1. Details of Module and its structure

Module Detail	
Subject Name	Physics
Course Name	Physics 02(Physics Part 2,Class XI)
Module Name/Title	Unit 9, Module 4, Degrees of Freedom Chapter 13, Kinetic theory of gases
Module Id	keph_201304_econtent
Pre-requisites	Assumptions of kinetic theory of gases, Kinetic interpretation of temperature, Average kinetic energy of a gas, Internal energy and laws of thermodynamics
Objectives	After going through this module, the learners will be able to; • Understand the meaning of degrees of freedom for monoatomic, diatomic, triatomic and polyatomic gases. • Interpret kinetic energy per degree of freedom, Law of equipartition of energy • Know about ratio of molar specific heats for monoatomic, diatomic and triatomic gases.
Keywords	Atomicity, Degrees of freedom, molar specific heat, law of equipartition of energy

2. Development Team

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1. UNIT SYLLABUS

Unit 9: Behaviour of perfect gases and kinetic theory

Chapter13: Behaviour of Perfect Gases and Kinetic Theory of Gases:

Equation of state of a perfect gas, work done in compressing a gas. Kinetic theory of gases - assumptions, concept of pressure. Kinetic interpretation of temperature; rms speed of gas molecules; degrees of freedom, law of equi-partition of energy (statement only) and application to specific heat capacities of gases; concept of mean free path, Avogadro's number.

2. MODULE-WISE DISTRIBUTION OF UNIT SYLLABUS 4 Modules

Module 1	• Microscopic and macroscopic view of interaction of heat with matter • Kinetic theory • Equation of state for a perfect gas • PV= nRT • Statement of gas laws – Boyles law, Charles' law, pressure law, Dalton law of partial pressure
Module 2	• Kinetic theory of gases • Assumptions made regarding molecules in a gas • Concepts of pressure • Derivation for pressure exerted by a gas using the kinetic theory model
Module 3	• Kinetic energy of gas molecules • rms speed of gas molecules • Kinetic interpretation of temperature • Derive gas laws from kinetic theory
Module 4	

	• **Degrees of freedom** • **Law of equipartition of energy** • **Specific heat capacities of gases depends upon the atomicity of its molecules** • **monoatomic molecule** • **diatomic molecules** • **polyatomic molecules**

MODULE 4

3. WORDS YOU MUST KNOW

States of matter: the three states solid, liquid and gas in which matter can exist depending upon external conditions of temperature and pressure.

Interatomic / intermolecular forces a force exists between atoms and molecules of matter. The origin of force is electrostatic; it depends upon nature of material, State in which the material is in, external conditions of temperature and pressure.

Kinetic Theory: a theory that the particles of a gas move in straight lines with high average velocity, continually encounter one another and thus change their individual velocities and directions, and cause pressure by their impact against the walls of a container called also kinetic theory of gases.

Microscopic variables: Microscopic variables deal with the state of each molecule in terms of the mass, position, velocity etc. of each molecule.

Macroscopic variables: Macroscopic variables are the physical quantities which describe the state of a system as a whole e.g. Pressure, Volume, Temperature etc. They can be easily measured with laboratory instruments.

Average speed is the arithmetic mean of the speeds of all the molecules of the gas.

Root mean square speed (rms value) is the square root of the mean of the squares of the velocity of the molecules of the gas.

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

This rms value of speed depends only on the temperature and the mass of the molecules..

The Boyle's law, Charles law and Avogadro's law can be obtained from the kinetic theory and the macroscopic variables of Pressure, Volume, and temperature can be related to the microscopic variables like the root mean square velocity and mass of individual molecules of the gas.

The speed of sound in gas is comparable to the root mean square speed of molecules but it is always less than the rms value of molecules of the gas.

4. INTRODUCTION

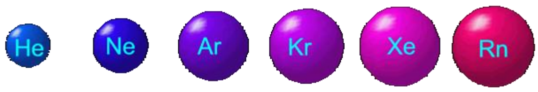
Gas molecules continuously move randomly in all possible directions. Predicting the direction of motion of a molecule is an impossible task. But a statistical analysis can tell the number of possible ways in which a molecule can move.

So, in the following module, we will analyse the motion of a gas molecule and the energy associated with the motion of the molecules.

5. ATOMICITY OF MOLECULES

The number of atoms in the molecule is called the atomicity of the molecule.

