# **13.** KINETIC THEORY OF GASES AND THERMODYNAMICS

## **KINETIC THEORY OF GASES (KTG)**

### **1. INTRODUCTION**

The kinetic theory of gases describes a gas as a large number of small particles (atoms or molecules), all of which are in constant, random motion. The rapidly moving particles constantly collide with each other and with the walls of the container. Kinetic theory explains macroscopic properties of gases, such as pressure, temperature, viscosity, thermal conductivity and volume, by considering their molecular composition and motion. The theory postulates that gas pressure is due to the impact of molecules or atoms moving at different velocities on the walls of a container.

But here we will only find the dependency of pressure on velocity and of velocity on temperature.

### 2. ASSUMPTIONS OF KTG

- (a) The collisions b/w gas molecules or between a molecule and the container are completely elastic.
- (b) Mass of gas molecules is negligible. So, the effect of gravity and gravitational force on each other can be neglected.
- (c) Volume of molecules is considered to be negligible.
- (d) Collision b/w molecules is governed by Newton's Law of Motion (i.e. Net force = Change in momentum per unit time)
- (e) Interaction force b/w particles is negligible. (That is, they exert no forces on one another.)
- (f) Molecules are considered to be in constant, random, and rapid motion. So, average velocity of particles in all the 3-directions will be zero i.e.  $\langle v_y \rangle = \langle v_y \rangle = \langle v_y \rangle = 0$ .

#### MASTERJEE CONCEPTS

These assumptions must always be kept in mind throughout the chapter.

Vaibhav Gupta (JEE 2009 AIR 54)

### **3. PRESSURE OF AN IDEAL GAS**

Applying Newton's Laws to an ideal gas under the assumptions of kinetic theory allows the determination of the average force on container walls. This treatment assumes that the collisions with the walls are perfectly elastic.





An overbar indicates an average quantity. In the expression for the average force per molecule

for N molecules. 
$$\overline{F} = \frac{m\left[v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots + v_{Nx}^2\right]}{L}$$
  
but this can be related to the average: 
$$\overline{v_x^2} = \frac{\left[v_{1x}^2 + v_{2x}^2 + v_{3x}^2 + \dots + v_{Nx}^2\right]}{N}$$

It is important to note that it is the average of the square of the velocity which is used, and that this is distinctly different from the square of the average velocity. The average of the square of the velocity is referred as square of root mean square speed.

i.e. 
$$V_{rms} = \sqrt{v^2}$$
; and for N molecules:  $\bar{F} = \frac{mNv_x^2}{L}$ 

And, since the molecular motion is random according to KTG, so  $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$ 

#### MASTERJEE CONCEPTS

Why are the RMS velocities the same in all the directions? Practically, if we use some pressure measuring device and use it from all directions, we would get the same value of pressure which indicates that RMS velocities must be same in all directions because it is directly proportional to RMS velocity.

#### Chinmay S Purandare (JEE 2012 AIR 698)

Thus,

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} = 3\overline{v_x^2};$$

Now, average force from N molecules can be re-written as  $F_{average} = \frac{mNv^2}{3I}$ 

Then the pressure in a container can be expressed as 
$$P = \frac{F_{avg}}{A} = \frac{mNv^2}{3LA} = \frac{mNv^2}{3V} = \frac{N}{3V}mv^2$$

$$P = \frac{1}{3}\rho v^2$$
  $\rho$ : density of gas molecules in the container; Therefore,  $V_{rms} = \sqrt{3\frac{P}{\rho}}$ 

Expressed in terms of average molecular kinetic energy:  $P = \frac{2N}{3V} \left[ \frac{1}{2}mv^2 \right]$ 

### 4. KINETIC INTERPRETATION OF TEMPERATURE

The expression for gas pressure developed from kinetic theory relates pressure and volume to the average molecular kinetic energy. Comparison with the ideal gas law leads to an expression for temperature sometimes referred to as the kinetic temperature.

PV = nRT

And we know from above that:  $PV = \frac{2}{3}N\left[\frac{1}{2}mv^2\right]$ ; Thus,  $T = \frac{2}{3}\frac{N}{nR}\left[\frac{1}{2}mv^2\right]$ 

:. Kinetic energy per mole of gas =  $\frac{3}{2}$  RT;

As R = Boltzmann's constant x Avogadro number; R =  $kN_{a}$ 

Thus, Average molecular kinetic energy is: 
$$KE_{avg} = \left[\frac{1}{2}mv^2\right] = \frac{3}{2}kT$$

Therefore,  $V_{rms} = \sqrt{\frac{3RT}{M_m}}$ ; Where  $M_m$  is the molecular weight of the gas.

#### **MASTERJEE CONCEPTS**

In  $V_{\rm rms} = \sqrt{\frac{3RT}{M}}$ , M is the molecular weight in Kg.

The temperature at which molecular speed becomes zero is called absolute zero i.e. 0 kelvin

#### Vaibhav Krishnan (JEE 2009 AIR 22)

**Illustration 1:** A tank used for filling helium balloons has a volume of 0.3m<sup>3</sup> and contains 2.0 mol of helium gas at 20.0°C. Assuming that the helium behaves like an ideal gas.

(a) What is the total translational kinetic energy of the molecules of the gas?

(b) What is the average kinetic energy per molecule?

Sol: Formula for total kinetic energy and kinetic energy per molecule is used.

(a) Using 
$$(KE)_{Trans} = \frac{3}{2}nRT$$

With n = 2.0 mol and T = 293 K, we find that (KE)<sub>Trans</sub> =  $\frac{3}{2}$ (2.0)(8.31)(293) = 7.3 x 10<sup>3</sup> J

(b) The average kinetic energy per molecule is  $\frac{3}{2}$ kT.

(JEE MAIN)

or 
$$\frac{1}{2}m\overline{v^2} = \frac{1}{2}m\overline{v^2}_{rms} = \frac{3}{2}kT = \frac{3}{2}(1.38x10^{-23})(293) = 6.07x10^{-21}J$$

Illustration 2: In a circle model of a rotation diatomic molecule of chlorine (Cl<sub>2</sub>), the two Cl atoms are 2.0 x 10<sup>-10</sup> m apart and rotate about their centre of mass with angular speed  $\omega = 2.0 \times 10^{12}$  rad/s. What is the rotational kinetic energy of one molecule of Cl<sub>2</sub>, which has a molar mass of 70.0 g/mol? (JEE ADVANCED)

**Sol:** Rotational kinetic energy of each molecule  $=\frac{1}{2}I\omega^2$ Movement of inertia,  $I = 2 (mr^2) = 2mr^2$ Here  $m = \frac{70 \times 10^{-3}}{2 \times 6.02 \times 10^{23}} = 5.81 \times 10^{-26} \text{kg}$  and  $r = \frac{2.0 \times 10^{-10}}{2} = 1.0 \times 10^{-10} \text{m}$  $I = 2(5.81) \times 10^{-26} (1.0 \times 10^{-10})^2 = 1.16 \times 10^{-45} \text{ kg} \text{-m}^2$ 



Figure 13.2

$$\therefore \qquad \qquad \mathsf{K}_{\mathsf{R}} = \frac{1}{2} \mathrm{I} \omega^2 = \frac{1}{2} \mathsf{x} (1.16 \, \mathsf{x} 10^{-45}) \, \mathsf{x} (2.0 \, \mathsf{x} 10^{12})^2 = 2.32 \mathsf{x} 10^{-21} \mathsf{J}$$

Note: At T = 300 K, rotational K.E, should be equal to  $\frac{1}{2}kT = \frac{1}{2}x(1.38 \times 10^{-23})x(300) = 2.07 \times 10^{-21} J$ 

### **5. TYPES OF SPEED**

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There are generally three types of speed defined which are physically important:

### 5.1 Root Mean Square (RMS) Speed v<sub>rms</sub>

It is the square root of the average of the square of velocities  $\overline{v^2}$  i.e.  $v_{rms} = \sqrt{v^2}$ 

As has been derived in the previous section, the value of v<sub>ms</sub> can be derived from the following formula:

$$v_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{\rho}}$$

#### 5.2 Mean/Average Speed v

It is the mean of the speeds of all the particles i.e.  $v_{av} = \frac{v_1 + v_2 + \ldots + v_N}{N}$ 

From the Maxwellian speed distribution law, we can show that  $v_{av} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi m}} = \sqrt{\frac{8P}{\pi m}}$ 

### 5.3 Most Probable Speed v<sub>mps</sub>

It is the mode of the speeds. That is, the speed which is possessed by most of the molecules of a gas at a given temperature T.

