

Answer Sheet No. $\qquad$

Sign. of Candidate $\qquad$

Sign. of Invigilator $\qquad$

## CHEMISTRY HSSC-I ( $2^{\text {nd }}$ Set Solution) <br> SECTION - A (Marks 17) <br> Time allowed: 25 Minutes

Section - A is compulsory. All parts of this section are to be answered on this page and handed over to the Centre Superintendent. Deleting/overwriting is not allowed. Do not use lead pencil.
Q. 1 Fill the relevant bubble for each part. Each part carries one mark.

1. The least number of molecules are present in 30 g of:
A. $\mathrm{N}_{2} \mathrm{O}$

B. NO
C. $\quad \mathrm{NO}_{2}$
D. $\quad \mathrm{N}_{2} \mathrm{O}_{3}$

2. The largest bound angle is present in:
A. $\mathrm{CH}_{4}$

B. $\mathrm{SCl}_{2}$
C. $\mathrm{NH}_{3}$
D. $\mathrm{BCl}_{3}$

3. The difference in angular momentum of electron which jumps from 3rd orbit to 6th orbit of hydrogen atom will be:
A. $3\left(\frac{h}{2 \pi}\right)$
$\bigcirc$
B. $3\left(\frac{h}{\pi}\right)$
C. $\quad 6\left(\frac{h}{2 \pi}\right)$D. $6\left(\frac{h}{\pi}\right)$

4. Which one of the following salts turns red litmus blue upon hydrolysis?
A. $\quad \mathrm{K}_{2} \mathrm{SO}_{4}$
B. NaCl
C. $\mathrm{Na}_{2} \mathrm{CO}_{3}$
D. $\mathrm{NH}_{4} \mathrm{Cl}$

5. Identify the unit of rate constant ( K ) for the given reaction:
$2 \mathrm{~A}+\mathrm{B} \longrightarrow$ Product when Rate $=\mathrm{K}[\mathrm{A}][\mathrm{B}]$
A.
$\mathrm{s}^{-1}$
$\bigcirc$
B. $\mathrm{mol} \mathrm{dm}^{-3} \mathrm{~s}^{-1}$
C. $\quad \mathrm{dm}^{3} \mathrm{~mol}^{-1} \mathrm{~s}^{-1}$
D. $\mathrm{dm}^{6} \mathrm{~mol}^{-2} \mathrm{~s}^{-1}$
6. The 3rd line in the Balmer Series of Bohr's Hydrogen spectrum is due to the transition of electron:
A. From $4^{\text {th }}$ shell to $1^{\text {st }}$ shell
B. From $4^{\text {th }}$ shell to $2^{\text {nd }}$ shell
C. From $5^{\text {th }}$ shell to $1^{\text {st }}$ shell
D. From $5^{\text {th }}$ shell to $2^{\text {nd }}$ shell
7. If Principal quantum number $(\mathrm{n})=3$, the total magnetic quantum numbers (m) will be:
A. 3
$\bigcirc$
B. 6
C. 9
D. 12

8. A gas $x$ diffuses four times faster than $\mathrm{SO}_{2}$ gas. The molar mass of gas $x$ will be:
A. $2 \mathrm{~g} / \mathrm{m}$
$\bigcirc$
B. $\quad 4 \mathrm{~g} / \mathrm{m}$
C. $16 \mathrm{~g} / \mathrm{m}$
D. $64 \mathrm{~g} / \mathrm{m}$
9. A real gas that obeys Vander Wall's equation $\left(p+\frac{a n^{2}}{v^{2}}+(v-n b)=\right.$ $n R T$ )behaves like an ideal gas when
A. 'a' is large \& ' $b$ ' is small
B. ' $a$ ' is small \& ' $b$ ' is large
C. 'a'\&'b' are large
D. 'a'\&'b' are small

10. NaCl is a crystalline solid which has face centered cubic structure. The $\mathrm{Na}^{+}$ion at the face of the unit cell is shared by:
A. Two unit cells
$\bigcirc$
B. Four unit cells
C. Six unit cell
D. Eight unit cells
11. The transition temperature of tin grey and tin white is:
A. $\quad 13.2^{\circ} \mathrm{C}$
B. $\quad 18^{\circ} \mathrm{C}$
C. $\quad 95.5^{\circ} \mathrm{C}$
D. $\quad 128.5^{\circ} \mathrm{C}$

12. The vapor pressure of a liquid depends upon the following, EXCEPT:
A. Nature of liquid
B. Temperature
C. Inter molecular forces
D. Amount of liquid
13. The standard electrode potential of different elements are measured with the help of Standard Hydrogen Electrode (SHE). The standard conditions at which SHE is operated are:
A. $\quad 2.00 \mathrm{M} \mathrm{HCl}$ solution, $1 \operatorname{atm~} \mathrm{H}_{2}$ at 0 K .
B. $\quad 1.00 \mathrm{M} \mathrm{HCl}$ solution, $1 \mathrm{~atm} \mathrm{H}_{2}$ at 298 K .
C. $\quad 1.00 \mathrm{M} \mathrm{HCl}$ solution, $2 \operatorname{atm} \mathrm{H}_{2}$ at 0 K .
D. 1.00 M HCl solution, $1 \mathrm{~atm}_{2}$ at 273 K .
14. 20 grams of glucose dissolved in water to prepare a solution of $10 \% \mathrm{w} / \mathrm{v}$ concentration. The volume of the solution will be:
A. $\quad 100 \mathrm{~cm}^{3}$
$\bigcirc$
B. $\quad 200 \mathrm{~cm}^{3}$
C. $\quad 2000 \mathrm{~cm}^{3}$
D. $2500 \mathrm{~cm}^{3}$

