

2nd Chapter

Thermodynamic Fundamentals and First law

Heat:

Heat is a nonmechanical exchange of energy between the system and the surroundings because of their temperature difference. It is also defined as internal energy or energy in transit.

Work:

In thermodynamics, the work is the quantity of energy transferred from one system to another.

$$W_b + \theta_b = 0_b$$

Relation between heat and work

Heat and work are two different ways of transferring energy from one system to another. Heat is the transfer of thermal energy between systems, while work is transfer of mechanical energy between two systems.

The relation between heat and work can be ~~seen~~ ^{get} by the first law of thermodynamics. First law states that the change in the amount of heat transferred by a system is the sum of increase in internal energy and amount of work done by the system.

Then if dQ amount of heat is transferred by the system and dW amount of work is done by increasing the amount of internal energy then,

$$dQ = dU + dW$$

Surrounding :

Anything outside system which can exchange energy with it and has a direct bearing on the behaviour of the system is called its surrounding. A system may be separated from its surroundings by a real or imaginary boundary through which heat or mechanical energy may pass. A thermodynamic system may contain no substance at all, but may consists of radiant energy or electric and magnetic field.

Universe :

The combination of a system and its surroundings is called an universe.

Thermodynamic walls / walls : (1st chapter)

Intensive properties :

An intensive property is a physical quantity whose value does not depend on the amount of the substance which it is measured.

Example - Pressure, density, concentration, temperature.

Extensive property:

An extensive property is a physical quantity whose value depends on the amount of the substance which it is measured.

Example - Volume, mass, enthalpy

Thermodynamic variables and equation of state:

The equation of state of the system is determined completely by the three variables. Pressure (P), Volume (V),

Temperature (T) .

For a system, in general there is an equation of state,

$$f(P, V, T) = 0$$

Therefore the pressure, volume, temperature, are not independent.

Then equation of state for an ideal gas,

$$PV = nRT$$

For van der waals equation of state is,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT ,$$

where, a and b are van der waals constant.

Limitation of equation of state :

- (i) The equation of state is not applicable to system which are not in thermodynamic equilibrium.
- (ii) Every thermodynamic system has its own equation of state independent of the others.
- (iii) An equation of state express the peculiar behaviour of one individual system which distinguishes it from the others.
- (iv) An equation of state is not a theoretical deduction from thermodynamics but is an experimental backing to it.

Thermodynamic equilibrium :

Any state of homogeneous system in which any two of the three variables P , V and T remain constant as long as the external conditions remain unchanged is said to be in thermodynamic equilibrium.

- (i) Mechanical equilibrium : For a system to be in mechanical equilibrium, there should be no microscopic movement within the system (i.e; no unbalanced force acting) or of the system with respect to its surroundings .

(ii) Thermal equilibrium: For a system to be in thermal equilibrium, there should be no temperature difference between the parts of the system or between the system and the surrounding.

(iii) Chemical equilibrium: For a system to be in chemical equilibrium there should be no chemical reaction within the system and also no movement of any chemical constituent from one part of the system to the other part.

(iv) Diffusive equilibrium: A ^{equilibrium} chemical is said to be diffusive equilibrium when the temperature are equal and their chemical potentials are same.

(v) Phase equilibrium: A equilibrium is said to be ^{in phase} in phase equilibrium when their chemical potential do not change with temperature;

$$\mu_{\text{ice}}(T_m, P) = \mu_{\text{liquid}}(T_m, P)$$

and particles from one phase can go to other phase without any energy change.

• When temperature of two phases

■ Non-Equilibrium thermodynamic:

Non-equilibrium thermodynamics is a branch of thermodynamics that deals with physical systems that are not in thermodynamic equilibrium but can be described in terms of variables (non-equilibrium state of variables) that represents an extrapolation of the variables used to specify the system in thermodynamic equilibrium.

■ Thermodynamic:

Thermodynamics is the study of movement of heat, which is the motion of molecules.

■ Thermodynamic process:

A thermodynamic process is any process that involves heat energy moving within a system or between the system.

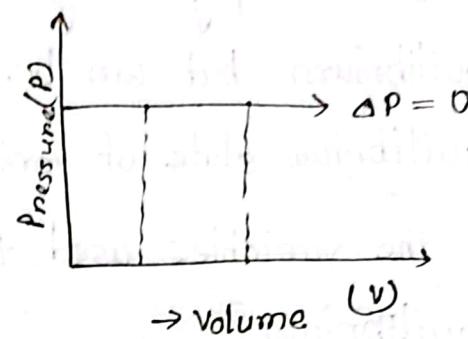
Different types of thermodynamic process —

• (i) reversible

(i) Isobaric process: An isobaric process is a thermodynamic process in which the pressure stay constant. $\Delta P = 0$

Suppose, Q is the heat absorbed by a system at constant pressure P and suppose its volume increases from V_1 to V_2 . Then we have,

$$\begin{aligned} Q &= (U_2 - U_1) + W \\ &= (U_2 - U_1) + P(V_2 - V_1) \\ &= (U_2 + PV_2) - (U_1 + PV_1) \\ &= H_2 - H_1 \end{aligned}$$

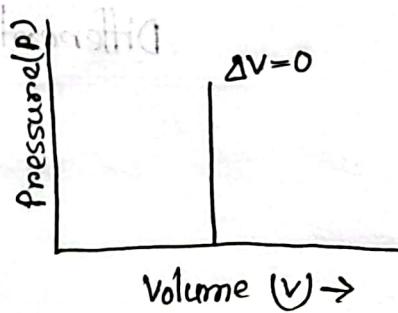


Here, $H = U + PV$

Here, H is the enthalpy of the system. Enthalpy is a property of a system and is defined as the sum of the systems internal energy and the product of its pressure and volume. H is also called heat function.

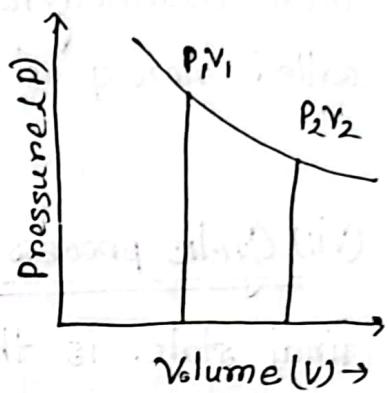
(ii) Isochoric process: An isochoric process is a thermodynamic process in which the volume remains constant. $\Delta V = 0$

It is also called isovolumetric process or isometric process. At constant volume, no external work is done. i.e; $\delta W = 0$



\therefore Heat absorbed is given by, $\delta Q = dU$.