$$v_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2P}{\rho}}$$

#### **MASTERJEE CONCEPTS**

The above quantities are easy to derive by some basic knowledge of calculus. However, only knowing them is also fine and observe that

1. V<sub>mps</sub>: V<sub>rms</sub>: V<sub>av</sub>:: 1: 1.224: 1.28 2. V<sub>mps</sub> = <V<sub>rms</sub> = < V<sub>avg</sub>

Nivvedan (JEE 2009 AIR 113)

Illustration 3: Consider an 1100 particles gas system with speeds distribution as follows:

1000 particles each with speed 100 m/s; 2000 particles each with speed 200 m/s

4000 particles each with speed 300 m/s; 3000 particles each with speed 400 m/s and 1000 particles each with speed 500 m/s Find the average speed, and rms speed. (JEE MAIN)

**Sol:** 
$$\left(V_{avg} = \frac{n_1v_1 + n_2v_2 + n_3v_3....}{n_1 + n_2 + n_3 + ....}\right)$$
 and  $V_{rms} = \sqrt{\frac{nv_1^2 + n_2v_2^2 + n_3v_3^2....}{n_1 + n_2 + n_3 + ....}}$ 

The average speed is:  $v_{av} = \frac{(1000)(100) + (2000)(200) + (4000)(300) + (3000)(400) + (1000)(500)}{1100} = 309 \text{ m/s}$ 

The rms speed is:  $v_{rms} = \sqrt{\frac{(1000)(100)^2 + (2000)(200)^2 + (4000)(300)^2 + (3000)(400)^2 + (1000)(500)^2}{1100}} = 328 \text{ m/s}$ 

**Note:** Here  $\frac{v_{rms}}{v_{av}} \neq \sqrt{\frac{3}{8 / \pi}}$  as values and gas molecules are arbitrarily taken.

 Illustration 4: Find the rms speed of hydrogen molecules at room temperature (=300 K).
 (JEE MAIN)

 Sol: Formula based
 (JEE MAIN)

Mass of 1 mole of hydrogen gas =  $2g = 2 \times 10^{-3} \text{kg} \implies v_{\text{rms}} = \sqrt{\frac{3\text{RT}}{M}} = \sqrt{\frac{3\text{x}8.31\text{x}300}{2\text{x}10^{-3}}} = 1.93\text{x}10^{3}\text{m/s}$ 

Illustration 5: Find the temperature at which oxygen molecules would have the same rms speed as of hydrogen molecules at 300 K. (JEE ADVANCED)

**Sol:** Compare the V<sub>rms</sub> of oxygen and hydrogen.

If T be the corresponding temperature 
$$\sqrt{\frac{3RT}{M_o}} = \sqrt{\frac{3R(300)}{M_H}} \Rightarrow T = (300) \left(\frac{M_o}{M_H}\right) = 4800 \text{ K}$$

# THERMODYNAMICS

### **1. INTRODUCTION**

You would have certainly noticed the whistle of the process cooker in the kitchen. Have you ever thought of reason for that? How small amount of water form large volume of vapours. Think of James Watt and his observation that red to invention of steam engine !

### 2. GAS LAWS

### 2.1 Boyle's Law

The Pressure-Volume Law (by Robert Boyle (1627-1691).

Boyle's law or the pressure-volume law states that the volume of a given amount of gas varies inversely with the applied pressure when the temperature and mass are kept constant.

$$V \propto \frac{1}{P}$$
; i.e.  $PV = C$ ; Therefore,  $P_1V_1 = P_2V_2$ 

When pressure goes up, volume goes down and vice-versa.

### 2.2 Charles' Law

The Temperature-Volume Law (by Jacques Charles (1746 - 1823).

This law states that the volume of a given amount of gas held at constant pressure is directly proportional to the Kelvin temperature.

 $v \propto T$ ; i.e. V / T = C; Therefore,  $V_1 / T_1 = V_2 / T_2$ 

As the volume goes up, the temperature also goes up, and vice-versa.

### 2.3 Gay-Lussac's Law

The Pressure Temperature Law (by Joseph Gay-Lussac (1778-1850).

This law states that the pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature.

 $P \propto T$ ; i.e. P/T = C; Therefore,  $P_1 / T_1 = P_2 / T_2$ 

### 2.4 Avogadro's Law

The Volume Amount Law (Amedeo Avogadro (1776-1856).

Gives the relationship between volume and amount when pressure and temperature are held constant. Remember amount is measured in moles. Also, since volume is one of the variables, that means the container holding the gas is flexible in some way and can expand or contract. If the amount of gas in a container is increased, the volume increases. If the amount of gas in a container is decreased, the volume decreases.

 $v \propto n$ ; i.e. V/n = C; Therefore,  $V_1 / n_1 = V_2 / n_2$ 

**The combined gas law:** The volume of a given amount of gas is proportional to the ratio of its Kelvin temperature and its pressure.

$$V \propto \frac{T}{P}$$
; i.e. PV/T = C Therefore,  $P_1 / V_1 = T_1 = P_2 V_2 / T_2$ 

As the pressure goes up, the temperature also goes up, and vice-versa.

The ideal gas law: On combining all the previous laws we get: PV = nRT

Where n: the number of moles and R: constant called the universal gas constant≈ 0.0821 L-atm / mol-K.

#### **MASTERJEE CONCEPTS**

For solving problems, it is not advisable to individually think over each and every case. Just remember this overall equation. PV = nRT

#### Nitin Chandrol (JEE 2012 AIR 134)

**Illustration 6:** An air bubble starts rising from the bottom of a lake. Its diameter is 3.6 mm at the bottom and 4 mm at the surface. The depth of the lake is 250 cm and the temperature at the surface is 40°C. What is the temperature at the bottom of the lake? Given atmospheric pressure = 76 cm of Hg and g = 980 cm/s<sup>2</sup>. (**JEE MAIN**)

**Sol:** Amount of air is constant, hence  $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$  applicable.

At the bottom of the lake, volume of the bubble  $V_1 = \frac{4}{3}\pi r_1^3 = \frac{4}{3}\pi (0.18)^3 \text{ cm}^3$ 

Pressure on the bubble;  $P_1$  = atmospheric pressure + pressure due to a column on 250 cm of water = 76 x 13.6 x 980 + 250 x 1 x 980 = (76 x 13.6 + 250) 980 dyne/cm<sup>2</sup>

At the surface of the lake, volume of the bubble  $V_2 = \frac{4}{3}\pi r_2^3 = \frac{4}{3}\pi (0.2)^3 \text{ cm}^3$ 

Pressure on the bubble;  $P_2$  = atmospheric pressure = (76 x 13.6 x 980) dyne/cm<sup>2</sup>

Now 
$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$
 or  $\frac{(76 \times 13.6 + 250)980 \times \left(\frac{4}{3}\right) \pi (0.18)^3}{T_1} = \frac{(76 \times 13.6) \times 980 \left(\frac{4}{3}\right) \pi (0.2)^3}{313}$ 

or  $T_1 = 283.37 \text{ K};$   $\therefore T_1 = 283.37 - 273 = 10.37^{\circ}\text{C}$ 

**Illustration 7:** P-V diagram of n moles of an ideal gas is as shown in figure. Find the maximum temperature between A and B. (JEE ADVANCED)

**Sol:** Find  $\frac{dT}{dV} = 0$ ,  $\frac{d^2T}{dV^2} < 0$  for  $T_{max}$  in T/V relation.

**Procedure**: For given number of moles of a gas,  $T \propto PV$ 

Although  $(PV)_A = (PV)_B$  or  $T_A = T_{B'}$  still it is not an isothermal process. Because in isothermal process P-V graph is a rectangular hyperbola while it is a straight line. So, to see the behaviour of temperature first we will find either T-V equation or T-P equation and from that equation we can judge how the temperature varies. From the graph first we will write P-V equation, then we will convert it either in T-V equation or in T-P equation.