15. A buffer solution resists the change of its pH upon adding small amount of strong acid or base. Which one of the following is an example of a buffer solution?
A. Mixture of $\mathrm{NH}_{4} \mathrm{Cl}_{(\mathrm{aq})}$ and $\mathrm{NH}_{4} \mathrm{NO}_{3(\mathrm{aq})}$
B. Mixture of $\mathrm{NH}_{4} \mathrm{Cl}_{(\mathrm{aq})}$ and $\mathrm{NaCl}_{(\mathrm{aq})}$
C. Mixture of $\mathrm{CH}_{3} \mathrm{COONa}_{(\mathrm{aq})}$ and $\mathrm{NH}_{4} \mathrm{Cl}_{(\mathrm{aq})}$
D. Mixture of $\mathrm{NH}_{4} \mathrm{Cl}_{\text {(aq) }}$ and $\mathrm{NH}_{4} \mathrm{OH}_{(\text {aq) }}$
16. If enthalpy of neutralization of the given reaction (a) is $-57.3 \mathrm{k} \mathrm{J} / \mathrm{mol}$. What would be the enthalpy change of reaction (b)?
(a) $\mathrm{KOH}_{(\mathrm{aq})}+\mathrm{HCl}_{(\mathrm{aq})} \rightarrow \mathrm{KCl}_{(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}$
(b) $\quad \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{KOH}_{(\mathrm{aq})} \rightarrow \mathrm{K}_{2} \mathrm{SO}_{4(\mathrm{aq})}+2 \mathrm{H}_{2} \mathrm{O}$ (l)
A. $\quad-28.65 \mathrm{k} \mathrm{J}$
C. $\quad-171.9 \mathrm{k} \mathrm{J}$

B. $\quad-114.6 \mathrm{~kJ}$
D. $\quad-229.2 \mathrm{k} \mathrm{J}$
C. 171.9 k
17. The unit of Kc for the following reversible reaction will be: $3 \mathrm{Fe}_{(\mathrm{s})}+4 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \rightleftharpoons \quad \mathrm{Fe}_{3} \mathrm{O}_{4(\mathrm{~s})}+4 \mathrm{H}_{2(\mathrm{~g})}$ Which one is the unit of Kc ?
A. $\quad$ No unit

B. $\mathrm{mole}^{2} \mathrm{dm}^{-3}$
D. $\mathrm{mol}^{-1} \mathrm{dm}^{3}$

Federal Board HSSC-I Examination
Chemistry Model Question Paper
(Curriculum 2006)
Time allowed: 2.35 hours
Total Marks: 68
Note: Answer any fourteen parts from Section 'B' and attempt any two questions from Section ' C ' on the separately provided answer book. Write your answers neatly and legibly.

## SECTION - B (Marks 42)

Q. 2 Attempt any FOURTEEN parts from the following. All parts carry equal marks.
$(14 \times 3=42)$
i. Justify the following:
a. One mole of $\mathrm{CO}_{2}, \mathrm{CH}_{4} \& \mathrm{H}_{2} \mathrm{O}$ has different masses but have same number of molecules.

Ans. One mole $\mathrm{CO}_{2}=6.022 * 10^{23}$ molecules $=44 \mathrm{~g}$
One mole $\mathrm{CH}_{4}=6.022 * 10^{23}$ molecules $=16 \mathrm{~g}$
One mole of $\mathrm{H}_{2} \mathrm{O}=6.022 * 10^{\wedge 23}$ molecules $=18 \mathrm{~g}$
This shows that one mole of different substances has same number of particles but different masses. This is because atomic mass, molecular masses or formula mass is equal to mole depends upon nature or molecules.
b. Energy of 3d sub shell is greater than 4 s .

Ans. $\quad 3 \mathrm{~d}=\mathrm{n}+1$ Rule
$3+2=5$
4s n+l
$4+0=4$
According to $(\mathrm{n}+\mathrm{l})$ rule, the orbital with lower ( $\mathrm{n}+\mathrm{l}$ ) will have lower energy. So 3d having greater
$(\mathrm{n}+\mathrm{l})$ value will have higher in energy than 4s.
ii. For the following reaction:

$$
\mathrm{Ca}(\mathrm{OH})_{2(\mathrm{aq})}+\mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}+\mathrm{CaSO}_{4(\mathrm{~s})}
$$