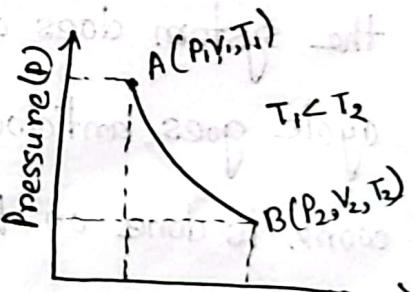
(ii) Isothermal process: An isothermal process is a thermodynamic process in which the temperature of the system remain constant $\therefore \Delta T = 0$. Example: The melting of ice of zero degree. In isothermal process, for an ideal gas, the product of pressure and volume is constant, $PV = \text{constant}$. This is known as Boyle's law.



(iv) Adiabatic process: An adiabatic process is a thermodynamic process in which there is no heat transfer from in or out of the system, $\therefore \Delta Q = 0$. Example: The vertical flow of air in the atmosphere.

$$PV^\gamma = \text{constant}$$

In adiabatic compression internal energy increases of a system and expansion internal energy decreases and the process take place suddenly or quickly.



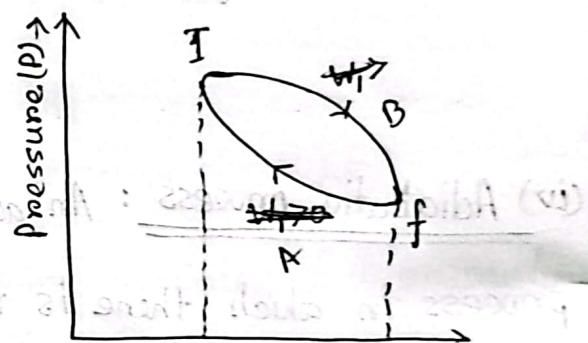
(v) Quasi-static process: Quasi-static process is one that take places so slowly that the system may be considered as passing through a succession of equilibrium state. (Reversible)

(vi) Non-quasi-static process : If a process is carried out in such a way that at every instant the system departs finitely from thermodynamic equilibrium state , such process is called non quasi - static process . [irreversible]

(vii) Cyclic process : The process in which the initial and the final state is the same is known as a cyclic process .

⇒ It is a sequence of process which leaves the in the same state in which it started.

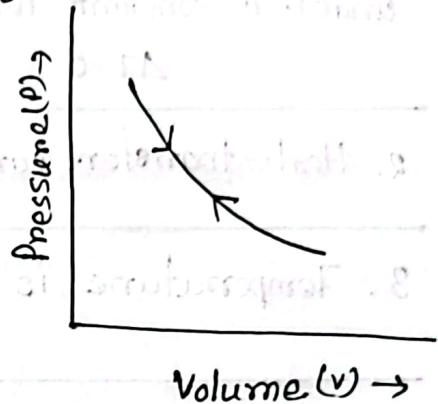
⇒ If the cycle goes clockwise, the system does work, If the cycle goes anticlockwise , then the work is done on the system every cycle.



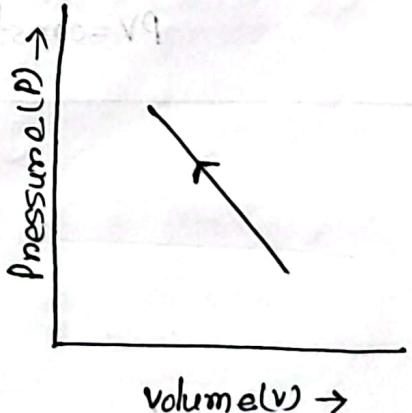
⇒ In non-cyclic process the series of changes involved do not return the system back to its original state .

(viii) Reversible process: A process in which the system and surrounding can be returned to the original conditions from the final state without producing any changes in the thermodynamic properties of the universe, if the process reversed.

Example: Current flows through a conductor with resistance.



(ix) Irreversible process: An irreversible process is a process in which both the system and surroundings do not return to their original conditions once the process is initiated.



Example : Transfer of heat from a hot object to a cold object.

Difference between Isothermal and adiabatic process:

| Isothermal | Adiabatic |
|--|---|
| 1. Isothermal process occurs under a constant temperature, $\Delta T=0$ | 1. Adiabatic process occurs under a constant heat, $\Delta Q=0$ |
| 2. Heat transfer can be observed. | 2. There is no heat transfer. |
| 3. Temperature is constant | 3. Temperature is not constant and can be changed |
| 4. Work done is due to the change in the net heat content of the system. | 4. Work done is due to the change in it's internal energy. |
| 5. In isothermal process, $PV=constant$ | 5. In adiabatic process, $PV^\gamma=constant$ |

Difference between reversible process and irreversible process:

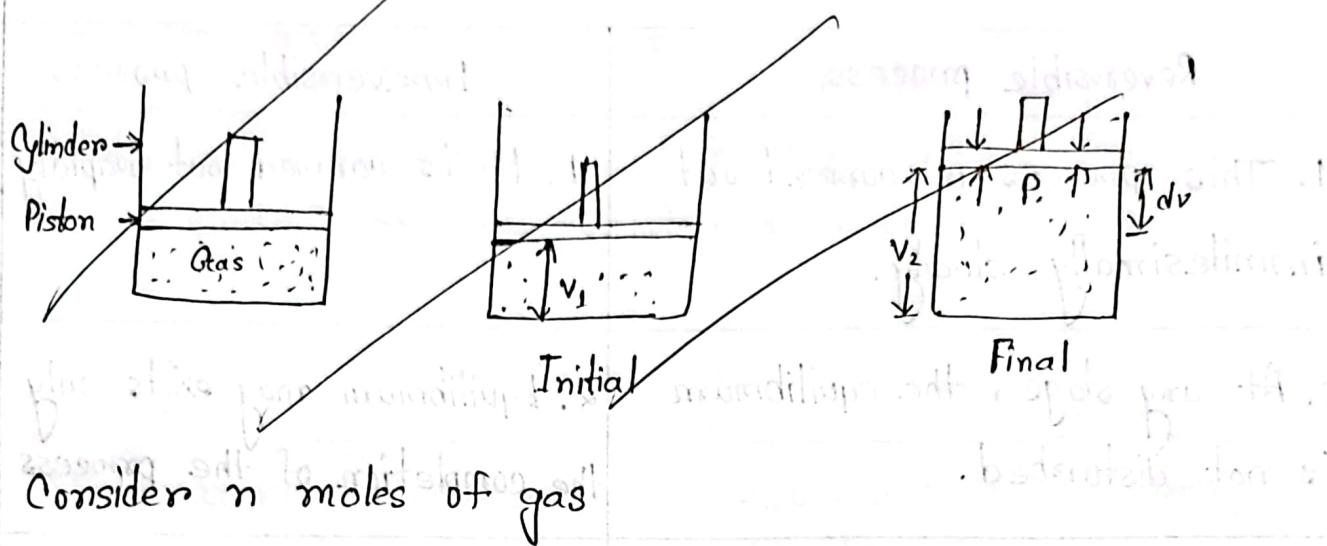
| Reversible process | Irreversible process |
|--|--|
| 1. This process is carried out infinitesimally slowly. | 1. It is carried out rapidly. |
| 2. At any stage, the equilibrium is not disturbed. | 2. Equilibrium may exists only after the completion of the process |
| 3. It takes infinite time for completion. | 3. It takes finite time for completion. |
| 4. Work obtained in this process is maximum. | 4. Work obtained in this process is not maximum. |
| 5. It is an ideal process. | 5. It is a real process. |