From the graph the P-V equation can be written as,

$$P = -\left(\frac{P_0}{V_0}\right)V + 3P_0 \quad (y = -mx + c) \text{ or } \qquad PV = -\left(\frac{P_0}{V_0}\right)V^2 + 3P_0V$$

or 
$$nRT = 3P_0V - \left(\frac{P_0}{V_0}\right)V^2$$
 (as PV = nRT) or  $T = \frac{1}{nR}\left[3P_0V - \left(\frac{P_0}{V_0}\right)V^2\right]$ 

This is the required T-V equation. This is quadratic in V. Hence T-V graph is a parabola. Now, to find maximum or minimum value of T we can substitute.

$$\frac{dT}{dV} = 0 \text{ or } 3P_0 - \left(\frac{2P_0}{V_0}\right)V = 0; \text{ or } V = \frac{3}{2}V_0$$

Further  $\frac{d^2T}{dV^2}$  is negative at V =  $\frac{3}{2}V_0$ 

Hence, T is maximum at V =  $\frac{3}{2}$ V<sub>0</sub> and this maximum value is,

$$T_{max} = \frac{1}{nR} \left[ (3P_0) \left( \frac{3V_0}{2} \right) - \left( \frac{P_0}{V_0} \right) \left( \frac{3V_0}{2} \right)^2 \right]; \text{ or } T_{max} = \frac{9P_0V_0}{4nR}$$

Thus, T-V graph is as shown in figure

$$T_A = T_B = \frac{2P_0V_0}{nR}$$
 and  $T_{max} = \frac{9P_0V_0}{4nR} = 2.25\frac{P_0V_0}{nR}$ 





Figure 13.4

#### 3. DEGREE OF FREEDOM (f)

Each independent mode by which a system can absorb energy (Kinetic + Potential) is called a degree of freedom. It is the number of independent motions possible or number of independent coordinates to specify the dynamic position of a body. A molecule can have translational K.E, rotational K.E and vibrational energy (potential, kinetic).

- (a) Monatomic Gas: It has 3 degrees of freedom, since it can have translational motion in any direction in space. It can rotate but due to its small moment of inertia, rotational energy is neglected. f = 3
- **(b) Diatomic gas and linear polyatomic gas:** It has 5 degrees of freedom (3 translational + 2 Rotational). Since, the moment of inertia about the axis joining the atoms is negligible, thus, it only has two rotational degrees of freedom. In all, f = 5.

At high temperature, its degree of freedom increases by 2 due to the vibrational energy (1 kinetic + 1 potential vibrational energy). Thus f = 7 at high temperature.

(c) Non-linear Polyatomic gas: It has 6 degrees of freedom (3 translational + 3 rotational). The one rotational degree of freedom which was neglected above, can't be neglected over here. Since, the moment of inertia about any of the three axes is not tending to zero i.e. f = 6.

At high temperature, its degree of freedom increases by 2 due to Vibrational energy

(1 kinetic + 1 potential) Thus, f = 8.

(d) Solid: Solids don't have any translational or rotational degrees of freedom. But at high temperature, it can vibrate along 3 axes. Thus it has 2 degrees of freedom per axis (i.e. potential + kinetic vibrational energy). Thus, at high temperature, solids have 6 degrees of freedom. i.e. f = 6

#### **MASTERJEE CONCEPTS**

 $f_{mix} = (n_1f_1 + n_2f_2 + \dots) / (n_1 + n_2 + \dots)$  is the equation for effective 'f' for a mixture of gases.

- Degrees of freedom of a diatomic and polyatomic gas depend on temperature and there is no clear cut demarcation line above which vibrational energy becomes significant. Moreover, this temperature varies from gas to gas. On the other hand for a monatomic gas, there is no such confusion. Degree of freedom here is 3 at all temperatures. Unless and until stated in the question you can take f = 3 for a monatomic gas, f = 5 for a diatomic gas and f = 6 for a non-linear polyatomic gas.
- When a diatomic or polyatomic gas dissociates into atoms it behaves as a monatomic gas, whose degrees of freedom are changed accordingly.

B Rajiv Reddy (JEE 2012 AIR 11)

### 4. INTERNAL ENERGY (U)

- (a) In thermodynamics, the internal energy is the total energy contained by a thermodynamic system. It is the energy needed to create the system but excludes any energy due to external force fields (e.g. Internal energy does not include the energy due to the motion of the system as a whole. It further excludes any kinetic or potential energy the body may have because of its location in external gravitational, electrostatic, or electromagnetic fields.).
- **(b)** Internal energy has two major components, kinetic energy  $(U_{kin})$  and potential energy  $(U_{pot})$ . The kinetic energy is due to the motion of the system's particles (translations, rotations, vibrations), and the potential energy is associated with the static rest mass energy of the constituents of matter. U = U<sub>pot</sub> + U<sub>kin</sub>
- (c) The internal energy of a system can be changed by heating the system or by doing work on it.
- (d) It is an extensive quantity. The internal energy is a state function of a system, because its value depends only on the current state of the system and not on the path taken or process undergone to arrive at this state
- (e) The SI unit of energy is the joule (J).

### 5. LAW OF EQUIPARTITION OF ENERGY

According to the law of equipartition of energy, the total energy of a molecule is equally distributed on the average among all the degrees of freedom. For an ideal gas at absolute temperature T, the energy is:  $\frac{1}{2}kT$  per molecule per degree of freedom. k = Boltzmann's constant;  $\frac{1}{2}RT$  per mole, R = gas constant.

Thus, if f be the number of degrees of freedom, the internal energy of n moles of the gas will be  $\frac{T}{2}$ nRT. Thus, U =  $\frac{f}{2}$ nRT

### 6. MOLAR HEAT CAPACITIES (C)

(a) The amount of heat needed to raise the temperature of one mole of a substance by one degree Celsius. i.e.

$$C = \frac{\Delta Q}{n\Delta T} \implies \Delta Q = nC\Delta T$$

- (i) S.I. unit is J/mol K
- (ii) The value of C depends on the process through which its temperature is raised.

- **(b)** Molar heat Capacity at constant Pressure C<sub>p</sub>: The amount of heat needed to raise the temperature of one mole of a substance by one degree Celsius at constant pressure.
- (c) Molar heat Capacity at constant Volume C<sub>V</sub>: The amount of heat needed to raise the temperature of one mole of a substance by one degree Celsius at constant volume.
  - (i)  $\gamma = \text{Ratio of } C_p \text{ to } C_v = \frac{C_p}{C_v}$ ;  $\gamma$  is also referred to as the adiabatic constant.

#### MASTERJEE CONCEPTS

You Can Write:

 $C_{Vmix} = (n_1Cv_1 + n_2Cv_2 + \dots) / (n_1 + n_2 + \dots)$   $C_{Pmix} = (n_1f_1 + n_2f_2 + \dots) / (n_1 + n_2 + \dots)$   $F_{mix} = (n_1f_1 + n_2f_2 + \dots) / (n_1 + n_2 + \dots)$ But  $\gamma_{mix} \neq (n_1\gamma_1 + n_2\gamma_2 + \dots) / (n_1 + n_2 + \dots)$   $\gamma_{mix} = 1 + 2 / f_{mix} \text{ (you will see it later that } \gamma = 1 + 2/f) = C_{Pmix} / C_{vmix}$ Anand K (JEE 2011 AIR 47)

### 7. ZEROTH LAW OF THERMODYNAMICS

If two bodies A and B are in thermal equilibrium and A and C are also in thermal equilibrium, then B and C are also in thermal equilibrium.

### 8. FIRST LAW OF THERMODYNAMICS

It is based on the law of conservation of energy. It states that

Heat supplied to the gas = Increment in internal energy + work done by the gas.

 $\Delta Q = \Delta U + \Delta W$ 

In differential form, dQ = dU + dW

We will be using the following sign convention:

(a) For heat transfer:  $\Delta Q$  is +ve for heat supplied;

 $\Delta Q$  is -ve for heat rejected

**(b)** For Work Done:  $\Delta W$  = +ve for work done by gas (in expansion of gas)

 $\Delta W$ =-ve for work done on the gas (in contraction of gas)

We know:

**Internal energy:** Earlier we have seen that  $U = \frac{n}{2} fRT$ 

Thus, change in internal energy  $\Delta U = \frac{n}{2} fR\Delta T$ 

or in differential from,  $dU = \frac{n}{2} fRdT$ 

**Note:** Change in Internal Energy is path independent whereas work done or heat energy released are path dependent. Internal Energy depends only on initial and final state of the system.

**Illustration 8:** Calculate the change in internal energy of 3.0 mol of helium gas when its temperature is increased by 2.0 K. (JEE MAIN)

Sol: Formulas based : f degree of freedom for monoatomic gas is 3.