Monoatomic gases: Molecules of these gases have only one atom and are called monoatomic having an atomicity equal to one. All the noble gases are monoatomic. Due to their stable electronic configuration, they do not react with the other atoms. The atoms of the molecules are considered as point particles. The chemical symbols of the noble gases as shown here:



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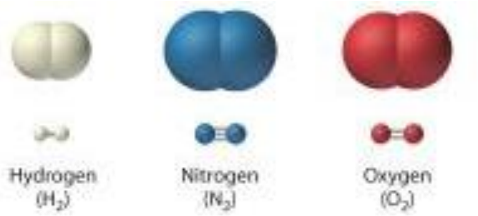
Diatomic gases: Molecules of these gases have two atoms and are called diatomic having atomicity equal to two. Most of the gases which are a part of the earth's atmosphere are diatomic.



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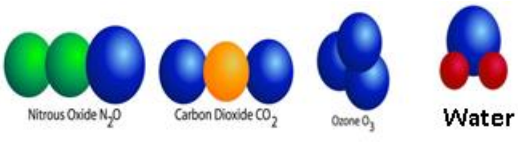
Triatomic gases: Molecules of these gases have three atoms and are called triatomic having atomicity equal to three. Some common example of triatomic gases is carbon dioxide, water vapour, nitrous oxide, ozone etc.



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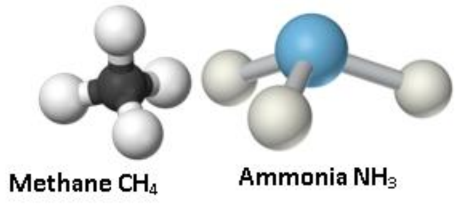
Polyatomic gases: Molecules of these gases may have two or more number of atoms. If there are n atoms in the molecule, the atomicity of the gas is n. Some common examples are methane, chlorofluorocarbons, ammonia etc.



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6. DEGREES OF FREEDOM

The number of independent ways in which a system can move is called the degree of freedom of the system. In case of kinetic theory of gases, we are interested in the motion of the molecules of the gas and the energy associated with this motion of the molecules. So, degree of freedom for molecules of gases is the

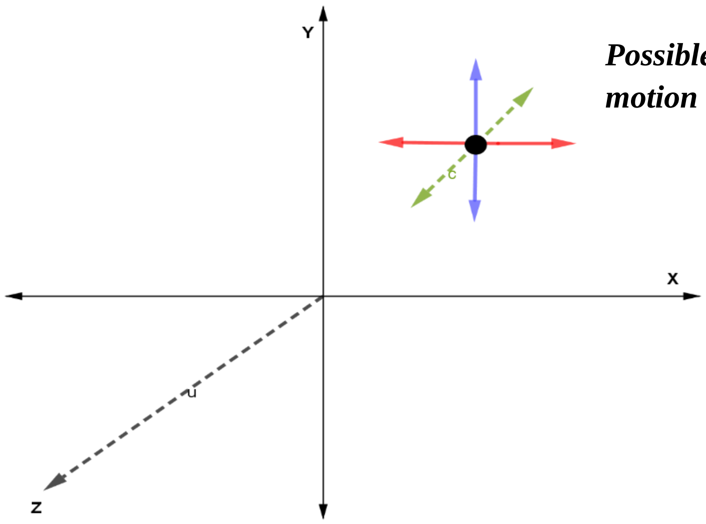
"The number of independent ways in which a molecule of gas can move"

The motion of a molecule can mainly be categorized as translational motion, rotational motion and vibrational motion. The number of degrees of freedom also defines the complete state of the molecule and the gas as a whole. Some movements of the molecules are restricted and are called constraints. These constraints mainly depend upon the type of the molecule. The type of molecule is decided by the number of atoms in the molecule and the arrangement of atoms in the molecule.

a) DEGREES OF FREEDOM DUE TO TRANSLATIONAL MOTION:

When the centre of mass of a particle moves from its initial position to a new position, we say that the particle is having a translational motion. This translation can be anywhere in the three dimensional space around it. But every such displacement from its earlier position to a new position can be resolved into components along the x-axis, y-axis and z-axis.

So, the translational motion of the molecule of a gas has three degrees of freedom associated with it. This is irrespective of the atomicity of the molecule. This means that whether it is a monoatomic, diatomic, triatomic or polyatomic molecule; it will have three translational degrees of freedom. These three degrees of freedom are due to the motion of the centre of mass of that molecule along x axis, along y axis and along the z-axis.