A \leftrightarrow A'

B \rightarrow

C \rightarrow

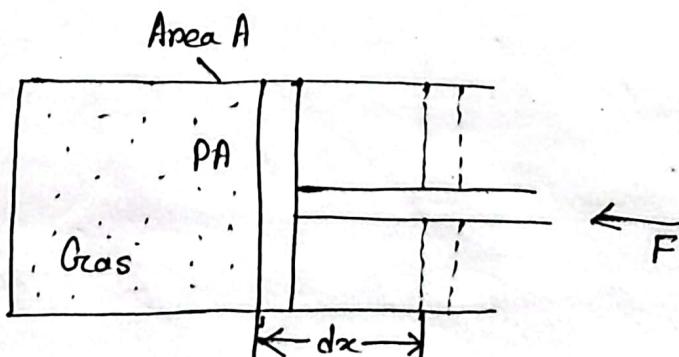
Work done in isothermal reversible process :



Consider n moles of gas

Work done in reversible process :

Suppose that a gas in the initial equilibrium state (P_1, v_1) is compressed to a new equilibrium state (P_2, v_2) by increasing the external force on the piston and allowing it to slide in.



Let at one of the intermediate equilibrium states during the reversible compression, the pressure P and the balancing force on the piston is F . Then,

$$F = PA$$

where, A is the area of the piston. If the force is increased infinitesimally so that the piston moves in by dx , the work done on the gas by surroundings applying the force F is,

$$dW = F dx$$

$$= PA dx$$

$$\therefore dW = -P dV \text{ (reversible)} [\because Adx = dv] \quad (1)$$

The minus sign in equation (1) indicates that during compression the volume is decreased, but work done on the gas is positive. The total work performed on the gas in the process is,

$$W = - \int_{V_1}^{V_2} P dV \text{ (reversible)} \quad (2)$$

This result is true for reversible processes.

By ideal gas equation,

$$\Rightarrow P = \frac{nRT}{V}$$

From equation (2),

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$\Rightarrow W = -nRT \int_{V_1}^{V_2} \frac{dv}{v}$$

$$= -nRT \left[\ln v \right]_{V_1}^{V_2}$$

$$\therefore W = -nRT \ln \left| \frac{V_2}{V_1} \right| \quad \text{--- (3)}$$

In terms of pressure -

For an isothermal expansion Boyle's law is applicable.

$$P_1 V_1 = P_2 V_2$$

$$\Rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

From equation (3) ,

$$W = -nRT \ln \left| \frac{P_1}{P_2} \right| \quad \text{--- (4)}$$

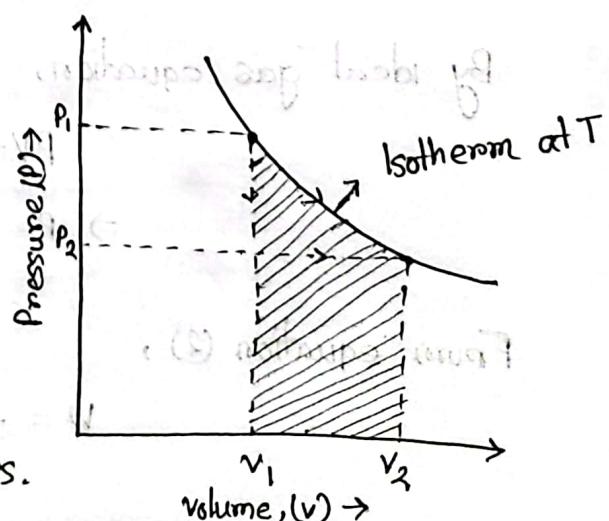
$$= -2.303 nRT \log \frac{P_1}{P_2} \quad \text{--- (5)}$$

Equation (3) , (4) and (5) all indicates the work done in isothermal reversible process .

$V_2 > V_1$ and so $\ln \left(\frac{V_2}{V_1} \right) > 0$ and the work done on the gas is negative .

Because in expansion the gas does positive work on its surroundings. If the gas is compressed from volume V_1 to V_2 then $V_2 < V_1$ and $\ln \left(\frac{V_2}{V_1} \right) < 0$, and the work done on the gas is positive , as it must be for compression.

In graph the shaded part is the workdone in isothermal reversible process.



E Work done in isothermal irreversible process :
Small work done in expansion process, with external pressure,

$$dW = -P_{ext} dV \quad \text{--- (1)}$$

Integrating from V_1 to V_2 ,

$$W = \int dW = \int_{V_1}^{V_2} -P_{ext} dV \quad \text{--- (2)}$$

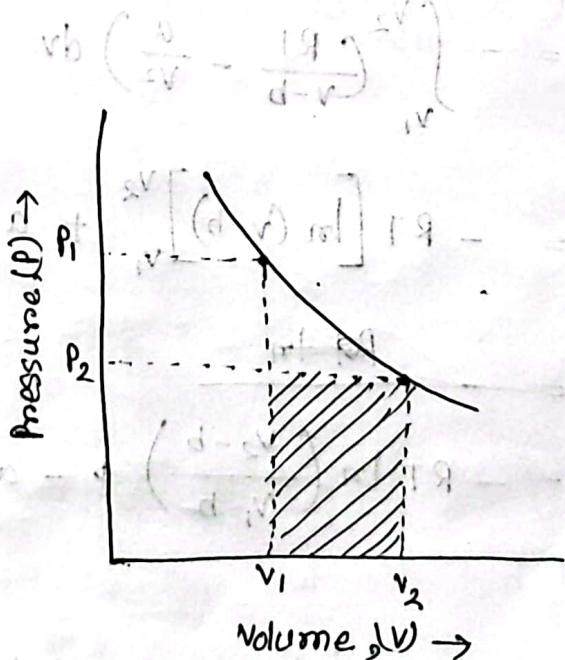
In irreversible process, external pressure is constant,

$$P_{ext} = \text{constant}$$

$$\therefore W = -P_{ext} (V_2 - V_1)$$

$$= -P_{ext} \Delta V$$

This is the work done in isothermal irreversible process.