Helium is a monatomic gas. Internal energy of n moles of the gas is,

$$U = \frac{3}{2} nRT; \qquad \therefore \quad \Delta U = \frac{3}{2} nR(\Delta T)$$

Substituting the values,  $\Delta U = \left(\frac{3}{2}\right)(3)(8.31)(2.0) = 74.8 \text{ J}$ 

Heat transfer: From molar heat capacity, we saw that  $\Delta Q = nC\Delta T$  or in differential form, dQ = nCdT

#### Work done: dW = PdV

For a finite change in volume from  $V_i$  to  $V_r$  this equation is then integrated between  $V_i$  to  $V_f$  to find the net work.

$$W = \int dw = \int_{v}^{v_f} P dV$$

Now, there are two methods of finding work done by a gas.

Method 1: This is used when the P-V equation is known to us. Suppose P as a function of V

is known to us. P = f(V) then work done can be found by,  $W = \int_{V}^{V} f(V) dV$ 

**Method 2:** Since, work done is the integration of pressure w.r.t volume. So, it is clear that work represents the area under P-V graph. But, always take care of the sign of the work done. If the volume increases or in case of cyclic process if it is clockwise then +ve work is done by the gas or vice versa.



Figure 13.5

**Illustration 9:** A certain amount of an ideal gas passes from state A to B first by means of process 1, then by means of process 2. In which of the process is the amount of heat absorbed by the gas greater? (JEE MAIN)

**Sol:**  $\Delta V$  is state function, remains constant. Hence work done directly proportional to heat obserbed.

 $Q_1 = W_1 + \Delta U_1$  and  $Q_2 = W_2 + \Delta U_2$ 

U is a state function. Hence,  $\Delta U$  depends only on the initial and final positions. Therefore,  $\Delta U_1 = \Delta U_2$ . But  $W_1 > W_2$  as the area under 1 is greater than area under 2. Hence,  $Q_1 > Q_2$ 

### 9. REVERSIBLE AND IRREVERSIBLE PROCESS

#### **9.1 Reversible Process**

A process in which the system and surroundings can be restored to the initial state from the final state without producing any change in the thermodynamic properties of the universe.

E.g. an infinitesimal compression of a gas in a cylinder assuming frictionless surfaces.

#### **9.2 Irreversible Process**

In irreversible processes, the system is not in equilibrium throughout the process. The initial state can't be obtained from the final state without producing changes in the universe.

E.g. heat transfer through a finite temperature difference.



Figure 13.6

### **10. DIFFERENT THERMODYNAMIC PROCESSES**

#### **10.1 Isochoric Process (V = Constant)**

 $C_{v}$  is the molar heat capacity for constant volume.

Since  $\Delta V = 0$ . Therefore,  $\Delta W = 0$ ; We know that,  $nC_v\Delta T = n\frac{f}{2}R\Delta T$  and  $= n\frac{f}{2}R\Delta T$ By 1<sup>st</sup> Law of Thermodynamics:  $\Delta Q = \Delta U + \Delta W$ ;  $\Delta Q = \Delta U + 0$ . Thus  $nC_v\Delta T = n\frac{f}{2}R\Delta T$ ; Therefore,  $\Delta Q = \Delta U \implies C_v = \frac{f}{2}R$ ; So in isochoric process we have  $\Delta Q = \Delta U = nC_{y}\Delta T$ ;  $\Delta W = 0$ 

Note: Since,  $\Delta U$  is an extrinsic property(property that is not inherent). So,  $\Delta U = nC_v \Delta T$  can be used for any process.

### **10.2 Isobaric Process (P = Constant)**



Thus,  $dQ = mC_{P}dT$ 

Since, dU is an extrinsic property, Thus,  $dU = nC_v dT$ 

We know PV = nRT ; 
$$\Rightarrow$$
 PdV + VdP = nRdT  $\Rightarrow$  PdV = nRdT [ $\because$  dP = 0]

And dW = PdV = nRdT

So, by using the 1<sup>st</sup> law of thermodynamics.

We get , dQ= dU + dW;  $\Rightarrow$  nC<sub>P</sub>dT = nC<sub>V</sub>dT + nRdT;  $\Rightarrow$ C<sub>P</sub> = C<sub>V</sub> + R

Thus, for the process, we have,  $\Delta W = P(V_f - V_i) = nR(T_f - T_i)$ ;  $\Delta Q = nC_p\Delta T$ ;  $\Delta U = nC_v\Delta T$ 

Note: We have seen, from above two process that,

$$C_V = \frac{f}{2}R$$
 and  $C_P = C_V + R$  ... (i)  
Thus,  $C_P = \left(\frac{f}{2} + 1\right)R$  ... by (i)

i nus,

We know,  $\gamma = \frac{C_{P}}{C_{V}}$ ;  $\Rightarrow \gamma = \frac{\left(\frac{f}{2}+1\right)R}{\left(\frac{f}{2}\right)R}$ ;  $\Rightarrow \gamma = 1 + \frac{2}{f}$  Thus,  $C_{V} = R / (\gamma - 1)$  And  $C_{P} = \gamma R / (\gamma - 1)$ 

Thus, for different degrees of freedom (i.e. for different gases) we have:

Types of Gas	Degrees of freedom	Total Energy	C <sub>P</sub>	C <sub>v</sub>	γ
Monatomic	3	$\frac{3}{2}$ RT	$\frac{5}{2}R$	$\frac{3}{2}R$	1.67
Diatomic	5	$\frac{5}{2}$ RT	$\frac{7}{2}R$	$\frac{5}{2}R$	1.4
Polyatomic( $\geq 3$ )	6	3RT	4R	3R	1.33









**Illustration 10:** A cylindrical vessel of 28cm diameter contains 20g of nitrogen compressed by a piston supporting a weight of 75kg. The temperature of the gas is 17°C. What work will the gas do, if it is heated to a temperature of 250°C? What amount of heat should be supplied? To what distance will the weight be raised? The process should be assumed to be isobaric; the heating of the vessel and the external pressure are negligible. **(JEE ADVANCED)** 

Sol: Use isobaric process equations .

$$\Delta W \text{ (work done)} = \int PdV = P\Delta V = P \times \frac{m}{M} \frac{R\Delta T}{P} = \frac{m}{M} R\Delta T \therefore \Delta W = \frac{20}{28} \times 8.3(250 - 17) = 1381J$$

$$\Delta Q = n C_p \Delta T = \frac{7}{2} nR \Delta T = 3.5 \times \frac{20}{28} \times 8.3 \times (250 - 17) = 4834.7J$$

$$h = \frac{\Delta V}{A} = \frac{nR\Delta T}{P} \times \frac{1}{A}$$

$$P = \left(P_0 + \frac{mg}{A}\right)$$

$$\Rightarrow h = \frac{20 \times 8.3 \times (250 - 17)}{28 \times 75 \times 9.8 + (10^5 \times \frac{22}{7} \times 14^2 \times 10^{-4})} \Rightarrow h = 0.2 \text{ m} = 20 \text{ cm}$$

#### 10.3 Isothermal Process (T = Constant)

$$\Delta T = 0 \; ; \; \Delta U = nC_V \Delta T = 0 \; ; \; \Rightarrow \; \Delta W = \Delta Q \; ;$$
  
We know, PV = nRT;  $\Rightarrow P = \frac{nRT}{V} \; ;$   
$$\therefore \Delta W = \int_{V_i}^{V_f} \frac{nRT}{V} dv = \left[ nRT \ln V \right]_{V_i}^{V_f} = nRT \ln \frac{V_f}{V_i}$$
  
Slope of P-V graph: PV=nRT;  $\Rightarrow (dP)V+P(dV)= nRdT$ 

Since, dT =0;

Thus, (dP)V+P(dV)=0;  $\Rightarrow dP/dV=-P/V$ 

So, in an isothermal process we have:  $\Delta U = 0$ 

$$\Delta Q = \Delta W = nRT ln \frac{V_f}{V_i} = nRT ln \frac{P_i}{P_f}; \qquad \text{Slope (isothermal)} = -\frac{P}{V}$$

And C (molar heat capacity) tends to infinity since even when temperature change is zero, heat transfer is non-zero.