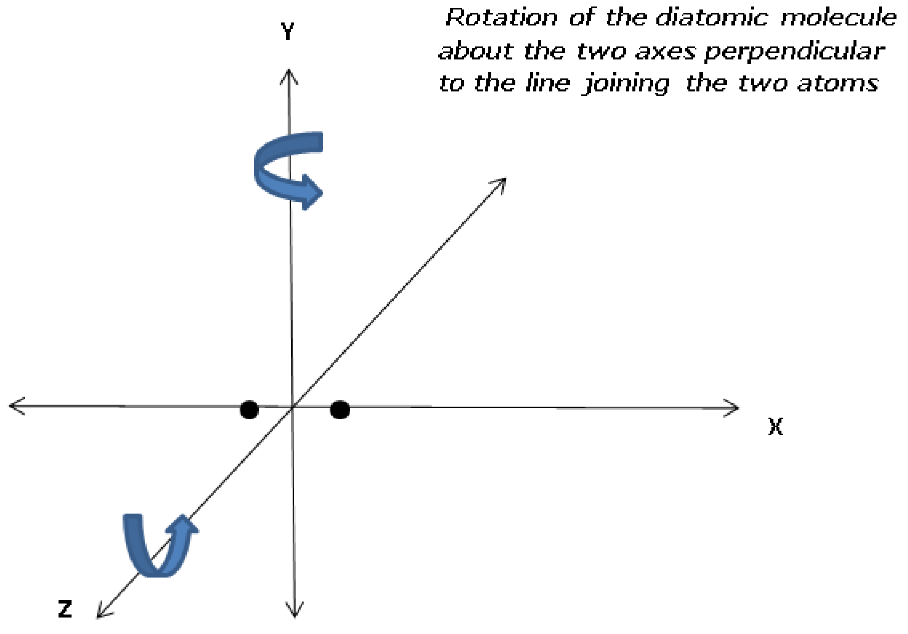
Possible translational motion of a molecule along

b) DEGREES OF FREEDOM ASSOCIATED WITH THE ROTATIONAL MOTION:

In addition to translational motion, a molecule can rotate about any axis passing through itself. So, there are maximum three degrees of freedom corresponding to the rotational motion of the molecule about three mutually perpendicular axes passing through it. The actual number of degrees of freedom associated with rotation depends upon the constraints on the molecule which does not allow some rotations along some axes. These constraints depend on the type of the molecule.

Monoatomic gases: The molecules of these gases have only one atom. This atom is so small that it can be considered to be a point particle with negligible dimensions. So for any axis passing through the atom, there can be no rotation about the axis as the atom lies on the axis itself. Hence the monoatomic gas molecules will not have any rotational degrees of freedom.

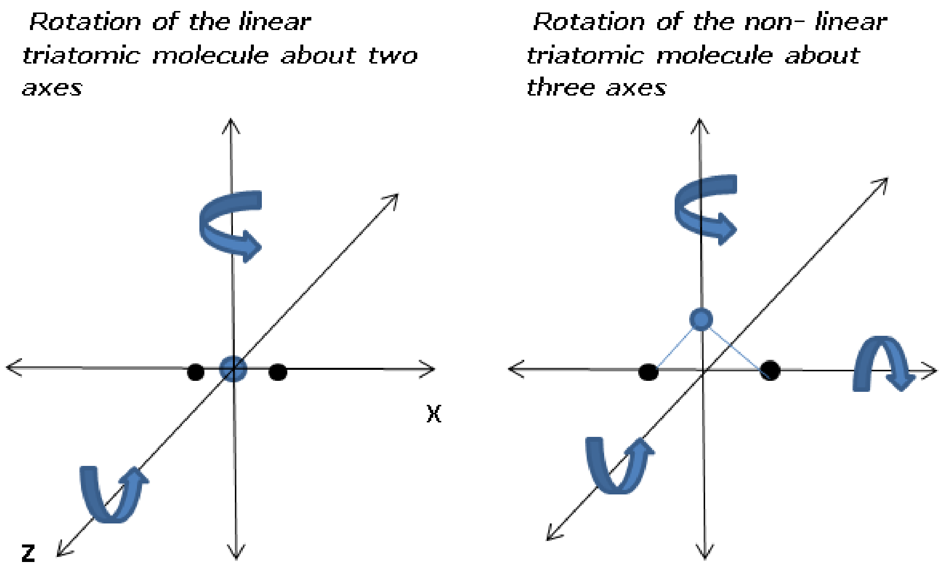
Diatomic gases: The molecules of these gases have two atoms. The separation between the atoms is nearly fixed and it is called the bond length. If the line joining the two atoms is taken along the x-axis then there can be no rotation about the x-axis as both the atoms lie on the x-axis. This is the constraint on the rotation of the molecule. But the molecule can rotate about the y and z axes passing through the line joining the two atoms. Hence diatomic molecules have two degrees of freedom associated with the rotational motion of the molecules about the above mutually perpendicular axes.