Shaded part is work done in isothermal irreversible process.

Q Calculate the work done for vander Waal's gas in isothermal reversible process.

→ The work done on gas by increasing external pressure in isothermal reversible process during compression is,

$$W = - \int_{v_1}^{v_2} P_{ext} dv \quad (1)$$

Now For Van der Waal's gas we know, for 1 mole gas,

$$\left(P + \frac{a}{v^2} \right) (v - b) = RT$$

$$\Rightarrow P = \frac{RT}{v-b} - \frac{a}{v^2} \quad (2)$$

From (1) and (2),

$$\begin{aligned} W &= - \int_{v_1}^{v_2} \left(\frac{RT}{v-b} - \frac{a}{v^2} \right) dv \\ &= - RT \left[\ln(v-b) \right]_{v_1}^{v_2} + a \left[\frac{-1}{v} \right]_{v_1}^{v_2} \\ &\quad \cancel{- R \ln} \\ &= - RT \ln \left(\frac{v_2-b}{v_1-b} \right) + a \left(\frac{1}{v_2} - \frac{1}{v_1} \right) \end{aligned}$$

For n mole,

$$W = - nRT \ln \left(\frac{v_2-b}{v_1-b} \right) - an^2 \left(\frac{1}{v_2} - \frac{1}{v_1} \right)$$

This is the work done for vanderwaal's gas.

EJ Work done in isothermal process :

When a gas is allowed to expand isothermally, work is done by it.

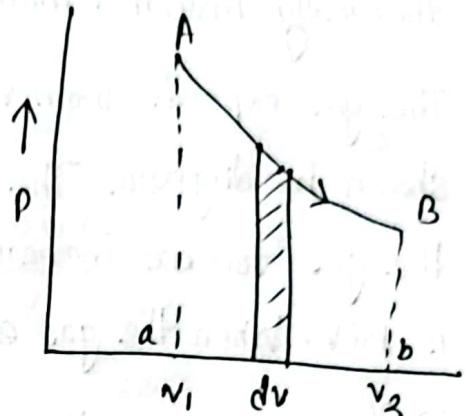
Let the initial and final volumes be v_1 and

v_2 respectively. The area shaded strip

represents the work done for a small change

in volume dv . For change in v_1 to v_2 ,

$$\text{Work done} = \int_{v_1}^{v_2} PdV = \text{area } ABba$$



Considering one gram molecules of the gas,

$$PV = RT$$

$$\Rightarrow P = \frac{RT}{V}$$

$$\therefore W = RT \int_{v_1}^{v_2} \frac{dv}{V}$$

$$= RT \times \ln \frac{v_2}{v_1} = RT \times 2.303 \log_{10} \left(\frac{v_2}{v_1} \right)$$

$$\text{Also, } P_1 V_1 = P_2 V_2$$

$$\Rightarrow \frac{P_1}{P_2} = \frac{V_2}{V_1}$$

$$\therefore W = 2.303 RT \log_{10} \left(\frac{P_1}{P_2} \right)$$

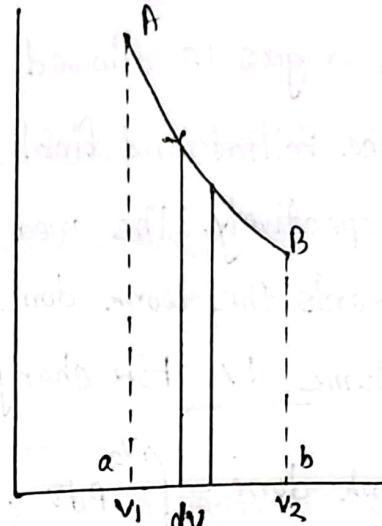
Here, the change in internal energy of the system is zero as the temperature is constant. So the heat absorbed by the system is equal to the work done by it.

Work done during an adiabatic process :

During an adiabatic process, the system is thermally insulated from the surroundings.

The gas expands from volume v_1 to v_2 as shown in diagram. The work done by the gas for an increase in volume dv is Pdv . When the gas expands from v_1 to v_2 ,

$$W = \int_{v_1}^{v_2} Pdv$$



During an adiabatic process,

$$PV^\gamma = \text{constant} = K$$

$$\Rightarrow P = \frac{K}{V^\gamma} \quad \text{--- (II)}$$

\therefore From (I) and (II),

$$W = K \int_{v_1}^{v_2} \frac{dv}{V^\gamma}$$

$$= K \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{v_1}^{v_2}$$

$$= \frac{K}{1-\gamma} \left[\frac{1}{V^{\gamma-1}} \right]_{v_1}^{v_2}$$

$$= \frac{K}{1-\gamma} \left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right]$$

Since A and B lies on the same adiabatic,

$$P_1 V_1^\gamma = P_2 V_2^\gamma = k$$

From (3),

$$\begin{aligned} W &= \frac{1}{1-\gamma} \left[\frac{k}{V_2^{\gamma-1}} - \frac{k}{V_1^{\gamma-1}} \right] \\ &= \frac{1}{1-\gamma} \left[\frac{P_2 V_2^\gamma}{V_2^{\gamma-1}} - \frac{P_1 V_1^\gamma}{V_1^{\gamma-1}} \right] \\ &= \frac{1}{1-\gamma} (P_2 V_2 - P_1 V_1) \quad \text{--- (4)} \end{aligned}$$

Taking T_1 and T_2 as the temperatures at points A and B respectively and considering one gram molecule of the gas,

$$P_1 V_1 = R T_1$$

$$P_2 V_2 = R T_2$$

Substituting the value in equation (4),

$$W = \frac{1}{1-\gamma} (R T_2 - R T_1)$$

$$\therefore W = \frac{R}{1-\gamma} (T_2 - T_1) \quad \text{--- (5)}$$

Hence the work done in adiabatic process depends only upon initial and final temperatures. Thus work done along any adiabatic between two isothermals is independent of the particular adiabatic.