**Illustration 11:** Three moles of an ideal gas being initially at a temperature  $T_0 = 273$ K were isothermally expanded  $\eta = 5.0$  time its initial volume and then isochorically heated so that the pressure in the final state became equal to that in the initial state. The total amount of heat transferred to the gas during the process equals Q = 80 kJ. Find the ratio  $\gamma = C_p / C_V$  for this gas. (JEE ADVANCED)

**Sol:** Try draw the process on P/V graph, during isothermal process, the change in internal energy is zero while in isochoric process work dne is zero. Take  $C_v = \frac{R}{y-1}$  and proceed to find y. Procedure:

(1) Find heat expression  $(Q_1)$  given in isothermal process

(2) Find heat expression (Q<sub>2</sub>) given in isochoric process



(3) Find total heat expression  $(Q=Q_1+Q_2)$ 

(4) Put the value of Q given in question in the expression obtained above

In Isothermal process, the heat transferred to the gas is given by

$$\begin{split} Q_{1} &= nRT_{0} \ln(V_{2} / V_{1}) = nRT_{0} \ln \eta \\ & \left[ \therefore \eta = (V_{2} / V_{1}) = (P_{1} / P_{2}) \right] \end{split}$$
 ... (i)

In isochoric process,  $Q_2 = \Delta U$  (W=0)

$$\therefore Q_2 = nC_v \Delta T = n\{R / (\gamma - 1)\}\Delta T \qquad ... (ii)$$

Now 
$$\frac{P_2}{P_1} = \frac{T_0}{T}$$
 or  $T = T_0 \left(\frac{P_1}{P_2}\right) = \eta T_0$  ... (iii)

$$\therefore \quad \Delta T = \eta T_0 - T_0 = (\eta - I) T_0$$

Substituting the value of  $\Delta T$  from equation (iii) in equation (ii), we get

$$Q_{2} = n \left(\frac{R}{\gamma - 1}\right) (\eta - 1) T_{0}; \qquad \therefore \quad Q = n R T_{0} \ln \eta + n \left(\frac{R}{\gamma - 1}\right) (n - 1) T_{0}$$
  
or 
$$\frac{Q}{n R T_{0}} - \ln \eta = \left(\frac{\eta - 1}{\gamma - 1}\right); \qquad \text{or} \qquad \gamma - 1 = \frac{\eta - 1}{\frac{Q}{n R T_{0}} - \ln \eta} \quad \therefore \gamma = 1 + \frac{\eta - 1}{\frac{Q}{n R T_{0}} - \ln \eta}$$

Substituting given values, we get  $\gamma = 1 + \frac{(5-1)}{\frac{80x10^2}{3x8.3x273} - \ln 5}$ ; Solving, we get  $\gamma = 1.4$ 

### **10.4 Adiabatic Process (** $\Delta$ **Q = 0)**

For adiabatic process: 
$$\Delta Q = 0$$
;  $\Delta U = -\Delta W$   
 $nC_V dT = -Pdv$   
By equation of gas:  $PV = nRT$ ;  $\Rightarrow Pdv + Vdp = nRdT$ ;  
 $\therefore ndT = \frac{Pdv + Vdp}{R}$   
 $\therefore$  Substituting in (i) we get:  $C_v \left(\frac{Pdv + Vdp}{R}\right) = -Pdv$   
 $\Rightarrow (C_v + R)Pdv = -C_v Vdp$ ;  $\Rightarrow \frac{C_pd_V}{C_V V} = \frac{-dp}{P} [C_v + R = C_p]$ ;  
 $\Rightarrow \gamma \frac{dV}{V} = -\frac{dP}{P}$ 

On integrating both sides we get,

$$\Rightarrow \gamma \int \int \frac{dv}{V} = -\frac{P_f}{P_i} \int \frac{dp}{P}; \Rightarrow \gamma \ln \frac{V_f}{V_i} = \ln \frac{P_i}{P_f}$$
$$\Rightarrow \frac{P_i}{P_f} = \left(\frac{V_f}{V_i}\right)^{\gamma}; \qquad (say)$$
$$\therefore PV^{\gamma} = Const$$



Adiabatic expansion of mono, dia and polyatomic gases

Figure 13.10

The relation found above can be written in many different ways using ideal gas equation (PV=nRT)

 $TV^{\gamma-1}$  = constant ;  $T^{\gamma}P^{1-\gamma}$  = constant

$$\begin{split} \mathsf{P}\mathsf{V}^{\gamma} &= \mathsf{Const} = \mathsf{K} \implies \mathsf{P} = \frac{\mathsf{k}}{\mathsf{V}^{\gamma}}; \ \therefore \Delta \mathsf{W} = \int_{\mathsf{V}_{i}}^{\mathsf{V}_{f}} \mathsf{P} d\mathsf{v} = \int_{\mathsf{V}_{i}}^{\mathsf{V}_{f}} \frac{\mathsf{k}}{\mathsf{V}^{\gamma}} d\mathsf{v} \\ &= \frac{\mathsf{K}\mathsf{V}_{f}^{1-\gamma} - \mathsf{K}\mathsf{V}_{i}^{1-\gamma}}{1-\gamma} = \frac{(\mathsf{P}_{f}\mathsf{V}_{f}^{\gamma})\mathsf{V}_{f}^{1-\gamma} - (\mathsf{P}_{i}\mathsf{V}_{i}^{\gamma})\mathsf{V}_{i}^{1-\gamma}}{1-\gamma} \\ &\implies \Delta \mathsf{W} = \frac{\mathsf{P}_{f}\mathsf{V}_{f} - \mathsf{P}_{i}\mathsf{V}_{i}}{1-\gamma} = \frac{\mathsf{n}\mathsf{R}}{1-\gamma}(\mathsf{T}_{f} - \mathsf{T}_{i}) \end{split}$$

Slope of P-V graph:

We know,  $PV^{\gamma}$  = constant

 $\frac{dp}{dV} = \frac{d}{dV} \left( \frac{constant}{V^{\gamma}} \right) = -\gamma \left( \frac{P}{V} \right); \text{ Thus, } (\text{Slope})_{adiabatic} = -\gamma \left( \frac{P}{V} \right)$ 

Because  $\gamma > 1$ , the isothermal curve is not as steep as that for the adiabatic expansion.

So, in adiabatic process we have:  $\Delta Q = 0$ 





Ρ



And C (molar heat capacity) is zero, since even when temperature change is not zero, heat transfer is zero.

Illustration 12: An ideal monatomic gas at 300K expands adiabatically to twice its volume. What is the final temperature? (JEE MAIN)

**Sol:** Adiabatic process  $PV^{\gamma}$  = constant or  $TV^{\gamma-1}$  = constant.

For an ideal monatomic gas,  $\gamma = \frac{5}{3}$ 

In an adiabatic process, 
$$TV^{\gamma-1} = constant$$
;  $\therefore T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$ 

or 
$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{\gamma-1} = (300) \left(\frac{1}{2}\right)^{\gamma-1}$$

**Illustration 13:** An ideal gas having initial pressure P, volume V and temperature T is allowed to expand adiabatically until its volume becomes 5.66 V while its temperature falls to T/2.

(a) How many degrees of freedom do the gas molecules have?

**Sol:** Apply 
$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$
 and hence  $\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$ 

$$\omega = \frac{nR}{1-\gamma} \left(\frac{T}{2} - T\right) = \frac{nRT}{2(\gamma - 1)} = \frac{nRT}{2 \times 0.4} = \frac{PV}{0.8}$$

(a) For adiabatic change,

$$TV^{\gamma-1} = T'(V')^{\gamma-1}$$
;  $T' = T/2, V' = 5.66V$   
 $TV^{\gamma-1} = (T/2)x(5.66V)^{\gamma-1}$ ;  $(5.66)^{\gamma-1} = 2$ 

It shows that the gas is diatomic for which the gas molecules have five degrees of freedom.

(b) Work done by the gas during adiabatic expansion, W, is given by,

$$W = \frac{PV - P'V'}{\gamma - 1}; As \frac{P'V'}{T} = \frac{PV}{T}, P' = \frac{PVT'}{V'T}$$
$$P' = \frac{1}{2}x\frac{1}{5.66}xP = \frac{P}{11.32}; \therefore W = \frac{1}{0.4}\left(PV - \frac{P}{11.32}x5.66V\right) = \frac{PV}{0.8} = 1.25PV.$$

### **10.5 Cyclic Process**

In a cyclic process, the thermodynamic process ends at the initial state.

Since, initial and final states are same, there,

 $\therefore \Delta Q = \Delta W$ ;  $\therefore |\Delta Q| = |\Delta W|$  = Area enclosed by the curve.

Sign of  $\Delta W$  is '+' if process is clockwise and '-' if process is anti-clockwise.

### **10.6 Polytropic Process**

For a process: **PV**<sup>x</sup> = **constant** where  $x \neq 1$ , also called a polytropic process.