Triatomic gases: The molecules of these gases have three atoms. If these three atoms are along a line, it is a linear molecule. But if the three atoms are along the vertex of a triangle it is a non-linear molecule.

If we again consider the line joining the three atoms of the linear molecule to be along the x axis, then there cannot be any rotation about the x axis. Rotation is possible only about the y and z axes passing perpendicular to the line joining the atoms. So like a diatomic molecule, the triatomic linear molecule will only have two degrees of freedom associated with the rotational motion of the molecule.

In a non-linear triatomic molecule, rotation about all the three axes is allowed. Hence there will be all three degrees of freedom associated with the rotation of the molecules.



Polyatomic molecules: The polyatomic molecule can have N (where N$\geq$ 2) number of atoms which may be linear or non-linear. We can extend the above analysis to a more general case to understand that there will be two rotational degrees of freedom for a linear polyatomic molecule and three rotational degrees of freedom for a non-linear polyatomic molecule.

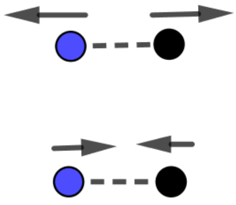
c) Degrees of freedom due to vibrational motion:

The atoms of a molecule can also vibrate and these vibrations of the atoms of a molecule slightly changes the inter-nuclear distances between the atoms of the molecule. These vibrations of the atoms of a molecule are complex and periodic. But they can be resolved into various vibrational modes each representing a simple harmonic motion of a particular frequency. They are also called normal modes of vibration.

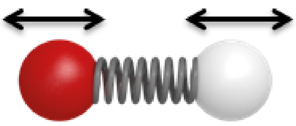
For non-linear molecules having N number of atoms, there are 3N – 6 vibrational modes and for linear molecules, there are 3N – 5 vibrational modes.

Monoatomic molecules: As there is only one atom in the molecule there are no vibrational modes.

Diatomic molecules: In these molecules, the vibration of the atoms occurs along the line joining the two atoms. This vibration can slightly increase or decrease the distance between the molecules. This vibration contributes towards one degree of freedom. At room temperature the amplitude of these vibrations is so small that it can be neglected. The **vibrational mode becomes significant only at high temperatures**.



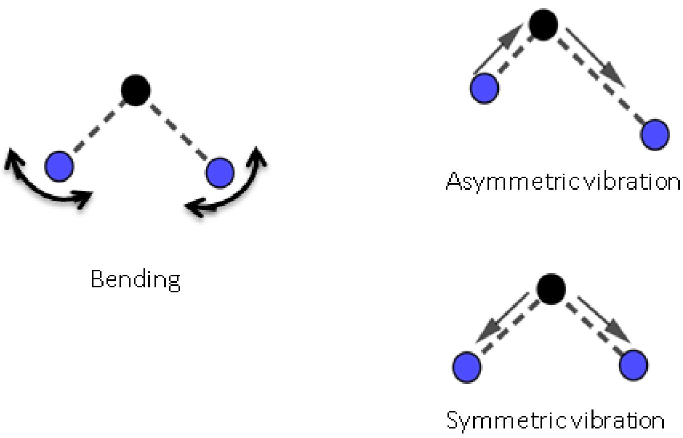
The periodic motion of the atoms can also be visualised from this physical model. The force between the atoms is compared with a spring and the periodic motion of the atoms causes this spring to expand and compress with a certain frequency.