Calculate the mass of calcium hydroxide needed to produce 680 g of calcium sulphate? $\quad(\mathrm{Ca}=40, \mathrm{O}=16, \mathrm{~S}=32, \mathrm{H}=1 \mathrm{~g} / \mathrm{mol})$

$$
\begin{aligned}
& \text { Ans. } \quad \mathrm{Ca}(\mathrm{OH})_{2}+\mathrm{H}_{2} \mathrm{SO}_{4} \rightarrow \quad 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{CaSO}_{4} \\
& \mathrm{~m}_{\mathrm{Ca}(\mathrm{OH}) 2}=\text { ? } \\
& \mathrm{m}_{\mathrm{CaSO}}=680 \mathrm{~g} \\
& 13 \mathrm{~g} \text { of } \mathrm{CaSO}_{4} \text { is produced by } \mathrm{Ca}(\mathrm{OH})_{2}=74 \mathrm{~g} \\
& 1 \mathrm{~g} \text { of } \mathrm{CaSO} \\
& 4 \\
& \text { is produced by } \mathrm{Ca}(\mathrm{OH})_{2}=74 / 136 \mathrm{~g} \\
& 1=680 \mathrm{~g}^{2} \text { of } \mathrm{CaSO}_{4} \text { is produced by } \mathrm{Ca}(\mathrm{OH})_{2}=(74 / 136 \mathrm{~g}) * 680 \\
& \qquad=370 \mathrm{~g}
\end{aligned}
$$

iii. $\quad \mathrm{Se}^{2-}$ selenide and $\mathrm{SO}_{3}{ }^{2-}$ Sulphite ions react spontaneously

$$
2 \mathrm{Se}^{2-}+2 \mathrm{SO}_{3}^{2-}+3 \mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{Se}+6 \mathrm{OH}^{-}+\mathrm{S}_{2} \mathrm{O}_{3}
$$

$\mathrm{E}^{\circ}$ cell $=0.35 \mathrm{v}$ If $\mathrm{E}_{0}$ Sulphite is -0.57 v , calculate $\mathrm{E}^{\circ}$ for selenium.
Ans. $2 \mathrm{Se}+2 \mathrm{SO}_{3}{ }^{2-}+3 \mathrm{H}_{2} \mathrm{O} \quad \rightarrow \quad 2 \mathrm{Se}+6 \mathrm{OH}^{-}+\mathrm{S}_{2} \mathrm{O}_{3}$
$\mathrm{E}^{0}\left(\mathrm{SO}_{3}{ }^{2-}\right)=-0.57 \mathrm{~V} \quad \mathrm{E}_{\text {cell }}=0.35 \mathrm{~V}$
$\mathrm{E}_{(\mathrm{S} 2+\mathrm{C}}=$ ?
$\mathrm{Se}^{+}+2 \mathrm{e}^{-} \rightarrow \mathrm{Se} \quad \mathrm{E}_{\text {cathode }}=\mathrm{E}_{0}=$ ? (cathode)
$2 \mathrm{e}-++2 \mathrm{SO}_{3}^{2-}+3 \mathrm{H}_{2} \mathrm{O} \quad \rightarrow 6 \mathrm{OH}^{-}+\mathrm{S}_{2} \mathrm{O}_{3} \quad \mathrm{E}=+0.57$ (anode)
$\mathrm{S}_{2} \mathrm{O}_{3}+6 \mathrm{OH}-3 \mathrm{H}_{2} \mathrm{O}+2 \mathrm{SO}_{3}^{-2}+2 \mathrm{e}^{-} \quad \mathrm{E}^{0}=0.57=\mathrm{E}$ anode
$\mathrm{E}^{0}{ }_{\text {CL }}=\mathrm{E}_{\text {cathode }}-\mathrm{E}_{\text {anode }}$
$0.35=\mathrm{E}_{\text {cathode }}-(-0.57)$
$\mathrm{E}_{\text {cathod }}=0.35 \mathrm{v}-0.57 \mathrm{v}$
$\mathrm{E}_{(\mathrm{Se} 2+)}=\mathrm{E}_{\text {cathode }}=-0.22$ volts
iv. What is metallic bond? Describe electron sea theory.

Ans. Metallic bonding is a type of bonding that arises from electrostatic forces of attraction between electrons and positively charged metal ions.

## Electron Sea/ Electron Gas Theory:

In metallic solids the positively charged portion of metallic atoms is surrounded by an atmosphere of free electrons. This is called electron sea or electron gas.
Two types of forces are responsible for metallic bonding.
i) Attractive forces between electrons and positive ions.
ii) Repulsive forces between positively charged nuclei.

The forces are equal and opposite so metallic solids are neutral as a whole.
v. How Mosley used x-rays Spectrum to predict the atomic number of elements? Give one use of x-rays in medical field and chemistry.

Ans. Mosely proved that the frequency of x-rays increase in a regular manner as number of protons increases in the nucleus. The plot of frequency of $x$ rays versus the square of protons number atomic number $(Z)$ of elements is called $x$ ray spectrum. From that $x$ ray spectrum if frequency of $x$ ray emitted by unknown element is measured than unknown element can be predicted from its atomic number.

## Use of X-ray In Medical Field.

- X-rays are used in radiography to locate fracture in bones.

Use of X- Rays In Chemistry

- $\quad$ X ray diffraction (XRD) technique is used to study crystal structure. X rays are also used to ionize gases.
vi. The species $\mathrm{H}_{2} \mathrm{O}, \mathrm{NH}_{3}$ and $\mathrm{CH}_{4}$ have bond angles of $104.5^{\circ}$, $107.5^{\circ}$, $109.5^{\circ}$ respectively. Prove by VSEPR theory, by drawing their structures.