 $\Delta W = (P_f V_f - P_i V_i) / 1 - x = nR \Delta T / 1 - x; \qquad C = C_v + \frac{R}{1 - x} = \frac{R}{\gamma - 1} + \frac{R}{1 - x}$ Slope of P-V diagram (also known as Indicator diagram) at any point is  $\frac{dP}{dV} = -x \frac{P}{V}$ 

### **11. FREE EXPANSION**

In a free expansion, the gas is allowed to expand into a vacuum. This happens quickly, so there is no heat transferred. No work is done, because the gas does not displace anything. According to the First Law, this means that:  $\Delta U = 0$ 

There is no change in internal energy, so the temperature stays the same.

On a PV diagram all you can do is plot the end-points. The process follows a path on the diagram that is not well-defined because the temperature is constant. The connection between the initial and final states is:  $P_iV_i = P_fV_f$ 

Thus,  $\Delta W=0$ ;  $\Delta Q=0$ ;  $\Delta U=0$ ; T=const. ; thus, PV = constant

**Illustration 14:** An insulated container is divided into two equal portions. One portion contains an ideal gas at pressure P and temperature T, while the other portion is a perfect vacuum. If a hole is opened between the two portions, find the change in internal energy and temperature of the gas? **(JEE ADVANCED)** 

**Sol:** No opposing force, hence work done is zero. As the system is thermally insulated,  $\Delta Q = 0$ 

Further as here the gas is expanding against vacuum (surroundings) the process is called free expansion and for it,  $\Delta W = \int P dv = 0 \qquad [as for vacuum P = 0]$ 

So in accordance with first law of thermodynamics, i.e.  $\Delta Q = \Delta U + \Delta W$ , we have  $0 = \Delta U + 0$ ,







.... (ii)

So in this problem internal energy of the gas remains constant, i.e.  $\Delta U = 0$ . Now as for an ideal gas  $U = 3/2 \mu RT$ , i.e.  $U \propto T$ ; so temperature of the gas will also remain constant, i.e.  $\Delta T = 0$ 

#### **MASTERJEE CONCEPTS**

- (a) A non-conducting container with no external source of heat energy will always undergo any change adiabatically.
- **(b)** A conducting (finitely conducting) container with no external source of heat energy will undergo change:
  - (i) Isothermally if the process is slow
  - (ii) Adiabatically if the process is fast
- (c) An infinitely conducting container with no external source of heat energy will always undergo any change isothermally.

#### Yashwanth Sandupatla (JEE 2012 AIR 821)

**Illustration 15:** A gas undergoes a process such that  $P \propto \frac{1}{T}$  If the molar heat capacity for this process is C= 33.24 J/mol-K, find the degree of freedom of the molecules of the gas. (JEE ADVANCED)

**Sol:** Heat capacity = amount of heat required for per unit change of temperature.  $C = \frac{Q}{\Lambda T}$ 

As 
$$P \propto \frac{1}{T}$$
 or  $PT = constant$  .... (i)

We have for one mole an ideal gas PV=RT

From Eqs. (i) and (iii)

$$P^2V = \text{constant or } PV^{1/2} = K \text{ (say)}$$
 ... (iii)

From first law of thermodynamics,  $\Delta Q = \Delta U + W$  or  $C\Delta T = C_V \Delta T + W$ 

or 
$$C = C_V + \frac{W}{\Delta T}$$
 ... (iv)

Here, 
$$\Delta W = \int P dV = K \int_{V_f}^{V_f} V^{-1/2} dv$$
;  $= \frac{P_f V_f - P_i V_i}{1 - (1/2)} = \frac{R(T_f - T_i)}{1/2} = \frac{RT}{1/2}$ ;  $\therefore \frac{W}{\Delta T} = 2R$ 

Substituting in Eq. (iv), we have  $C = C_v + 2R = \frac{R}{\gamma - 1} + 2R$ 

Substituting the values,  $33.24 = R\left(\frac{1}{\gamma-1}+2\right) = 8.31\left(\frac{1}{\gamma-1}+2\right)$ 

Solving this we get  $\gamma = 1.5$ ; Now,  $\gamma = 1 + \frac{2}{F}$  or degree of freedom  $F = \frac{2}{\gamma - 1} = \frac{2}{1.5 - 1} = 4$ 

**Alternate Solution:** In process PV<sup>x</sup> = constant, molar heat capacity is given by  $C = \frac{R}{\gamma - 1} + \frac{R}{1 - x}$ 

The given process is 
$$PV^{1/2}$$
 = constant or  $x = \frac{1}{2}$ ;  $C = \frac{R}{\gamma - 1} + \frac{R}{1 - \frac{1}{2}} = \frac{R}{\gamma - 1} + 2R$ 

Now, we may proceed in the similar manner.

Illustration 16: An ideal gas expands isothermally along AB and does 700 J of work.

(a) How much heat does the gas exchange along AB?

(b) The gas then expands adiabatically along BC and does 400 J of work. When the gas returns to A along CA, it exhausts 100J of heat to its surroundings. How much work is done on the gas along this path? (JEE MAIN)

**Sol:** Apply  $Q = \Delta U + W$  for the forces AB, BC & then CA separately. Remember  $\Delta U$  is a state function.

(a) AB is an isothermal process. Hence,  $\Delta U_{AB} = 0$  and  $Q_{AB} = W_{AB} = 700 \text{ J}$ (b) BC is an adiabatic process. Hence,  $Q_{BC} = 0$ ;  $W_{BC} = 400 \text{ J}$  (given)

$$\therefore \qquad \Delta U_{BC=} - W_{BC} = -400 J$$

ABC is a cyclic process and internal energy is a state function. Therefore,  $(\Delta U)_{whole cycle} = 0 = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CA}$ 

and from first law of thermodynamics,  $Q_{AB} + Q_{BC} + Q_{CA} = W_{AB} + W_{BC} + W_{CA}$ 

Substituting the values,  $700 + 0 - 100 = 700 + 400 + \Delta W_{CA}$ 

$$\therefore \quad \Delta W_{CA} = -500 J$$

Negative sign implies that work is done on the gas.

### **12. HEAT ENGINE & EFFICIENCY**

Heat Engine is a device which converts the input heat energy into mechanical energy by using a cyclic process.

It absorbs a quantity of heat  $Q_1$  from a source and performs an amount of work W and returns to the initial state after rejecting some heat  $Q_2$ to a sink. The working substance which is gas or liquid undergoes a cyclic thermodynamic process. The source is at a higher temperature than the sink.

The efficiency  $\eta$ , of a heat engine is given by

$$\eta = \begin{pmatrix} \text{Work done by the working substance} \\ (an ideal gas in our case) during a cycle} \\ \text{Heat supplied to the gas during the cycle} \end{pmatrix} = \frac{W}{Q_1}$$

From conservation of energy.  $Q_1 = W + Q_2$ 

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}; \quad \text{Thus,} \quad \therefore \quad \text{Efficiency}(\eta) = 1 - \frac{\text{Heat released}}{\text{Heat absorbed}}$$

**Illustration 17:** The P-V diagram of 0.2 mol of a diatomic ideal gas is shown in figure. Process BC is adiabatic. The value of  $\gamma$  for this gas is 1.4. (JEE ADVANCED)

- (a) Find the pressure and volume at points A, B and C.
- (b) Calculate  $\Delta Q$  ,  $\Delta W\,$  and  $\Delta U$  for each of the three processes.





Figure 13.13

(c) Find the thermal efficiency of the cycle. Take 1 atm =  $1.0 \times 10^5$  N/m<sup>2</sup>.

**Sol:** Try to start from A where  $P_A$  and  $T_A$  are known. (a)  $P_A = P_C = 1$  atm = 1.01 x 10<sup>5</sup> N/m<sup>2</sup> Process AB is an isochoric process.

$$\therefore \qquad P \propto T \qquad \text{or } \frac{P_B}{P_A} = \frac{T_B}{T_A} \ ;$$

:. 
$$P_{B} = \left(\frac{T_{B}}{T_{A}}\right) P_{A} \left(\frac{600}{300}\right) (1atm) = 2atm = 2.02 \times 10^{5} \text{ N/m}^{2}$$

From ideal gas equation  $V = \frac{nRT}{P}$ 

:. 
$$V_A = V_B = \frac{nRT_A}{P_A} = \frac{(0.2)(8.31)(300)}{(1.01 \times 10^5)} \approx 5.0 \times 10^{-3} \text{ m}^3$$
; = 5 litre

$$V_{C} = \frac{nRT_{C}}{P_{C}} = \frac{(0.2)(8.31)(455)}{(1.01x10^{5})} = 7.6x10^{-3} \text{ m}^{3} \approx 7.6 \text{ litre}$$

А	1 atm	5 lt
В	2 atm	5 lt
С	1 atm	7.6 lt

(b) **Process AB** is an isochoric process. Hence,  $\Delta W_{AB} = 0$ 

$$\Delta Q_{AB} = \Delta U_{AB} = nC_{v}\Delta T = n\left(\frac{5}{2}R\right)(T_{B} - T_{A}) = (0.2)\left(\frac{5}{2}\right)(8.31)(600 - 300) \approx 1246 \text{ J}$$

**Process BC** is an adiabatic process. Hence,  $\Delta Q_{BC}=0$ 

$$\Delta W_{BC} = -\Delta U_{BC}$$
  
$$\Delta U_{BC} = nC_v \Delta T = nC_V (T_C - T_B) = (0.2) \left(\frac{5}{2}R\right) (455 - 600) = (0.2) \left(\frac{5}{2}\right) (8.31) (-145) J \approx -602 J$$

 $\therefore \qquad \Delta W_{BC} = -U_{BC} = 602 J$ 

*.*..

