IUPAC，the International Union of Pure and Applied Chemistry．

INTERNATIONAL UNION OF
PURE AND APPIIED CHEMISTRY




[^0]:    © Homi Bhabha Centre for Science Education, Tata Institute of Fundamental Research V. N. Purav Marg, Mankhurd, Mumbai 400088