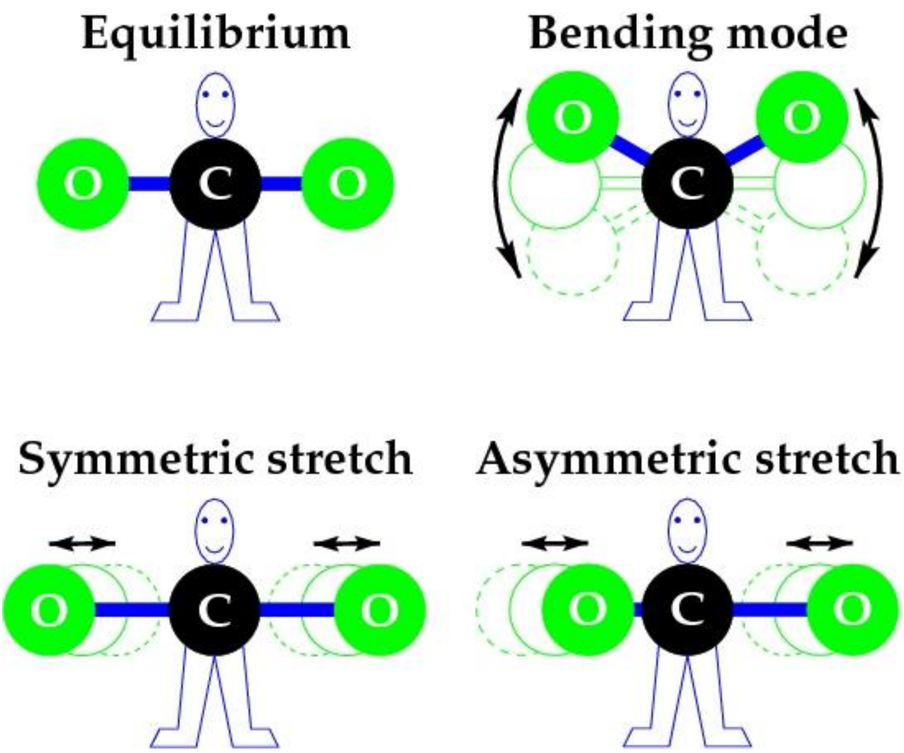


Triatomic molecule: Here the vibration of the atoms can be mainly resolved into asymmetric vibration, symmetric vibration and bending. All these vibrational modes are associated with a particular frequency. The number of vibrational modes is given by 3N-6 where N is the number of atoms in the molecule. For triatomic molecules, it comes out to be 3 vibrational modes for the non-linear molecules.

For the linear molecules, there are 3N-5 vibrational modes and is equal to 4 vibrational modes for linear triatomic molecules. But again these vibrations become significant at high temperatures. At room temperatures, we can neglect the vibration of the atoms of the molecule.

Vibrational modes of a non-linear triatomic molecule





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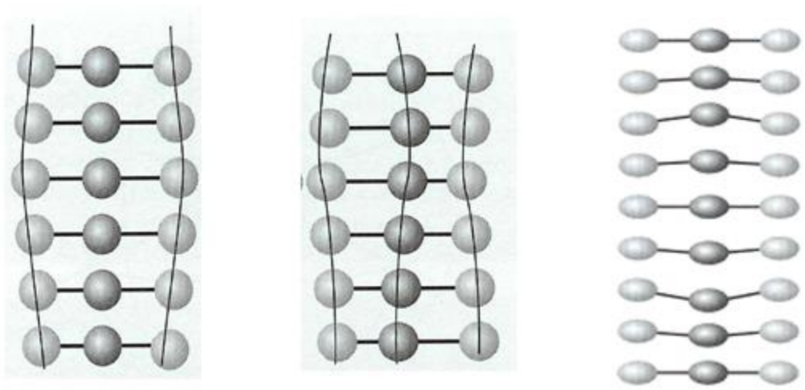
Polyatomic molecules: Even the vibration of a non-linear polyatomic molecule involves asymmetric and symmetric vibrational modes and also the bending of molecules. The number of vibrational modes is again given by 3N-6, where N is the number of atoms.



Symmetric and Anti symmetric vibrational *Bending*

Summary of the degrees of freedom

Type of molecule	Degrees of freedom associated with			Total Degrees of freedom
	Translational motion	Rotational motion	Vibrational motion	
Monoatomic	**3**	**0**	**0**	**3**
Diatomic	**3**	**2**	**1**	**6**
Triatomic (linear)	**3**	**2**	**4**	**9**
Triatomic (non-linear)	**3**	**3**	**3**	**9**
Polyatomic (linear)	**3**	**2**	**3N-5**	**3N**
Polyatomic (Non-linear)	**3**	**3**	**3N-6**	**3N**

Points to be noted:

- **All types of molecules have three translational degrees of freedom.**
- **The rotational degree of freedom is less for linear molecules as compared to non-linear molecules.**
- **At room temperatures, the degrees of freedom need not include the vibrational modes. For molecules to vibrate in their normal modes they require much higher energies which is not possible at the room temperature.**
- **Vibrational modes become appreciable at high temperatures and are used in Raman spectroscopy and nuclear magnetic spectroscopy.**

7. LAW OF EQUIPARTITION OF ENERGY

According to this law**:**

For a system in equilibrium, there is an average energy of ½ kT per molecule associated with each degree of freedom.

(Where k is the Boltzmann constant and T is the temperature of the system)

This energy associated with each degree of freedom is in the form of kinetic energy and potential energy.