Slope of Adiabatic and isothermals :

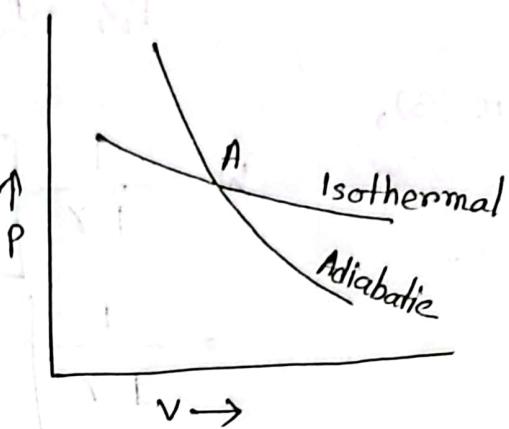
In an isothermal process,

$$PV = \text{constant}$$

Differentiating,

$$PdV + VdP = 0$$

$$\Rightarrow \frac{dP}{dV} = -\frac{P}{V} \quad \underline{(1)}$$



In an adiabatic process,

$$PV^\gamma = \text{constant}$$

Differentiating,

$$PV^{\gamma-1}dV + V^\gamma dP = 0$$

$$\Rightarrow \frac{dP}{dV} = -\frac{\gamma P}{V} \quad \underline{(2)}$$

From (1) and (2) we can say that the slope $\left(\frac{dP}{dV}\right)$ of an adiabatic is γ times the slope of the isothermal.

State function :

A state function is a property of a system whose value does not depend on the path taken to reach the specific value. It depends only on the state of the system.

Example - mass, pressure, density, energy etc.

Non state function / Path function:

Depends on the path.

Example - Heat, work.

First law of thermodynamics :

When a certain amount of heat Q is supplied to a system which does external work W in passing from one state to another state, the amount of heat Q is equal to the sum of the increase in the internal energy of the system and the work done by the system. Then, the law is expressed as,

$$Q = (U_2 - U_1) + W$$

The differential form is,

$$dQ = dU + dW$$

■ Significance of the first law:

- (i) It is applicable to any process by which a system undergoes a physical or chemical change.
- (ii) It introduces the concept of the internal energy.
- (iii) It provides method for determining the change in the internal energy.
- (iv) First law defined 3 things - Internal energy, heat, conservation of energy.

■ Limitation of 1st law:

The first law of thermodynamics is based on the principle of conservation of energy of a system. Though it is applicable to every process in nature between the equilibrium states, it does not specify the condition under which a system can use its heat energy to produce a supply of mechanical work. It also does not say how much of the heat energy can be converted into work.

$$W_b + Q_b = Q_b$$

■ zeroth law of thermodynamics :

[1st chapter]

■ Significance of zeroth law -

This law signifies that temperature is a fundamental indicator of thermal equilibrium. If two bodies of same temperature come in contact with each other there is no net exchange of heat and those bodies are said to be in thermal equilibrium. It gives the definition of temperature.

■ Limitations of zeroth law -

zeroth law of thermodynamics only tells us about equality of temperature. It does not give any clue how the heat is being transferred. It does not speak of energy conservation. zeroth law only helps in the calibration of thermometers.

$$W - Q = (U_2 - U_1)$$

With all the states in system connected with each other

2 state at different temperatures

Q1 Internal energy :

The energy content of a system is called its internal energy. It is the sum of following form of energy of the system.

- (i) kinetic energy due to translational, rotational and vibrational motion of the molecules, all of which depends only on the temperature.
- (ii) Potential energy due to measure the intermolecular forces, which depends on the separation between the molecules.
- (iii) the energy of electrons and nuclei.

In practice, it is not possible to measure the total internal energy of a system in any given state. Only change in its value can be measured.

If the state of the system is changed from an initial state 1 to final state 2 by supplying heat Q to the system and if W is the work done, then increase in the internal energy of the system is given by,

$$(U_2 - U_1) = Q - W$$

where U_1 is the internal energy in state 1 and U_2 the internal energy in state 2.

Internal energy for ideal (perfect) gas:

For an ideal gas, the internal energy is only kinetic energy of its molecules. It is proportional to kT and hence only depends upon temperature (T), k being Boltzmann constant. The internal energy of a perfect gas is independent of its volume and only depend on temperature.

Internal energy for real gas:

For a real gas, say a gas obeying Van der Waal's equation, the internal energy is the sum of the kinetic and potential energies of molecules due to their mutual forces of attraction. The force of attraction between the molecules depends upon the intermolecular distance and is thus a function of volume. Hence for a real gas, internal energy is a function of both, the temperature and volume.

out resulted Δ_{in} is not same as $(W-Q)$ answer but

~~Q~~ Internal energy does not depend on path / Internal energy as a state function :

→ Suppose Q is the heat supplied to a working substance and

W is the work done by it in taking the system from state 1 to state 2. then increase in

internal energy,

$$(U_2 - U_1) = Q - W$$

$$\Rightarrow Q = (U_2 - U_1) + W \quad (1)$$

If the state of the system is changed from the same initial state 1 to same final state 2 by different paths

B and C we have,

For path B,

$$Q_B = (U_2 - U_1) + W_B \quad (2)$$

For path C,

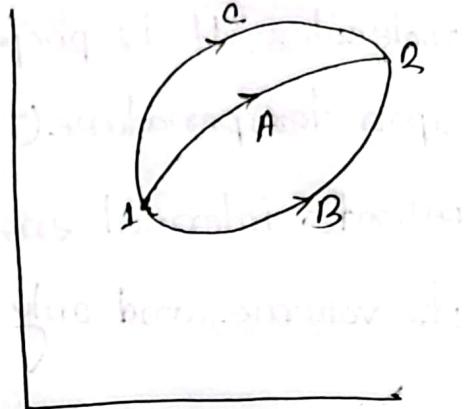
$$Q_C = (U_2 - U_1) + W_C \quad (3)$$

From (2) and (3),

$$Q_B + Q_C = W_B + W_C$$

$$\Rightarrow Q_B - W_B = Q_C - W_C$$

That means $(Q - W)$ is same for all path between two,



states.

Thus when a system changes from one state to another, the change of internal energy of the system has a definite value, independent of the paths between the two states.

Hence internal energy is called as state function or independent of path.

Heat capacity:

Heat capacity of a body is defined as the amount of heat absorbed or rejected to change the temperature by one unit.