## Water



It is $\mathrm{AB}_{2} \mathrm{E}_{2}$ type molecule with two bond pairs and two lone pairs. As repulsion between two lone pairs is greater than repulsion between two bond pairs, so bond angle decreases from 109.5 to 104.5
Total electron pair Bond pair Lone Pair

## Ammonia:



The expected angle in $\mathrm{NH}_{3}$ is $109.5^{\circ}$ as it has 4 electron pairs, but as one of electron pair is a lone pairs and three bond pairs so the angle decreases to $107.5^{\circ}$. Lone pair bond pair repulsion is greater than bond pair repulsion. Hence angle is reduced to $107.5^{\circ}$. It is $\mathrm{AB}_{3} \mathrm{E}$.

Total electron pair 4

Bond pair
3

Lone Pair
1

Methane:


It has perfect tetrahedral geometry because 4 electron pairs are bond pairs, so these are arranged in such a way that there is maximum distance and minimum repulsion between them, so the angle is $109.5^{\circ} . \mathrm{It}$ is $\mathrm{AB}_{4}$ type.
Total electron pair Bond pair Lone Pair
4
4
0
vii. Briefly describe the shape of subshells when the values of $l$ are $0,1 \& 2$.

Ans.
l=0 s subshell-----spherical
l=1 p subshell----dumbell shape
l=2 d subshell----- sausage shape

l=0 s subshell-----spherical
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l=2 d subshell----- sausage shape
viii. Explain the shape and polarity of $\mathrm{H}_{2} \mathrm{O}$ on the basis of dipole moment.

Ans.
Molecules having zero dipole moment are non polar molecules. Molecules having some value of dipole moment are polar. Water is a triatomic V- shaped molecule because it is polar and has dipole moment 1.84 D . This is because of vector sum of the forces are not equal to zero. That is why water is a polar molecule.

ix. State Joule Thomson Effect and give one application.

Ans.
Statement: When a highly compressed gas is allowed to escape out through a throttle, the temperature of the gas falls to such an extent, that it changes into liquid form.
Application: Self cooling pop can (container)
A small container holding liquid $\mathrm{CO}_{2}$ is built right into the can. When the can is opened, the liquid $\mathrm{CO}_{2}$ vaporizes and escapes out of the top of the can. The heat absorbed by the vaporizing $\mathrm{CO}_{2}$ can lower the temperature of the POP by $16^{\circ} \mathrm{C}$ in a few seconds. Thus the temperature is lowered considerably.
x. Boiling point of $\mathrm{HF}\left(19.5^{\circ} \mathrm{C}\right)$ is low as compared to $\mathrm{H}_{2} \mathrm{O}\left(100^{\circ} \mathrm{C}\right)$ although the electronegativity of Fluorine is greater than Oxygen. Explain.

Ans. Though the strength of single hydrogen bond in HF is stronger than $\mathrm{H}_{2} \mathrm{O}$. But the no of hydrogen bonds formed by water molecules with neighboring molecules are more than in HF. Hydrogen is trapped in between two fluorine atoms and form one hydrogen bond while in $\mathrm{H}_{2} \mathrm{O}$ two hydrogen bonds are formed. That is why boiling point of $\mathrm{H}_{2} \mathrm{O}$ is greater than HF.
H-F.......H-F.........H-F
xi. Briefly describe the factors on which London forces depend?

## Ans. Factors affecting London dispersion force are:

1. Atomic or Molecular Size: With the increase in size of atom or molecule, the dispersion becomes easy and these forces become prominent.
2. Polarizability: It is a quantitative measure of the ease with which electron charge density is distorted. Large atoms have more electrons and large electronic cloud than small atoms. Polarizability increases with increased molecular and atomic size.
3. No of atoms in a molecule: Elongated molecules make contact with neighbouring molecules over a greater surface than do small molecules. Greater the no of atoms, greater will be London dispersion forces of the molecule.
xii. Give three properties of covalent crystals.

## Ans. Properties of Covalent Crystals:

1. They are bad conductors of electricity with the exception of graphite.
2. They have definite shape and oriented in three directions with a network structure.
3. They may be called as macromolecules due to their giant covalent structures.
xiii. How can you measure the depression in freezing point using Beckman's Freezing point apparatus.

Ans. There are many methods but Beckmann's method is easy to perform. The apparatus consists of three major parts:
a. A freezing tube with a side arm. It contains solvent or solution and is fitted with a stirrer and Beckmann's thermometer.
b. An outer larger tube into which the freezing tube is adjusted. The air jacket in between these tubes help to achieve a slower and more uniform rate of cooling.
c. A large jar containing a freezing mixture. Around 20 to 25 g of the solvent is taken in the freezing tube. The bulb of the thermometer is immersed in the solvent. First of all, approximate freezing point of the solvent is measured by directly cooling the freezing point tube in the freezing mixture.