- **Energy in Translational degrees of freedom**:

There are three translational degrees of freedom for every molecule which correspond to its translational movement along the x-axis, y- axis and z- axis.

So, every molecule has a total translational kinetic energy

$$= \frac{1}{2} mv_x^2 + \frac{1}{2} mv_y^2 + \frac{1}{2} mv_z^2$$

where v_x, v_y and v_z are the x-component, y-component and z-component of the velocity of the molecule and m is the mass of the molecule.

So, according to equipartition of energy, the total translational energy per molecule

$$= 3 \times \frac{1}{2} kT = \frac{3}{2} kT$$

Monoatomic gases have only three translational degrees of freedom, so the total energy per molecule of a monoatomic gas = 3/2 kT

Total energy per mole of a monoatomic gas = $\frac{3}{2}$ **kT** x N= $\frac{3}{2}$ **RT**

- **Energy in Rotational degrees of freedom**:

There are three possible rotational degree of freedom corresponding to the rotation of the molecule about three mutually perpendicular axis.

The total rotational energy associated with the these rotations is given by

$$\frac{1}{2} I_1 \omega_1^2 + \frac{1}{2} I_2 \omega_2^2 + \frac{1}{2} I_3 \omega_3^2$$

where I_1 , I_2 , I_3 are the moment of inertia of the molecule respectively about the three mutually perpendicular axis and ω_1 , ω_2 , ω_3 are the angular velocity of the molecule about the three axes.

Every linear molecule has only two rotational degrees of freedom. This is because there is no rotation possible along the axis joining the atoms of the molecules as they are almost point particles.

The molecule can rotate only about two mutually perpendicular axis which is also perpendicular to the line joining the atoms.

So, according to equipartition of energy:

the total rotational energy of a linear molecule = 2 x ½ kT = kT

A non-linear molecule can have all three rotational degrees of freedom

So the total rotational energy of a non-linear molecule = 3 x ½ kT = $\frac{3}{2}$ **kT**

- **Energy in vibrational degrees of freedom**:

Atoms of a molecule can move with respect to one another, leading to vibrational degrees of freedom.

Each vibration is associated with both kinetic and potential energy, Hence, the energy associated with each vibrational mode

$$= \frac{1}{2} mv^2 + \frac{1}{2} kx^2$$

This corresponds to the energy of two degrees of freedom per vibrational mode

$$= 2 \times \frac{1}{2} kT = kT$$

At the room temperature, most of the molecules are in their ground vibrational state. So, the vibrational modes which are active at high temperatures contribute very little to the total energy of the molecule. Hence at room temperature, we neglect the vibrational degrees of freedom and the corresponding energy associated with it in the total energy of a molecule.

Neglecting the vibrational energy, we get the average total kinetic energy per molecule at room temperature as follows.

Molecule	Example	Degrees of freedom			Average kinetic energy per molecule
		Translational	Rotational	Total	
Monoatomic	**He, Ne, Ar**	**3**	**0**	**3**	$\frac{3}{2}$**kT**
Diatomic	O_2, N_2	**3**	**2**	**5**	$\frac{5}{2}$**kT**
Triatomic (linear)	CO_2, **HCN**	**3**	**2**	**5**	$\frac{5}{2}$**kT**
Triatomic (Non-linear)	H_2O	**3**	**3**	**6**	**3kT**

Internal energy of a gas:

Internal energy of a gas is the sum of the kinetic and potential energy of the molecules. But in kinetic theory of gases, we assume that there is no force of attraction or repulsion between the molecules of the gas. In the absence of mutual forces between the molecules, the potential energy of the gas is zero. So, the total internal energy of the ideal gas only consists of its kinetic energy**.** It depends on the number of degrees of freedom of the molecules**.**

If the number of degrees of freedom is f,

Internal energy (U) for one mole of a gas $= \frac{f}{2} RT$

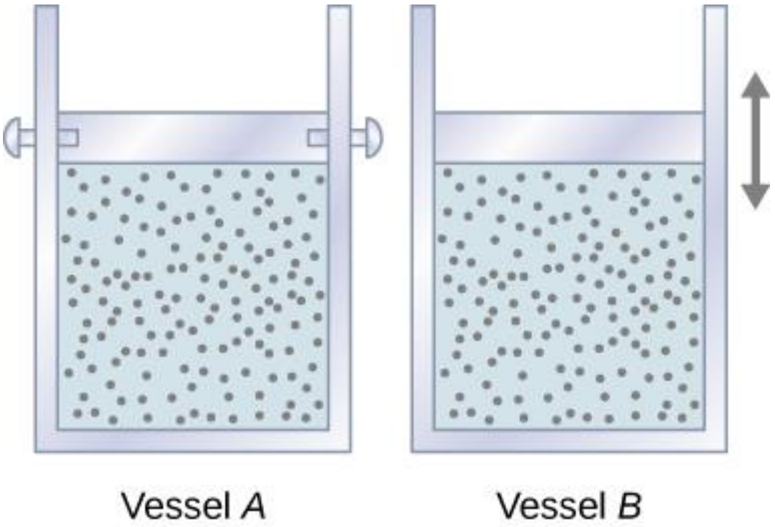
So, the internal energy of a gas increases with the increase in temperature. At very high temperatures, the vibrational degrees of freedom also become active which further increases the internal energy.