If a material of mass m absorbs heat Q , so that its temperature rises through ΔT ,

$$\text{Heat capacity} = \frac{Q}{\Delta T}$$

$$\text{or } S = \frac{dQ}{dT}$$

$$q \left(\frac{\partial Q}{\partial T} \right)_D = q$$

$$[\text{where } q = \left(\frac{\partial Q}{\partial T} \right)_D \text{ is } q \text{ in D's work}]$$

■ Molar specific heat :

The molar specific heat is the amount of energy that is required to increase the temperature of one mole of substance by one unit.

$$C = \frac{S}{m} = \frac{1}{m} \frac{dQ}{dT}$$

where m = mole.

$$\text{Or, } C = \frac{Q}{m \cdot \Delta T}$$

A gas has two types of specific heat -

(i) Molar specific heat at constant pressure, C_p

(ii) Molar specific heat at constant volume, C_v

[molar अर्थात् definition - a unit mass के लिये एक एक मोल]

■ ~~Molar~~ specific heat at constant pressure, C_p :

It is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1°C , when its pressure is kept constant. It is represented by C_p and is given by,

$$C_p = \left(\frac{dQ}{dT} \right)_p$$

$$\text{When molar } C_p = \frac{1}{m} \left(\frac{dQ}{dT} \right)_p \quad [m = \text{mole}]$$

◻ Specific heat at constant volume (C_V):

It is defined as the amount of heat required to raise the temperature of unit mass of a gas through 1°C . when its volume is kept constant. It is represented by C_V and is given by,

$$C_V = \left(\frac{dQ}{dT}\right)_V$$

In mole, $C_V = \frac{1}{m} \left(\frac{dQ}{dT}\right)_V$

where $m = \text{mole}$

(v) similarly tends to zero as to do.

◻ C_P is greater than C_V :

Heat capacity of a gas is different under these two conditions.

Let heat is supplied to a gas and is allowed to expand at constant pressure. The heat is used up in doing two things

(i) it raises the temperature of the gas (i.e; increase in its internal energy)

(ii) it does work in expanding the gas against the external pressure.

$$\textcircled{1} \quad dQ = dU + dW$$

$$\Rightarrow dQ = dU + PdV$$

On the other hand, when gas is heated at constant volume, no work is done ($dW = PdV = 0$) and hence whole heat supplied is used to raise its temperature. Thus more heat is required for increasing in temperature of the gas through 1°C at constant pressure than at constant volume. Hence specific heat of a gas at constant pressure (C_p) is greater than the specific heat ~~at~~ of a gas at constant volume (C_v).

$$\text{i.e;} \quad C_p > C_v$$

~~conditions such that work done by the system is zero~~

~~General equation between two specific heats C_p and C_v :~~

The internal energy of a system is a single valued function of the state variable, pressure, volume, temperature etc. In this case of gas any two variables P, V, T are sufficiently to define its state! If V and T are chosen as independent variables,

$$U = f(V, T) \quad \text{--- (1)}$$

$$V, T \rightarrow \text{Work} = PdV$$

Differentiating U we get,

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (2)$$

According to 1st law of thermodynamics,

$$\begin{aligned} dQ &= dU + dW \\ \Rightarrow dQ &= dU + PdV \end{aligned}$$

Substituting the value of dU in equation (2),

$$dQ - PdV = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \quad (3)$$

Dividing by dT ,

$$\begin{aligned} \frac{dQ}{dT} &= \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{\partial V}{\partial T} + P \frac{\partial V}{\partial T} \\ \Rightarrow \frac{dQ}{dT} &= \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \frac{\partial V}{\partial T} \end{aligned} \quad (4)$$

If the gas is heated at constant volume, $dV=0$ and $\frac{dV}{dT}=0$

and, $\left(\frac{\partial Q}{\partial T}\right)_V = C_V$

From (4),

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (5)$$

And when the gas is heated at constant pressure,

$$dP=0 \quad \text{and} \quad C_P = \left(\frac{\partial Q}{\partial T}\right)_P$$

From (4),

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow C_p = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P \quad [\text{From (5)}]$$

$$\therefore C_p - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \cdot \left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (6)}$$

~~Eqn~~
This is the general equation between two specific heats, and relation between C_p and C_V .

From Joule's experiment, for an ideal gas gas on opening the stopcock, no work was done and no heat transfer took place.

$$dQ = Q_T = dU = 0$$

Or $dU = 0$ so no change in internal energy

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0$$

~~E~~ For ideal gas deduce $C_p - C_v$:

⇒ We have the relation,

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \quad \text{--- (1)}$$

For ideal gas of one mole,

$$PV = RT$$

At constant Pressure differentiating, w.r.t T

$$P \left(\frac{\partial V}{\partial T} \right)_P = R$$

$$\Rightarrow \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} \quad \text{--- (2)}$$

From equation (1),

$$C_p - C_v = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \frac{R}{P} \quad \text{--- (3)}$$

At constant temperature for ideal gas change is internal energy is zero,

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

∴ From (3),

$$C_p - C_v = \left[P + 0 \right] \frac{R}{P}$$

$$\therefore C_p - C_v = R$$

This formula is known as Mayer's relation.

~~Q~~ For van der Waal's gas deduce $C_p - C_V$:

→ We have the relation,

$$C_p - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P \quad (1)$$

and,

$$\left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] = T \left(\frac{\partial P}{\partial T} \right)_V \quad (2)$$

From (1) and (2),

$$C_p - C_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_P \quad (3)$$

For Van der Waal's gas or real gas,

$$\left(P + \frac{a^2}{V^2} \right) (V - b) = RT \quad (4)$$

Differentiating (4) with respect to T keeping P as constant

$$0 + \left(-\frac{2a^2}{V^3} \right) \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{(V-b)} + \frac{-RT}{(V-b)^2} \left(\frac{\partial V}{\partial T} \right)_P$$

$$\Rightarrow -\frac{2a^2}{V^3} \left(\frac{\partial V}{\partial T} \right)_P + \frac{RT}{(V-b)^2} \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{V-b}$$

$$\Rightarrow \left(\frac{\partial V}{\partial T} \right)_P \left[\frac{RT}{(V-b)^2} - \frac{2a^2}{V^3} \right] = \frac{R}{V-b}$$

$$\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P - \frac{RT}{(v-b)^2} \left[1 - \frac{(v-b)^2 2a}{RTv^3} \right] = \frac{R}{v-b}$$

$$\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P \left[1 - \frac{2a(v-b)^2}{RTv^3} \right] = \frac{v-b}{T}$$

$$\Rightarrow + \left(\frac{\partial v}{\partial T}\right)_P = \frac{(v-b)}{\left[1 - \frac{2a(v-b)^2}{RTv^3} \right]} \quad (5)$$

