## Case Study - 4

## Specific Heat Capacity of Solids -

We can use the law of equipartition of energy to determine specific heats of solids. Consider a solid of N atoms, each vibrating about its mean position. An oscillation in one dimension has average energy of $2 \times 1 / 2 \mathrm{kBT}=\mathrm{k}_{\mathrm{B}} \mathrm{T}$. In three dimensions, the average energy is $3 \mathrm{k}_{\mathrm{B}} \mathrm{T}$. For a mole of solid, $\mathrm{N}=\mathrm{N}_{\mathrm{A}}$, and the total energy is U $=3 \mathrm{k}_{\mathrm{B}} \mathrm{T} \times \mathrm{N}_{\mathrm{A}}=3 \mathrm{RT}$
Now at constant pressure $\Delta \mathrm{Q}=\Delta \mathrm{U}+\mathrm{P} \Delta \mathrm{V}=\Delta \mathrm{U}$, since for a solid $\Delta \mathrm{V}$ is negligible. Hence,
$\mathrm{C}=\Delta \mathrm{U} / \Delta \mathrm{T}=3 \mathrm{R}$.

## Specific Heat Capacity of Water

We treat water like a solid. For each atom average energy is 3 Kb T. Water molecule has three atoms, two hydrogen and one oxygen. So it has $U=3 \times 3 k_{B} T$ $\times$ NA $=9$ RT and

$$
\mathbf{C}=\Delta \mathbf{Q} / \Delta \mathbf{T}=\Delta \mathbf{U} / \Delta \mathbf{T}=9 \mathbf{R}
$$

This is the value observed and the agreement is very good. In the calorie, gram, degree units, Water is defined to have unit specific heat. As 1 calorie $=4.179$ joules and one mole of water are 18 grams, the heat capacity per mole is $\sim 75 \mathrm{~J}$ mol-1 K-1 $\sim 9 \mathrm{R}$. However with more complex molecules like alcohol or acetone the arguments, based on degrees of freedom, become more complicated.

## 1. For solids ratio of specific heats $\gamma$ is

a. 3 R
b. 5 R
c. $9 R$
d. None of these
2. For water ratio of specific heats $\gamma$ is
a. 5 R
b. $9 R$
c. 3 R
d. None of these

## 3. For water total energy is

a. 3RT
b. 5RT
c. 9RT
d. None of these
4. What is specific heat capacity of solids?
5. What is specific heat capacity for water?

## Answer key-4

1. A
2. B
3. A
4. Specific Heat Capacity of Solids

We can use the law of equipartition of energy to determine specific heats of solids. Consider a solid of N atoms, each vibrating about its mean position. An oscillation in one dimension has average energy of $2 \times 1 / 2 \mathrm{kBT}=\mathrm{k}_{\mathrm{B}} \mathrm{T}$. In three dimensions, the average energy is $3 \mathrm{k}_{\mathrm{B}} \mathrm{T}$. For a mole of solid, $\mathrm{N}=\mathrm{N}_{\mathrm{A}}$, and the total energy is $U=3 \mathrm{k}_{\mathrm{B}} \mathrm{T} \times \mathrm{N}_{\mathrm{A}}=3 \mathrm{RT}$
Now at constant pressure $\Delta \mathrm{Q}=\Delta \mathrm{U}+\mathrm{P} \Delta \mathrm{V}=\Delta \mathrm{U}$, since for a solid $\Delta \mathrm{V}$ is negligible. Hence, $\mathrm{C}=\Delta \mathrm{U} / \Delta \mathrm{T}=3 \mathrm{R}$.

## 5. Specific Heat Capacity of Water

We treat water like a solid. For each atom average energy is 3 Kb T. Water molecule has three atoms, two hydrogen and one oxygen. So it has $U=3 \times$ $3 \mathrm{k}_{\mathrm{B}} \mathrm{T} \times \mathrm{NA}=9 \mathrm{RT}$ and $\mathrm{C}=\Delta \mathrm{Q} / \Delta \mathrm{T}=\Delta \mathrm{U} / \Delta \mathrm{T}=9 \mathrm{R}$.