Process CA is an isobaric process. Hence,

$$\Delta Q_{CA} = nC_{P}\Delta T = n\left(\frac{7}{2}R\right)(T_{A} - T_{C}) = (0.2)\left(\frac{7}{2}\right)(8.31)(300 - 455)$$

#### **12.1 Types of Heat Engine**

- (a) **External combustion engine:** In which heat is produced by burning the fuel in a chamber outside the main body (working substance) of the engine. Steam engine is an external combustion engine. The thermal efficiency of a steam engine varies from 10 to 20%.
- (b) Internal combustion engine: In which heat is produced by burning the fuel inside the main body of the engine. Petrol engine and diesel engines are internal combustion engine. Here, we will just discuss about only one heat engine i.e. Carnot engine.



Figure 13.15

### 12.2 Carnot Engine

Carnot Cycle is the most efficient heat engine which undergoes a cycle of two isothermal and two adiabatic processes. It absorbs heat Q<sub>1</sub> by expanding isothermally at T<sub>1</sub> along AB and then expands adiabatically along BC to temperature T<sub>2</sub>. It is compressed isothermally at T<sub>2</sub> rejecting heat Q<sub>2</sub> along CD and is compressed adiabatically along DA. Its efficiency  $\eta$  is given by:

$$\eta = 1 \! - \! \frac{T_2}{T_1}$$



Figure 13.16

#### **Derivation of efficiency in Carnot engine:**



Figure 13.17: P-V diagram of the carnot cycle

#### **MASTERJEE CONCEPTS**

Try to prove that carnot engine is the most efficient one among all engines working in the same temperature range. You will come across a nice use of the second law of thermodynamics!

#### GV Abhinav (JEE 2012 AIR 329)

Process	w	q	ΔU	Δ <b>H</b>
I	$-nRT_{h} ln \left(\frac{V_{2}}{V_{1}}\right)$	$nRT_{h}In\left(\frac{V_{2}}{V_{1}}\right)$	0	0
11	$-n\overline{C}_{v}(T_{I}-T_{h})$	0	$n\overline{C}_v(T_l - T_h)$	$n\overline{C}_{p}(T_{I}-T_{h})$
111	$-nRT_{I}In\left(\frac{V_{4}}{V_{3}}\right)$	$nRT_{I}ln\left(\frac{V_{4}}{V_{3}}\right)$	0	0

Work, heat,  $\Delta$  U. and,  $\Delta$  H(nc<sub>n</sub> $\Delta$ T) in the P-V diagram of the Carnot Cycle.

Process	w	q	ΔU	ΔΗ
IV	$-n\overline{C}_{v}(T_{h}^{-}-T_{l}^{-})$	0	$n\overline{C}_v(T_h - T_l)$	$n\overline{C}_{p}(T_{h}-T_{l})$
Cycle	$-nRT_{h} ln \left(\frac{V_{2}}{V_{1}}\right) - nRT_{l} ln \left(\frac{V_{4}}{V_{3}}\right)$	$nRT_{h} ln\left(\frac{V_{2}}{V_{1}}\right) + nRT_{l} ln\left(\frac{V_{4}}{V_{3}}\right)$	0	0

The efficiency of the Carnot engine is defined as the ratio of the energy output to the energy input.

$$\begin{aligned} & \text{Efficiency} = \frac{\text{Net work done by heat engine}}{\text{Heat absorbed by heat engine}} = \frac{-\text{Wsys}}{q_h} = \frac{n\text{RT}_h \ln\left(\frac{V_2}{V_1}\right) + n\text{RT}_l\left(\frac{V_4}{V_3}\right)}{n\text{RT}_h \ln\left(\frac{V_2}{V_1}\right)} \end{aligned} \\ & \text{Since processes II (2-3) and IV (4-1) are adiabatic.} \left(\frac{T_2}{T_3}\right)^{C_V/R} = \frac{V_3}{V_2}, \text{and} \left(\frac{T_1}{T_4}\right)^{C_V/R} = \frac{V_4}{V_1} \end{aligned} \\ & \text{and since } T_1 = T_2 \text{ and } T_3 = T_4, \ \frac{V_3}{V_4} = \frac{V_2}{V_1} \end{aligned} \\ & \text{Therefore Efficiency} = \frac{n\text{RT}_h \ln\left(\frac{V_2}{V_1}\right) - n\text{RT}_l \ln\left(\frac{V_2}{V_1}\right)}{n\text{RT}_h \ln\left(\frac{V_2}{V_1}\right)}; \qquad \boxed{\text{Efficiency} = \frac{T_h - T_l}{T_h} = 1 - T_l / T_h} \end{aligned}$$

#### **MASTERJEE CONCEPTS**

- By the second law of thermodynamics we can say that, it is impossible to construct an engine, operating in a cycle, which will extract heat from a source and convert the whole of it into work. It implies that it is impossible to make heat flow from a colder body to a hotter body without the help of an external agency or an engine from outside.
- That efficiency of Carnot engine is maximum (not 100%) for given temperatures T<sub>1</sub> and T<sub>2</sub>. But still Carnot is not a practical engine because many ideal situations have been assumed while designing this engine which can practically not be obtained.

#### Anurag Saraf (JEE 2011 AIR 226)

**Illustration 18:** Carnot's engine takes in a thousand kilo calories of heat from a reservoir at 827°C and exhausts it to a sink at 27°C. How much work does it perform? What is the efficiency of the engine? (JEE MAIN)

Sol: 
$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$
 and for cannot cycle  $\eta = 1 - \frac{T_2}{T_1}$ , hence  $\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$   
Given,  $Q_1 = 10^6$  Cal  $T_1 = (827 + 273) = 1100$ K and  $T_2 = (27 + 273) = 300$ K

as, 
$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}$$
  $\therefore$   $Q_2 = \frac{T_2}{T_1}Q_1 = \left(\frac{300}{1100}\right)(10^6) = 2.72 \times 10^5 \text{ cal}$ 

Efficiency of the cycle, 
$$\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100$$
 or  $\eta = \left(1 - \frac{300}{1100}\right) \times 100 = 72.72\%$ 

### **PROBLEM-SOLVING TACTICS**

- (a) Most of the problems of  $T_{max}$ ,  $P_{max}$  and  $V_{max}$  are solved by differentiating. Sometimes the graph will be given and sometimes, the equation will be given. For problems of finding  $P_{max}$ , you will require either the P-V or P-T equation.
- (b) From the sections of thermodynamic, graphical questions are usually asked so one must have a thorough understanding of PV diagrams at least. It is generally advised to convert other graphs namely TV and PT graph to PV graph before solving to visualize it easily. Also in many cases we can directly get asked quantities like work done because it involves integration of area under the PV graph.
- (c) Silly mistakes must be avoided because there is not much variety in problems and not so much to think. Remember the following points:-
  - (i) Be very careful in signs of Q and W while solving questions of thermodynamics.
  - (ii) Be careful in noting the type of gas used in question whether it is monatomic or diatomic.
  - (iii) Be careful with units of given quantities and asked quantities.
  - (iv) You can list more from your personal experience.
- (d) It would be helpful to note keywords in a question (like noting down slow and fast changes because slow changes imply reversible change whereas fast change imply irreversible change).
- (e) It is always helpful to make a separate list of known quantities and asked quantities and then think of a way, a link between them.
- (f) Questions are mostly based on various reversible or irreversible processes which have their own set of formulae. And no more processes can be found other than these. Hence, these concepts must be strong and you should know the algorithm of each one thoroughly.