When volume v is constant,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{v-b} \quad (6)$$

Putting this in equation 3,

$$C_p - C_V = \frac{R}{(v-b)} \times \frac{(v-b)}{\left[1 - \frac{2a(v-b)^2}{RTv^3} \right]}$$

$$\Rightarrow C_p - C_V = \frac{R}{\left[1 - \frac{2a(v-b)^2}{RTv^3} \right]} = \frac{R}{b}$$

When b is very small then $v-b \approx v$

$$\therefore C_p - C_V = \frac{R}{\left[1 - \frac{2av^2}{RTv^3} \right]} = R \frac{R}{\left[1 - \frac{2a}{RTv} \right]} = R \left[1 + \frac{2a}{RTv} \right]$$

A

Q Adiabatic equation of a perfect gas :

Prove that, (i) $PV^\gamma = \text{constant}$

(ii) $TV^{\gamma-1} = \text{constant}$

(iii) $T P^{\{(1-\gamma)/\gamma\}} = \text{constant} / \frac{P^{\gamma-1}}{T^\gamma} = \text{constant}$

(i) Prove that $PV^\gamma = \text{constant} \rightarrow$

Consider 1 gram of working substance perfectly insulated from the surroundings. Let the external work done by the gas,

$$dW = PdV \quad [\because dQ = 0]$$

Applying the first law of thermodynamics,

$$dQ = dU + PdV \quad (1)$$

Specific heat at constant volume,

$$C_V = \left(\frac{dU}{dT}\right)_V$$

$$\Rightarrow dU = C_V dT \quad (2)$$

From equation (1),

$$dQ = C_V dT + PdV \quad (3)$$

For ideal gas, $PV = RT$

$$\Rightarrow PdV + VdP = RdT$$

$$\Rightarrow PdV = RdT - VdP \quad (4)$$

From equation (3) and (4),

$$\begin{aligned} dQ &= C_v dT + R dT - v dP \\ &= (C_v + R) dT - v dP \end{aligned}$$

We know,

$$C_p - C_v = R$$

$$\Rightarrow C_v + R = C_p$$

$$\therefore dQ = C_p dT - v dP \quad \text{--- (5)}$$

For adiabatic process, $dQ = 0$ then from (5) and (3)

$$C_p dT = v dP \quad \text{--- (6)}$$

$$C_v dT = -P dV \quad \text{--- (7)}$$

$$(6) \div (7)$$

$$\gamma = \frac{C_p}{C_v} = - \frac{v dP}{P dV}$$

$$\Rightarrow -\gamma \frac{dV}{V} = \frac{dP}{P}$$

$$\Rightarrow -\gamma \int \frac{dV}{V} = \int \frac{dP}{P}$$

$$\Rightarrow -\ln V \cdot \gamma = \ln P$$

$$\Rightarrow -\gamma \ln V + \ln k = \ln P$$

$$\Rightarrow \ln P + \ln V^\gamma = \ln k$$

$$\Rightarrow \ln P V^\gamma = \ln K$$

$$\Rightarrow P V^\gamma = \text{constant}$$

(ii) Prove that, $T V^{\gamma-1} = \text{constant}$

\Rightarrow For ideal gas,

$$P V = R T$$

$$\Rightarrow P = \frac{R T}{V}$$

We know that

$$P V^\gamma = \text{constant}$$

$$\Rightarrow \frac{R T}{V} V^\gamma = \text{constant}$$

$$\Rightarrow R T V^{\gamma-1} = \text{constant}$$

R is constant it is ~~Boltzmann's constant~~ ^{Real gas}

$$\therefore T V^{\gamma-1} = \text{constant}.$$

(iii) Prove that, $T P^{\frac{1-\gamma}{\gamma}} = \text{constant}$

\Rightarrow For ideal gas,

$$P V = R T$$

$$\Rightarrow V = \frac{R T}{P}$$

We know that,

$$PV^\gamma = \text{constant}$$

$$\Rightarrow P \left(\frac{RT}{P}\right)^\gamma = \text{constant}$$

$$\Rightarrow \frac{R^\gamma T^\gamma}{P^{\gamma-1} p^\gamma} = \text{constant}$$

$$\Rightarrow \frac{T^\gamma}{P^{\gamma-1}} = \text{constant}$$

$$\Rightarrow \frac{P^{\gamma-1}}{T^\gamma} = \text{constant} \rightarrow [\text{Proved}]$$

$$\Rightarrow T^{-\gamma} P^{\gamma-1} = \text{constant}$$

$$\Rightarrow \ln T^{-\gamma} + \ln P^{\gamma-1} = \text{constant}$$

$$\Rightarrow -\gamma \ln T + (\gamma-1) \ln P = \text{constant}$$

Dividing by $-\gamma$,

$$\Rightarrow \ln T - \frac{(\gamma-1)}{\gamma} \ln P = \text{constant}$$

$$\Rightarrow \ln T + \frac{(1-\gamma)}{\gamma} \ln P = \text{constant}$$

$$\Rightarrow \ln T P^{\frac{(1-\gamma)}{\gamma}} = \text{constant}$$

$$\Rightarrow T P^{\frac{(1-\gamma)}{\gamma}} = \text{constant} \rightarrow [\text{Proved}]$$

~~Q~~ Differential relation between different state variable:

→ The equation of state, $f(P, V, T) = 0 \quad \dots \quad (1)$

$$P = f(V, T) \quad \dots \quad (2)$$

$$\therefore dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT$$

For isobaric process, $dP = 0$

$$\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV = 0$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V dT = -\left(\frac{\partial P}{\partial V}\right)_T dV$$

Dividing by dT we get,

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

This equation represents chain rule.