## Case Study - 5

Molar specific heat at constant pressure is defined as amount of heat required to raise the temperature of 1 mol of a gas through 1 Kelvin at constant pressure. It is denoted by $\mathrm{C}_{\mathrm{P}}$.
Molar specific heat at constant volume is defined as amount of heat required to raise the temperature of 1 mol of a gas through 1 Kelvin at constant volume. It is denoted by $\mathrm{C}_{\mathrm{v}}$.
Monatomic Gases: The molecule of a monatomic gas has only three translational degrees of freedom. Thus, the average energy of a molecule at temperature T is $(3 / 2) \mathrm{kBT}$. The total internal energy of a mole of such a gas is $\mathrm{U}=(3 / 2)$ RT.
The molar specific heat at constant volume $\mathrm{c}_{\mathrm{v}}$ is given by
$\mathrm{C}_{\mathrm{v}}=\mathrm{dU} / \mathrm{dT}=(3 / 2) \mathrm{R}$
For an ideal gas,
$\mathrm{C}_{\mathrm{p}}-\mathrm{C}_{\mathrm{v}}=\mathrm{R}$
Where $C_{p}$ is the molar specific heat at constant pressure. Thus, $C_{P}=(5 / 2) R$ The ratio of specific heats IS $\gamma=c_{p} / c_{v}=5 / 3$.
Diatomic Gases: a diatomic molecule treated as a rigid rotator, like a dumbbell, has 5 degrees of freedom: 3 translational and 2 rotational. Using the law of equipartition of energy, the total internal energy of a mole of such a gas is $U=$ (5/2) RT.
The molar specific heat at constant volume $c_{v}$ is given by
$\mathrm{C}_{\mathrm{v}}=\mathrm{dU} / \mathrm{dT}=(5 / 2) \mathrm{R}$
For an ideal gas,
$\mathrm{C}_{\mathrm{p}}-\mathrm{C}_{\mathrm{v}}=\mathrm{R}$
Where $C_{p}$ is the molar specific heat at constant pressure. Thus, $C_{P}=(7 / 2) R$ The ratio of specific heats IS $\gamma($ for rigid diatomic $)=c_{p} / c_{v}=7 / 5$.
For non rigid diatomic molecules they have additional mode of vibrations therefore $\gamma=c_{\mathrm{p}} / \mathrm{c}_{\mathrm{v}}=9 / 7$.
Polyatomic Gases: In general a polyatomic molecule has 3 translational, 3 rotational degrees of freedom and a certain number ( f ) of vibrational modes. According to the law of equipartition of energy, it is easily seen that one mole of such a gas has
$\mathrm{C}_{\mathrm{v}}=(3+\mathrm{f}) \mathrm{R}$ and $\mathrm{C}_{\mathrm{p}}=(4+\mathrm{f}) \mathrm{R}$ and $\gamma=(4+\mathrm{f}) /(3+\mathrm{f})$.
In kinetic theory of gases there are several molecules in gas randomly moving and colliding with each other .the average distance between the two successive collisions is called mean free path.

The mean free path 1 is the average distance covered by a molecule between two successive
collisions :
$\mathrm{L}=\frac{1}{\sqrt{2} n \pi d 2}$
Where n is the number density and d the diameter of the molecule.

1. For monatomic molecules The molar specific heat at constant volume $c_{v}$ is given by
a. $(3 / 2) \mathrm{R}$
b. $(5 / 2) \mathrm{R}$
c. $(7 / 5) R$
d. None of these
2. For monatomic molecules The molar specific heat at constant pressure $c_{p}$ is given by
a. $(3 / 2) \mathrm{R}$
b. $(5 / 2) R$
c. $(7 / 5) \mathrm{R}$
d. None of these
3. Define Molar specific heat at constant pressure

## 4. Molar specific heat at constant volume.

## 5. Define mean free path and give its formula.

## Answer key-5

1. A
2. B
3. Molar specific heat at constant pressure is defined as amount of heat required to raise the temperature of 1 mol of a gas through 1 Kelvin at constant pressure. It is denoted by $\mathrm{C}_{\mathrm{P}}$.
4. Molar specific heat at constant volume is defined as amount of heat required to raise the temperature of 1 mol of a gas through 1 Kelvin at constant volume. It is denoted by $\mathrm{C}_{\mathrm{v}}$.
5. In kinetic theory of gases there are several molecules in gas randomly moving and colliding with each other .the average distance between the two successive collisions is called mean free path. The mean free path 1 is the average distance covered by a molecule between two successive collisions :
$\mathrm{L}=\frac{1}{\sqrt{2} n \pi d 2}$
Where n is the number density and d the diameter of the molecule.