### FORMULAE SHEET

#### **Kinetic Theory of Gases**

$$PV = \frac{1}{3}nM_mV_{rms}^2 = nRT$$
  
Kinetic energy per mole of gas =  $E = \frac{1}{2}M_mV_{rms}^2 = \frac{3}{2}RT$ 

$$V_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3P}{\rho}}$$

$$\begin{split} V_{av} &= \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8P}{\pi \rho}} & \text{M is the molar mass in kilogram per mole.} \\ V_{mp} &= \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2P}{\rho}} & \text{V}_{mps} : V_{av} : V_{mps} : \sqrt{3} : \sqrt{\frac{8}{\pi}} : \sqrt{2} ; & V_{mps} : V_{av} : 1 : 1.224 : 1.28 & \text{The mean free path of a gas molecule is the average distance between two successive collisions. It is represented by $\lambda$.} \\ \lambda &= \frac{kT}{\sqrt{2\pi}d^2\rho} & \text{Here, } \begin{array}{l} \sigma = \text{Diameter of themolecule} \\ k = \text{Boltzmann's constant} \end{array} \end{split}$$

The	modynamics	
(a)	<b>Boyle's law:</b> According to this law, for a given mas of a gas the volume of a gas at constant temperature (called isothermal process) is inversely proportional to its pressure, i.e., $V \propto \frac{1}{p}$ (T = constant) or PV = constant	P T=constant V Figure 13.18
(b)	<b>Charle's law:</b> According to this law, for a given mass of a gas, the volume of a gas at constant pressure (called isobaric process) is directly proportional to its absolute temperature, i.e., $V \propto T$ (P= constant) or $\frac{V}{T}$ = constant	P=constant T(in K) Figure 13.19
(c)	<b>Gay Lussac's law or Pressure law:</b> According to this law, for a given mass of a gas the pressure of a gas at constant volume (called isochoric process) is directly proportional to its absolute temperature, i.e., $P \propto T$ (V= constant) or $\frac{P}{T}$ = constant	P V=constant T(in K) Figure 13.20
(d)	<b>Avogadro's law:</b> According to this law, at same temperature and pressure equal volumes of all gases contain equal number of molecules.	

Ideal gas equation	$PV = nRT  OR  \rho = \frac{PM}{RT}$
Degree of freedom of monoatomic gas	f = 3 (all translational)

Degree of freedom of a diatomic and linear polyatomic gas	f = 5 (3 translational + 2 rotational) at room temperatures and $f = 7(3 translational + 2 rotational + 2 vibrational) at high temperatures.$
Degree of freedom of nonlinear polyatomic gas	f = 6 (3 translational + 3 rotational) at room temperatures and $f = 8$ (3 translational + 3 rotational + 2 vibrational) at high temperatures.
Degree of freedom of solid	An atom in a solid has no degrees of freedom for translational and rotational motion. At high temperatures due to vibration along 3 axes it has $3 \times 2 = 6$ degrees of freedom. f = 6 (all vibrational) at high temperatures.

$$C = \frac{\Delta Q}{n\Delta T}$$
 or  $\Delta Q = nC\Delta T$ 

#### For a gas the value of C depends on the process through which its temperature is raised.

Types of gas	Degrees of freedom	Total energy	C <sub>p</sub>	C <sub>v</sub>	γ
Monoatomic	3	$\frac{3}{2}$ RT	$\frac{5}{2}R$	$\frac{3}{2}R$	1.67
Diatomic	5	$\frac{5}{2}$ RT	$\frac{7}{2}R$	$\frac{5}{2}R$	1.4
Polyatomic( $\geq 3$ )	6	3RT	4R	3R	1.33

Ratio of specific heat :- 
$$\gamma = \frac{C_P}{C_V} = \frac{f+2}{f}$$
  $\xrightarrow{\text{monoatomic}}$  5/3 = 1.67  
 $\frac{f}{f}$   $\frac{f+2}{f}$   $\frac{f}{f}$   $\frac{f+2}{f}$   $\frac{f+2}$ 

Note: C of a gas depends on the process of that gas, which can be infinite in types.

and  $f = \frac{2}{\gamma - 1}$ ;  $C_v = \frac{R}{\gamma - 1}$ ;  $C_p = \frac{\gamma R}{\gamma - 1}$ 

Often the first law must be used in its differential form, which is dU = dQ - dW

This can also be written as dQ = dU + dW

 $\Delta$  Q is +ve for heat supplied

 $\Delta$  Q is -ve for heat rejected

1.  $\Delta W = +ve$  for work done by the gas (in expansion of gas)

 $\Delta$  W = -ve for work done on the gas (in contraction of gas)

- 2. For change in internal energy of the gas, apply  $\Delta U = nC_v \Delta T$  or in differential form,  $dU = nC_v dt = \frac{f}{2}nRdT$
- 3. For heat transfer, apply  $Q = nC\Delta T$

or in differential form dQ = nCdT dW = PdV $W = \int dW = \int_{V_i}^{V_f} PdV$  = Area under P-V curve

Isothermal	Q = W	0	$nRT \ln\left(\frac{V_{f}}{V_{i}}\right) = nRT \ln\left(\frac{P_{i}}{P_{f}}\right)$
Adiabatic	0	nC <sub>v</sub> ΔT	$\frac{P_i V_i - P_f V_f}{\gamma - 1} = -\Delta = \frac{nR\Delta T}{\gamma - 1}$
Isobaric	nC <sub>p</sub> ΔT	nC <sub>v</sub> ΔT	$P(V_f - V_i)$
Isochoric	$Q = \Delta U$ = nC <sub>V</sub> $\Delta T$	nC <sub>v</sub> ΔT	0

$$(Slope)_{isothermal} = -\frac{P}{V}$$
  $(Slope)_{adiabatic} = -\gamma \left(\frac{P}{V}\right)$ 

 $T_1$ 

$$\eta = \begin{pmatrix} \text{Work done by the working substance} \\ \frac{(\text{an ideal gas in our case}) \text{ during a cycle}}{\text{Heat supplied to the gas during the cycle}} \end{pmatrix} \times 100 = \frac{W_{\text{Total}}}{Q_{+\text{ve}}} \times 100 = \left\{ 1 - \left| \frac{Q_{-\text{ve}}}{Q_{+\text{ve}}} \right| \right\} \times 100$$
For Carnot Engine:  $\eta = 1 - \frac{T_2}{T_1}$ 

### **Solved Examples**

### **JEE Main/Boards**

**Example 1:** An electric bulb of volume 250cm<sup>3</sup> was sealed off during manufacture at the pressure of 10<sup>-3</sup>mm of Hg at 27°C. Find the number of air molecules in the bulb.

**Sol:** 
$$PV = \frac{N}{A}RT = N\frac{R}{A}T = NkT$$

Let N be the number of air molecules in the bulb.

$$V_1 = 250 \text{ cm}^3$$
,  $P_1 = 10^{-3} \text{ mm of Hg}$ ,

$$T_1 = 273 + 27 = 300^{\circ}K$$

As  $P_1V_1 = NkT$  where k is constant, then

At N.T.P., one mole of air occupies a volume of 22.4 litre,

 $V_0 = 22400 \text{ cm}^3$ ,  $P_0 = 760 \text{ mm of Hg}$ ,

T = 273° K and N<sub>0</sub> =  $6 \times 10^{23}$  molecules

$$\therefore 760 \times 22400 = 6x10^{23} \times k \times 273$$
 ... (ii)

Dividing equation (i) by equation (ii), we get

$$\frac{10^{-3} \times 250}{760 \times 22400} = \frac{N \times 300}{6 \times 10^{23} \times 273}$$

$$N = \frac{10^{-3} \times 250 \times 6 \times 10^{23} \times 273}{760 \times 22400 \times 300} = 8.02 \times 10^{15} \text{ mole}$$

Example 2: One gram-mole of oxygen at 27°C and one atmospheric pressure is enclosed in a vessel.

(a) Assuming the molecules to be moving with  $V_{rms}$ , find the number of collisions per second which molecules make with one square meter area of the vessel wall.

(b) The vessel is next thermally insulated and moved with a constant speed  $v_0$ . It is then suddenly stopped.

The process results in a rise of the temperature of the gas by 1°C. Calculate the speed  $v_0$ .

**Sol:** Formula based:  $n = \frac{P}{kT} \& V_{rms} = \sqrt{\frac{3N_AkT}{M_p}}$ . Recall

the assumption of KTG. Kinetic energy changed to internal energy.