~~Q~~ Verify the relation for ideal gas or prove that,

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$$

→ We know that,

For one mole of ideal gas,

$$PV = RT$$

At constant pressure, differentiating w.r.t. T,

$$P \left(\frac{\partial V}{\partial T} \right)_P = R$$

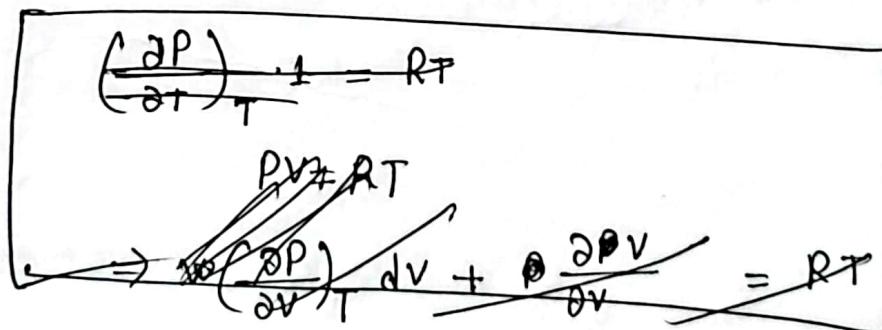
$$\Rightarrow \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{P} \quad \text{--- (1)}$$

At constant volume, differentiating w.r.t. P,

$$V \cdot 1 = R \left(\frac{\partial T}{\partial P} \right)_V$$

$$\Rightarrow \left(\frac{\partial T}{\partial P} \right)_V = \frac{V}{R} \quad \text{--- (2)}$$

At constant Temperature, differentiating w.r.t. V,



$$PV = RT$$

$$\Rightarrow P = \frac{RT}{V}$$

$$\Rightarrow \left(\frac{\partial P}{\partial V} \right)_T = RT \left(-\frac{1}{V^2} \right)$$

$$\Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT}{V^2} \quad \text{--- (B)}$$

$$\therefore \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -\frac{RT}{V^2} \cdot \frac{R}{P} \cdot \frac{V}{R}$$

$$= -\frac{RT}{PV}$$

$$= -\frac{PV}{PV} \quad [\because PV=RT]$$

$$= -1$$

$$\therefore \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \quad \boxed{\text{Proved}}$$

$$\begin{aligned} & \frac{PV}{RT} = \frac{1}{-1} \\ & PV = RT \end{aligned}$$

$$\left(\frac{1}{PV} - 1\right) RT = \frac{1}{T} \left(\frac{96}{V_6}\right)$$

Molecular and atomic specific heat :

Let Q be the total energy (in heat unit) associated with a gm-molecule of gas. Specific heat of the gas molecule,

$$C_V = \frac{dQ}{dT} \quad \text{--- (1)}$$

Since $C_P - C_V = R$

$$\Rightarrow C_P = C_V + R$$

$$\Rightarrow C_P = \frac{dQ}{dT} + R \quad \text{--- (2)}$$

Dividing (2) by (1)

$$\frac{C_P}{C_V} = \gamma = 1 + \frac{R}{\left(\frac{dQ}{dT}\right)} \quad \text{--- (3)}$$

The kinetic theory and the law of equipartition of energy enables us to determine the values of C_P , C_V and γ for different types of gas and solids.

(1) Monoatomic gas :

A monoatomic gas molecule has only translational motion in space and as such it has got 3 degree of freedom and its total energy $\frac{3}{2}kT$. Since a gm-molecule contain N_A molecules the total energy is given by,

$$Q = N_0 \frac{3}{2} kT = \frac{3}{2} RT$$

$$\therefore \kappa = \frac{R}{N_0}$$

$$\therefore C_V = \frac{dQ}{dT} = \frac{3}{2} R = 2.98 \text{ cal/mole/deg.}$$

$$\text{and } C_P = \frac{3}{2} R + R = \frac{5}{2} R$$

$$\text{also, } \kappa = \text{specific heat}, \gamma = \frac{C_P}{C_V} = \frac{5}{3} = 1.666$$

(2) Diatomic gas :

It will have three degrees of translational motion. Apart from these, the system will also capable of rotation about any of the two axes perpendicular to the line of centres of the two constituent atoms. Altogether it will have five degrees of freedom. Total energy,

$$Q = N_0 \cdot 5 \cdot \frac{1}{2} kT = \frac{5}{2} RT$$

$$\therefore C_V = \frac{dQ}{dT} = \frac{5}{2} R$$

$$\text{and, } C_P = \frac{5}{2} R + R = \frac{7}{2} R$$

$$\text{and, } \gamma = \frac{C_P}{C_V} = \frac{7}{5}$$

(3) Triatomic gas :

A triatomic gas molecule will have three translational and three rotational degree of freedom. Hence total 6 degrees of freedom. So total energy,

$$Q = N_0 \cdot 6 \frac{1}{2} kT = 3RT$$

$$\therefore C_V = \frac{dQ}{dT} = 3R = 5.961 \text{ cal/mole/deg.}$$

$$\therefore C_P = 3R + R = 4R = 7.948 \text{ cal/mole/deg.}$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{4R}{3} = 1.33.$$

(4) Solids :

Molecules of a solid may be regarded as elastic spheres capable of vibrating in a simple harmonic motion having three degrees of freedom. The molecules are held in position within a sphere of attraction due to other molecules and so a vibrating molecules will posses kinetic energy as well as potential energy in equal amount. The molecules of solid have total six degree of freedom. Total energy,

$$Q = 3RT = N_0 6 \frac{1}{2} kT$$

$$C_V = \frac{dQ}{dT} = 3R$$

$$\begin{aligned} C_P &= 3R + R = 4R \\ \therefore \gamma &= \frac{4R}{3} = 1.33. \end{aligned}$$

For solids the distinction between C_p and C_v disappears on account of the almost negligible expansion in volume that occurs due to heating under constant pressure.

According to Riehantz the ratio $\frac{C_p}{C_v}$ lies between 1.01 to 1.04

In Brief:

| Types | Degrees of freedom | Total energy for No molecules | $C_v = \frac{dQ}{dT}$ | $C_p = C_v + R$ | $\gamma = \frac{C_p}{C_v}$ |
|------------|--------------------|--|-----------------------|-----------------|--|
| monoatomic | 3 | $Q = N_0 \frac{3}{2} kT = \frac{3}{2} RT$ | $\frac{3}{2} R$ | $\frac{5}{2} R$ | $\frac{5}{3}$ |
| Diatomic | 5 | $Q = N_0 \frac{5}{2} kT = \frac{5}{2} RT$ | $\frac{5}{2} R$ | $\frac{7}{2} R$ | $\frac{7}{5}$ |
| Triatomic | 6 | $Q = N_0 \cdot 6 \cdot \frac{1}{2} kT = 3RT$ | $3R$ | $4R$ | $\frac{4}{3}$ |
| Solid | 6 | $Q = N_0 \cdot 6 \cdot \frac{1}{2} kT = 3RT$ | $3R$ | $4R$ | According to Riehantz it lies between 1.01 to 1.04 |