Internal energy of the gas can increase, if heat is given to the gas or work is done on the gas.

8. MOLAR SPECIFIC HEATS OF GASES

If heat is given to a vessel containing gas, the heat will cause an increase in the internal energy of the gas. If the lid of the vessel is movable, then some of the heat will be used in the expansion of the gas. If the lid is fixed, then all the heat given to the gas will only increase the internal energy of the gas.

Vessel A and Vessel B contain one mole of an ideal gas. The lid of vessel A is fixed while the lid of vessel B is moveable.



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If the heat given to vessel A is ΔQ, by the first law of thermodynamics, all the heat given only increases the internal energy (the work done is zero as the lid is fixed) and

We have,

$$\mathbf{\Delta Q = \Delta U}$$

If the temperature of the gas rises by ΔT, then

$$\Delta Q = C_v \, \Delta T$$

Here, C_v is the heat required to raise the temperature of one mole of a gas by one degree Celsius at constant volume. It is called the molar specific heat of the gas at constant volume.

$$\Delta Q = C_v \, \Delta T = \Delta U$$

If the heat given to vessel B is ΔQ′, by the first law of thermodynamics the heat given increases the internal energy (ΔU) and some work is also done (ΔW) as the gas expands (as the lid is movable) and we have

$$\mathbf{\Delta Q' = \Delta U + \Delta W}$$

If the temperature of the gas rises by ΔT, then

$$\mathbf{\Delta Q' = C_p \, \Delta T}$$

Here C_p is the heat required to raise the temperature of one mole of a gas by one degree Celsius at constant volume. It is called the molar specific heat of the gas at constant pressure.

$$\mathbf{\Delta Q' = C_p \, \Delta T = \Delta U + \Delta W}$$

$$= \Delta U + P\Delta V$$

Here work done ΔW is equal to PΔV which is the product of pressure and increase in volume of the gas. By ideal gas equation it is also R**ΔT,**

Hence, we have

$$C_p\, \Delta T = C_v\, \Delta T + R\, \Delta T$$

$$C_p - C_v = R$$

The ratio of the molar specific heats C_p and C_v is an important quantity which is used in adiabatic processes and determining the speed of sound in gases.

$$\frac{C_p}{C_v} = \gamma$$

The value of this ratio γ is depended on the atomicity of the molecule of gas.

The increase in internal energy ΔU of one mole of a gas due to rise in temperature ΔT is given by

$$\Delta U = \frac{f}{2} R\Delta T$$

Where f is number of degrees of freedom

Molar specific heat at constant volume is given by

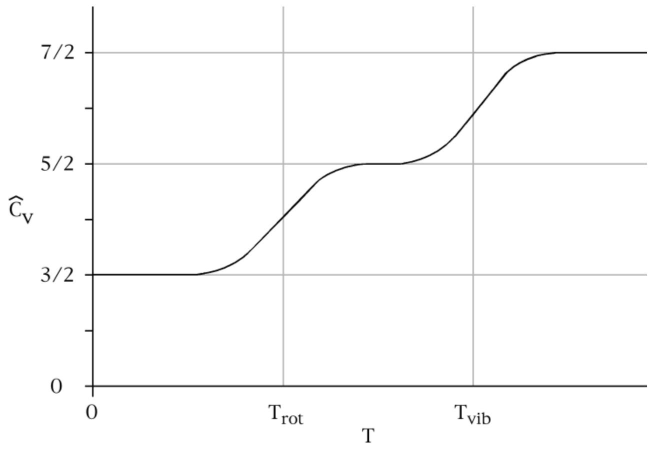
$$C_v = \frac{\Delta U}{\Delta T} = \frac{f}{2} R$$

The number of degrees of freedom (f) of a molecule depends on the temperature of the gas. As the temperature increases more degrees of freedom become active as seen from the graph. This increases the value of molar specific heat capacity.