The freezing tube is then put in the air jacket and cooled slowly. In this way, accurate freezing point of the solvent is determined. Now, the solvent is re-melted by removing the tube from the water bath and weighed amount of 0.2 to 0.3 g of the solute is introduced in the side tube. The freezing point of the solution is determined while stirring the solution. The difference of the two freezing points gives the value of $\Delta T$, and the following formula is used to calculate the molar mass of solute.

$$
\mathrm{M} 2=\frac{\mathrm{Kf} \quad 1000 \mathrm{~W} 2}{\Delta \mathrm{TfW} 1}
$$

xiv. What is the oxidation numbers of the relevant elements on each side of the following equation, state which atom is oxidized and which is reduced? Show your working.
$2 \mathrm{FeCl}_{3}+\mathrm{SO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \longrightarrow 2 \mathrm{FeCl}_{2}+\mathrm{H}_{2} \mathrm{SO}_{4}+2 \mathrm{HCl}$
Ans. Fe is reduced while $\mathrm{SO}_{2}$ is oxidized.
$2 \mathrm{Fe}^{+3} \mathrm{Cl}_{3}{ }^{-1 \times 3}+\mathrm{S}^{+4} \mathrm{O}_{2}^{-2 \times 2}+2 \mathrm{H}_{2}{ }^{+1 \times 2} \mathrm{O}^{-2} \longrightarrow 2 \mathrm{Fe}^{+2} \mathrm{Cl}_{2}^{-1 \times 2}+\mathbf{H}_{2}^{+1 \times 2} \mathbf{S}^{+6} \mathrm{O}_{4}^{-2 \times 4}+\mathbf{2} \mathrm{H}^{+1} \mathrm{Cl}^{-1}$
xv. Standard enthalpy change of combustion of a substance is energy change when one mole of a substance is completely burnt in oxygen at standard conditions i.e $25^{\circ} \mathrm{C}$ and 1 atm pressure. Using following standard enthalpy changes of combustion of propanol $\Delta \mathrm{HCO}_{2}=-293 \mathrm{KJ} / \mathrm{mol} \quad \Delta \mathrm{H} \mathrm{H}_{2} \mathrm{O}=-286 \mathrm{KJ} / \mathrm{mol} \quad \Delta \mathrm{Hc} \mathrm{C}_{3} \mathrm{H}_{7} \mathrm{OH}=-1560 \mathrm{KJ} / \mathrm{mol}$ Calculate enthalpy change of formation of propanol.

Ans.
i. $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{OH}+9 / 2 \mathrm{O}_{2} \longrightarrow 3 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O} \quad \Delta \mathrm{H}_{1}=-1560 \mathrm{KJ} / \mathrm{mol}$
ii. $\mathrm{C}+\mathrm{O}_{2} \longrightarrow \mathrm{CO}_{2} \Delta \mathrm{H}_{2}=-393.5 \mathrm{KJ} / \mathrm{mol}$
iii. $\mathrm{H}_{2}+1 / 2 \mathrm{O}_{2} \longrightarrow \mathrm{H}_{2} \mathrm{O} \Delta \mathrm{H}_{3}=-286.7 \mathrm{KJ} / \mathrm{mol}$

Reverse eq i. xing eq ii. By 3 and eq iii. By 4 and then add.
$3 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{C}_{3} \mathrm{H}_{7} \mathrm{OH}+9 / 2 \mathrm{O}_{2} \Delta \mathrm{H}_{1}=+1560 \mathrm{KJ} / \mathrm{mol}$
$3 \mathrm{C}+3 \mathrm{O}_{2} \longrightarrow 3 \mathrm{CO}_{2} \Delta \mathrm{H}_{2}=-3 \times 393.5=1180.5$
$4 \mathrm{H}_{2}+2 \mathrm{O}_{2} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O} \Delta \mathrm{H}_{3}=-4 \times 286.7=1146.8 \mathrm{KJ}$.
$1 / 2 \mathrm{O}_{2}+3 \mathrm{C}+4 \mathrm{H}_{2} \mathrm{O} \longrightarrow \mathrm{C}_{3} \mathrm{H}_{7} \mathrm{OH}$
$\Delta \mathrm{H}=\Delta \mathrm{H}_{1}+\Delta \mathrm{H}_{2}+\Delta \mathrm{H}_{3}$
$=1560-1180.5-1146.8$
$\Delta \mathrm{H}=-767.3 \mathrm{KJ} / \mathrm{mol}$
xvi. The dissociation constant of an acid is a measure of its strength. Derive an expression for the dissociation constant of an acid " $\mathrm{CH}_{3} \mathrm{COOH}$ ".

Ans.
Suppose a weak acid $\mathrm{CH}_{3} \mathrm{COOH}$ is dissolved in water.
$\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{CH}_{3} \mathrm{COO}^{-1}+\mathrm{H}_{3} \mathrm{O}^{+1}$
$\mathrm{Kc} \equiv\left[\mathrm{H}_{2} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-1}\right]$
[ $\left.\mathrm{CH}_{3} \mathrm{COOH}\right]\left[\mathrm{H}_{2} \mathrm{O}\right]$
$\mathrm{Kc}\left[\mathrm{H}_{2} \mathrm{O}\right]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-1}\right]$
$\left[\mathrm{CH}_{3} \mathrm{COOH}\right]$
As water is a solvent its concentration will remain constant
$\mathrm{Kc}\left[\mathrm{H}_{2} \mathrm{O}\right]=\mathrm{Ka}$
So

$$
\mathrm{Ka}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-1}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}
$$

xvii. In the equilibrium
$\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}=90 \mathrm{KJ} / \mathrm{mol}$
predict the effect on the position of equilibrium if temperature is increased and pressure is decreased.