The molar specific heat at constant pressure is given by

$$C_p = C_v + R = \frac{f}{2} R + R$$

$$C_p = \frac{f+2}{2} R$$



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Hence, the ratio $\gamma = \frac{f+2}{f}$

It is evident from the above formula that this ratio of molar specific heats depends on the number of degrees of freedom of a molecule which in turn depends on the type of molecule and the temperature of the gas.

This ratio of molar specific heat is given below in the table for various types of molecules i.e. monoatomic, diatomic and triatomic. This ratio is given at the room temperature. At higher temperatures, the value of this ratio will increase when the vibrational modes becomes active.

Molecule	Total degrees of freedom(f)	Molar specific heat of gas at Constant volume (C_v)	Constant pressure (C_p)	Molar specific heat ratio (γ) C_p/C_v
Monoatomic	3	$\frac{3}{2}$R	$\frac{5}{2}$R	$\frac{5}{3}$ = 1.67
Diatomic	5	$\frac{5}{2}$R	$\frac{7}{2}$R	$\frac{7}{5}$ = 1.4
Triatomic (non-linear)	6	$\frac{6}{2}$R	$\frac{8}{2}$R	$\frac{8}{6}$ = 1.33

EXAMPLE:

The heat capacity at constant volume of a certain amount of a monatomic gas is 62.35 J/K.

(a) Find the number of moles of the gas.

(b) What is the internal energy of the gas at T = 300 K?

(c) What is the heat capacity of the gas at constant pressure?

SOLUTION:

Heat capacity at constant volume per mole of a monoatomic gas (C_v)

= 3/2 R

= 1.5 x 8.314 = 12.47 J $mol^{-1}K^{-1}$

a. Number of moles of the gas(n) = $\frac{\text{Total Heat capacity at constant volume}}{C_v}$

$= \frac{62.35}{12.47}$ = 5 moles of gas

b. Internal energy of the gas at T = 300K is 3/2 nRT = n C_v T

= 62.35 x 300 = 18,705 J = 18.705 kJ

c. Heat capacity at constant pressure per mole of a monoatomic gas (C_p)

$= C_v + R$

$= 12.47 + 8.314 = 20.784$

Total heat capacity at constant pressure of the gas = 5 x 20.784 = 103.92 J

EXAMPLE:

The heat capacity of a certain amount of a particular gas at constant pressure is greater than that at constant volume by 33.256 J/K.

(a) How many moles of the gas are there?

(b) If the gas is monatomic, what are C_v and C_p?

(c) If the gas consists of diatomic molecules that rotate but do not vibrate, what are C_v and C_p?

SOLUTION:

a. Given: $n(Cp - Cv) = 33.256$ J/K

$nR = 33.256$ J/K

$n = 33.256/R = 33.256/8.314$

= 4 moles

b. If the gas is monoatomic,

$C_v = 3/2\ R = 12.471$ J/mol/K

$C_p = 5/2\ R = 20.785$ J/mol/K

c. If the gas is diatomic,

$C_v = 5/2\ R = 20.785$ J/mol/K

$C_p = 7/2\ R = 29.1$ J/mol/K

9. SUMMARY

Atomicity: The number of atoms in a molecule is called the atomicity of the molecule

Degrees of freedom: The number ways in which a molecule can move**.** The motion of the molecule is mainly categorized in three types, i.e. translational, rotational and vibrational motion. Hence, there is translational degree of freedom, rotational degrees of freedom and vibrational degrees of freedom of molecules.

At room temperature, the vibrational degrees of freedom are frozen.

i) **Monoatomic gases:** They have three translational degrees of freedom.

ii) **Diatomic gases:** Apart from three translational degrees of freedom they have two rotational degrees of freedom.

iii) **Triatomic gases** (non-linear) **:** They have three translational degrees of freedom and three rotational degrees of freedom.

Law of equipartition of energy: For a system in equilibrium, there is an average energy of ½ kT per molecule associated with each degree of freedom.

(Where k is the Boltzmann constant and T is the temperature of the system)

Molar specific heat of gases: Heat required in raising the temperature of one mole of a gas by one degree Celsius. It can be at constant volume (C_v) or at constant pressure (C_p)

Molar specific heat at constant pressure (C_p) is greater than molar specific heat at constant volume (C_v) by an amount equal to the gas constant.

$$C_p - C_v = R$$

Ratio of molar specific heat of gases γ: It depends on the atomicity of the molecules and also on the temperature of the gas.

Value of γ for monoatomic gases = 1.67, diatomic gases = 1.4 and triatomic gases = 1.33 at room temperature.