Ans. a. Reaction will move forward because reaction is endothermic. So decomposition of $\mathrm{PCl}_{5}$ is favourable at high temperature.
b. When pressure is decreased reaction will move forward because number of moles of product is greater than reactants.
xviii. Values of equilibrium constants can be calculated from measured values of concentrations or partial pressures. Write relationship between Kp and Kc in the following reactions?
(a) $\quad \mathrm{COCl}_{2(\mathrm{~g})} \quad \rightleftharpoons \mathrm{CO}_{(\mathrm{g})}+\mathrm{Cl}_{2}(\mathrm{~g})$
(b) $\quad \mathrm{N}_{2(\mathrm{~g})}+3 \mathrm{H}_{2(\mathrm{~g})} \rightleftharpoons 2 \mathrm{NH}_{3(\mathrm{~g})}$

Ans. $\mathrm{Kp}=\mathrm{Kc}[\mathrm{RT})^{\Delta \mathrm{n}}$
a. $\quad \Delta \mathrm{n}=2-1=1$
$\mathrm{Kp}=\mathrm{Kc}(\mathrm{RT})^{1}$
$\mathrm{Kp}=\mathrm{Kc} \mathrm{RT}$.
b. $\quad \Delta \mathrm{n}=2-4=-2$
$\mathrm{Kp}=\mathrm{Kc}(\mathrm{RT})^{-2}$
xix. A solution containing 0.13 M potassium acetate and 0.07 M acetic acid. Calculate the pH of buffer solution. The value of ionization constant for acid is $1.81 \times 10^{-5}$.

Ans. $\quad\left[\mathrm{CH}_{3} \mathrm{COOK}\right]=0.13 \mathrm{M}$

$$
\begin{aligned}
& \mathrm{Ka}=1.808 \times 10^{-15} \mathrm{Pka}=-\log \mathrm{Ka} \\
& =-\log 1.808 \times 10^{-5} \\
& =4.74
\end{aligned}
$$

$\mathrm{pH}=\mathrm{Pka}+\log \left[\mathrm{CH}_{3} \mathrm{COOK}\right]$
[ $\left.\mathrm{CH}_{3} \mathrm{COOH}\right]$

$$
\begin{aligned}
& =4.74+\log \frac{0.13}{0.07} \\
\mathrm{pH} & =5
\end{aligned}
$$

xx. Calculate the molarity of $4.6 \% \mathrm{w} / \mathrm{w}$ solution of NaOH .

Ans. $\quad 4.6 \% \mathrm{w} / \mathrm{v} \mathrm{NaOH}$ means.
4.6 g NaOH in $=100 \mathrm{~cm}^{3}$ of solution

Mole $=46 / 40$

Mole $=1.15 \mathrm{~mol}$
Molarity $=\underline{\text { No of mole of solute }}$
Volume of solution in $\mathrm{dm}^{3}$
Molarity $=1.15 / 1$
Molarity $=1.15 \mathrm{M}$

## SECTION - C(Marks 26)

Note: Attempt any TWO questions. All questions carry equal marks.
Q. 3 a. Derive energies expression for ${ }_{2}^{4} \mathrm{He}^{+1}$ according to Bohr's atomic model. (7)

Ans. The total energy E of an electron revolving around the nucleus is the sum of its kinetic and the potential energies.

$$
\begin{equation*}
\mathrm{E}_{\mathrm{T}}=\text { K.E. }+ \text { P.E. } \tag{i}
\end{equation*}
$$

The kinetic energy of moving electron of mass $m$ and velocity v is

$$
\begin{equation*}
\text { K.E. }=\frac{1}{2} m v^{2} . \tag{ii}
\end{equation*}
$$

The potential energy is given by the following equation

$$
\begin{equation*}
\text { P.E. }=-\frac{Z e^{2}}{4 \pi \epsilon_{0} r} \tag{iii}
\end{equation*}
$$

Taking the sum of equations (i) and (ii),

$$
\begin{align*}
& \mathrm{En}=\frac{1}{2} m \mathrm{v}^{2}+\left(-\frac{Z e^{2}}{4 \pi \epsilon_{0} r}\right) \\
& \mathrm{En}=\frac{1}{2} m \mathrm{v}^{2}-\frac{Z e^{2}}{4 \pi \epsilon_{0} r} \tag{iv}
\end{align*}
$$

We know that the electron can revolve only in those orbits, where the centripetal force $\frac{\mathrm{mv}^{2}}{r}$ and the coulombic forces are equal. So comparing the centripetal and columbic forces we get the following equation

$$
\begin{align*}
\frac{m v^{2}}{\mathrm{r}} & =\frac{Z e^{2}}{4 \pi \epsilon_{\mathrm{o}} r^{2}} \\
\text { or } \quad m v^{2} & =\frac{Z e^{2}}{4 \pi \epsilon_{\mathrm{o}} r}
\end{align*}
$$

Eliminate the factor of velocity v from equation (iv) by using equation (v).

$$
\begin{equation*}
\mathrm{E}=+\frac{Z e^{2}}{8 \pi \epsilon_{\mathrm{o}} r}-\frac{Z e^{2}}{4 \pi \epsilon_{\mathrm{o}} r} \tag{vi}
\end{equation*}
$$

By simplifying we get the following Equation (vii) which gives the expression for radius of orbit (r). Put value of $r$ from equation (vii) into equation (vi) we get equation (viii) which gives the energies of $n$ orbits.

$$
\begin{align*}
\mathrm{r} & =\frac{n^{2} h^{2} \epsilon_{0}}{\pi m z e^{2}}  \tag{vii}\\
\text { so } \quad \mathrm{E}_{\mathbf{n}} & =-\frac{Z^{2} e^{4} m}{8 \in_{\mathbf{0}}^{2} n^{2} h^{2}} \tag{viii}
\end{align*}
$$

The value of $Z$ (atomic number) of Helium is 2 . Put $Z=2$ in equation viii.
$\mathrm{E}_{\mathrm{n}}=-\frac{e^{4} m}{8 \epsilon_{\mathbf{0}}{ }^{2} h^{2}} \times\left(\frac{Z^{2}}{n^{2}}\right)$

$$
\begin{aligned}
& E_{n}=-\frac{e^{4} m}{8 \epsilon_{o}^{2} h^{2}} \times\left(\frac{2^{2}}{n^{2}}\right) \\
& E_{n}=-\frac{e^{4} m}{8 \epsilon_{o}^{2} h^{2}} \times\left(\frac{4}{n^{2}}\right)
\end{aligned}
$$



Equation ix gives the energy of the n orbitals of $\mathrm{He}^{+1}$
b. $\quad 40 \mathrm{dm}^{3} \mathrm{HCl}(\mathrm{g})$ at STP reacts with 50 g Zn which is placed in water to form $\mathrm{ZnCl}_{2}$ andH ${ }_{2}$. Calculate the mass of $\mathrm{H}_{2}$ produced and unreacted reactant left.

$$
\begin{align*}
& (\mathrm{Zn}=65, \mathrm{Cl}=35.5, \mathrm{H}=1)  \tag{3+3}\\
& \mathrm{Zn}+2 \mathrm{HCl} \longrightarrow \mathrm{ZnCl}_{2}+\mathrm{H}_{2}
\end{align*}
$$

Ans.
Mass of $\mathrm{H}_{2}$ Produced
Moles of $\mathrm{Zn}=50 / 65=0.769$
Moles of $\mathrm{HCl}=40 / 22.414=1.784$
Mole ratio:
$\mathrm{Zn} \quad: \quad \mathrm{H}_{2}$
1 : 1
0.769 : x
$\mathrm{X}=\mathbf{0 . 7 6 9}$
Mole Ratio:
$\mathrm{HCl}: \mathrm{H}_{2}$
2 : 1
1.784: x
$\mathrm{X}=1.784 \times 1 / 2=\mathbf{0 . 0 8 9 2}$
Since Zn produced less number of moles of $\mathrm{H}_{2}$ hence it is a limiting reactant and the moles of $\mathrm{H}_{2}$ produced will be $=0.769$
Mass of $\mathrm{H}_{2}=0.769 \times 2=1.538 \mathrm{gm}$
Mass of non limiting reactant left:
The number of moles of HCl required to react with 0.769 mol of Zn can be calculated by applying mol ratio between them according to the balance chemical equation.
Mol Ratio
$\mathrm{Zn}: \mathrm{HCl}$
1 : 2
0.769 : $\quad \mathrm{x}$
$\mathrm{X}=0.769 \times 2=1.538$
Moles of HCl left unreacted $=1.784-1.538=0.246$
Mass of HCl left unreacted $=0.246 \times 36.5=8.979 \mathrm{gm}$
Q. 4 a. Explain and draw stepwise Born Haber Cycle for measurement of $\Delta \mathrm{H}_{\text {latticefor }}$ potassium chloride ( KCl ) by using supposed values according to the steps. (5+3)

Ans. Lattice energy cannot be determined directly. However, it can be determined indirectly by means of Born Haber's cycle.
Suppose the enthalpy formation of $\mathrm{KCl}(\mathrm{s}) \Delta \mathrm{H}_{\mathrm{f}} \quad$ is -x $\mathrm{kJ} / \mathrm{mol}$. The formation reaction can be considered as taking place in several steps, one of which is the formation of lattice. This complete sequence of reaction is called a Born Haber cycle.
Step-I: Sublimation of solid potassium.
Let the energy of sublimation for $\mathrm{K}(\mathrm{s})$ is a kJ mole ${ }^{-1}$
$\mathrm{K}_{(\mathrm{s})} \longrightarrow \mathrm{K}_{(\mathrm{g})} \quad \Delta \mathrm{H}_{\mathrm{s}}=+\mathrm{akJ} /$ mole
Step-II: Ionization of $\mathrm{K}_{(\mathrm{g})}$ atom to form $\mathrm{K}^{+}{ }_{\mathrm{g})}$ ion. This process corresponds to the first ionization energy for K .
$\mathrm{K}_{(\mathrm{g})} \longrightarrow \mathrm{K}^{+}{ }_{(\mathrm{g})}+\mathrm{e}^{-} \quad \Delta \mathrm{H}=+\mathrm{bkJ} /$ mole
Step-III: Dissociation of $\mathrm{Cl}_{2}$ molecules. We need to form one mole of Cl atoms by breaking the $\mathrm{Cl}-\mathrm{Cl}$ bond in 1 mole of $\mathrm{Cl}_{2}$ molecules. The energy required to break this bond is known as enthalpy of atomization for $\mathrm{Cl}_{2}$.
$1 / 2 \mathrm{Cl}_{2(\mathrm{~g})} \longrightarrow$
$\mathrm{Cl}_{(\mathrm{g})}$
$\Delta \mathrm{H}=+\mathrm{ckJ} / \mathrm{mole}$

All these three steps are endothermic.
Step-IV: Formation of $\mathrm{Cl}_{(\mathrm{g})}$ ion. Energy is released in this step equal to the electron affinity for Cl .


Step-V: Formation of solid KCl from the gaseous $\mathrm{K}^{+}(\mathrm{g})$ and $\mathrm{Cl}^{-}(\mathrm{g})$ ions. This corresponds to the lattice energy $(\Delta \mathrm{H} l)$ for $\mathrm{KCl}(\mathrm{s})$ which is to be calculated.
$\mathrm{K}^{+}{ }_{(\mathrm{g})}+\mathrm{Cl}_{(\mathrm{g})} \longrightarrow \mathrm{KCl}_{(\mathrm{s})} \Delta \mathrm{H}_{l}=$ ?

## Born Haber cycle



$$
\begin{aligned}
& \Delta \mathrm{H}_{\mathrm{f}}=\Delta \mathrm{H}_{\mathrm{s}}+\Delta \mathrm{H}_{\mathrm{II} .}+\Delta \mathrm{H}_{\mathrm{at}}+\Delta \mathrm{H}_{\mathrm{E} . \mathrm{A}}+\Delta \mathrm{H}_{\text {lattice }} \\
& \Delta \mathrm{H}_{\text {lattice }}=\Delta \mathrm{H}_{\mathrm{f}}-\Delta \mathrm{H}_{\mathrm{s}}+\Delta \mathrm{H}_{\mathrm{IIE}}+\Delta \mathrm{H}_{\mathrm{at}}+\Delta \mathrm{H}_{\mathrm{E} . \mathrm{X}} \mathrm{\lambda}
\end{aligned}
$$

b. Explain the potential energy diagram for the given reaction and propose reaction mechanism
(3+2)

$$
\begin{aligned}
& 2 \mathrm{H}_{2}+2 \mathrm{NO} \longrightarrow 2 \mathrm{H}_{2} \mathrm{O}+\mathrm{N}_{2} \\
& \text { Rate }=\mathrm{K}\left[\mathrm{H}_{2}\right][\mathrm{NO}]^{2}
\end{aligned}
$$



Ans. The given potential energy diagram shows two peaks. Thus the reaction mechanism must involve two elementary steps.
The activation energy for step 1 is higher than step 2 . Which suggests that step 1 will be slow and rate determining step.
The rate law suggests that two molecules of NO and one molecule of $\mathrm{H}_{2}$ are involved in the slow or rate determining step.
The proposed mechanism of the reaction could be.

| $2 \mathrm{NO}+\mathrm{H}_{2} \longrightarrow$ | $\mathrm{H}_{2} \mathrm{O}+\mathrm{N}_{2}+[\mathrm{O}]$ | (slow) |
| :--- | :--- | :--- |
| $\mathrm{H}_{2}+[\mathrm{O}]$ | $\mathrm{H}_{2} \mathrm{O}$ | (fast) |
| $2 \mathrm{NO}+2 \mathrm{H}_{2} \longrightarrow$ | $2 \mathrm{H}_{2} \mathrm{O}+\mathrm{N}_{2}$ | (Overall reaction) |

Q. 5 a. Define the following terms witha suitable example:
i. Isomorphism
ii. Polymorphism
iii. Anisotropy

Ans.

## Isomorphism

Different crystalline substances having the same crystalline shapes are called Isomorphs, and this phenomenon is called isomorphism. This is due to the same ratio of atoms in different crystalline substances.
For example
$\mathrm{ZnSO}_{4}$ and $\mathrm{NiSO}_{4}$ are isomorphism because both have the same crystalline shape, i.e. orthorhombic.

## Polymorphism

The substance existing in more than one crystalline form is called polymorphous substance and the phenomena as polymorphism.
For example NaCl is found in cubic and octahedral forms.

## Anisotropy

A crystalline substance shows different intensity of properties in different directions this phenomenon is called anisotropic. It is because crystal has different arrangements in different directions. For example Refractive index, co-efficient of thermal expansion, electrical and thermal conductivities give different intensity of properties indifferent directions.
b. Summarize and illustrate the elevation of boiling point using graph.

Ans.

## Boiling Point:

A liquid boils at a temperature where its vapour pressure becomes equal to the atmospheric pressure. This temperature is called boiling point of that liquid.

## Elevation of boiling point:

When a non-volatile and non-electrolyte solute is added to a solvent, its vapour pressure is decreased due to the decrease of the number of solvent surface particles. This decreases the rate of evaporation of solvent, which in turns decreases the vapour pressure. Therefore, a solution must be heated to a higher temperature than the boiling point of pure solvent to equalize its vapour pressure to the external pressure. Thus addition of solute to a pure solvent causes an elevation of the boiling point of solution.
The difference between the boiling point of solution and that of pure solvent is called
 Elevation of Boiling Point.

