Thermodynamic Terms

System: The macroscopic part of the universe under study in thermodynamics is called the system. e.g. a reaction vessel, an engine, an electrochemical cell, a biological cell, etc.

Surroundings: The rest of universe that can interact with the system is called the surroundings. We make our observations from the surroundings.

Boundary (or wall): A system is confined to a definite place in space by a boundary (or wall). A boundary separates a system from the surroundings.

- A wall can be either rigid or non-rigid (movable).
- A wall is said to be permeable if it allows matter to pass through it; otherwise, it is impermeable.
- A wall is said to be adiabatic if it does not allow passage of heat through it.
- A wall that allows passage of heat through it is said to be a diathermic wall.

Types of Systems:

Open system: An open system is one where transfer of both matter and energy between system and surroundings can occur through the boundary.

Closed system: A closed system is one where transfer of energy between system and surroundings can occur. It can't exchange matter with the surroundings.

Isolated system: An isolated system is one that does not interact in any way with its surroundings. For an isolated system, neither matter nor energy can be transferred between system and surroundings.

Properties of a system: The properties of a system are its physical characteristics that we can observe directly with our senses or by using scientific tools and methods. Measurable properties of a system may be divided into two classes:

(i) **Extensive property**: An extensive thermodynamic property is one which depends on the amount of matter in the system. Value of an extensive property is equal to the sum of its values for the parts of the system. Examples of extensive property are mass, volume, pressure, internal energy, enthalpy, free energy, entropy, heat capacity.

(ii) **Intensive property**: Properties that do not depend on the amount of matter in the system are called intensive. e.g., density, pressure, molar properties (like molar volume, molar energy, molar entropy etc.) surface tension, viscosity, specific heat, refractive index, temperature, etc.

State of a system: A system is said to be in a definite state when each of its properties has a definite value. However, it is not necessary to specify all the properties to define the state. Thermodynamics uses *composition, pressure, volume and temperature* to define the state of a system. Experiments show that, for a homogeneous system with a fixed composition, the thermodynamic state is specified when the two variables P, T are specified. An equation relating P, V, T and composition is called an equation of state. For an ideal gas, equation of state is

$$PV = nRT$$

State variable or thermodynamic variable: A state variable is one that has a definite value when the state of a system is specified. e.g. P, V, T and composition.

Change in state: Change in state of a system is completely defined when the initial and final states are defined.

Path: It is the sequence of intermediate steps or stages arranged in order, followed by the system in going from its initial to final state.

Equilibrium:

An isolated system is in equilibrium when its observable properties (macroscopic properties) remain constant with time.

A non-isolated system is in equilibrium when the following two conditions hold:

(a) The system's macroscopic properties remain constant with time

(b) Removal of the system from contact with its surroundings causes no change in the properties of the system.

If condition (a) holds but (b) does not hold, the system is in a **steady state**.

The equilibrium concept can be divided into the following three kinds of equilibrium:

Mechanical equilibrium: A system is said to be in mechanical equilibrium if there are no unbalanced forces acting on or within the system, hence the system undergoes no acceleration, and there is no turbulence in the system. This is possible if pressure remains the same in all parts of the system.

Material equilibrium (or chemical equilibrium): If the concentrations of the chemical species in various parts of the system are constant with respect to time, the system is said to be in material equilibrium (or chemical equilibrium). This is possible when there are no net chemical reactions or transfers of matter within a system.

Thermal Equilibrium: A system is in thermal equilibrium if the temperature remains the same in all parts of the system. For thermal equilibrium between a system and its surroundings, there must not be any flow of heat to and from the system.

For thermodynamic equilibrium, all three kinds of equilibrium must be present.

Process: A process is the method of operation by means of which a change in state is carried out in a system.

Different types of processes:

(i) **Cyclic process:** If a system after undergoing through a series of changes in its state comes back to its initial state, then the process is termed as cyclic process.

(ii) **Isothermal process:** A process that is carried out under conditions of constant temperature is called an isothermal process. The constancy of temperature is maintained by either extracting heat from the system or supplying heat to it.

(iii) **Adiabatic process:** A process in which there is no exchange of heat between the system and the surroundings is known as an adiabatic process. The system is enclosed by an adiabatic wall. In an adiabatic process there is a change in the temperature of the system.

(iv) **Isochoric process:** A process in which the volume of the system remains constant.

(v) **Isobaric process:** A process that is carried out under conditions of constant pressure.

(vi) **Reversible process:** A reversible process is one where the system is always in infinitesimally close to equilibrium.

- In a reversible process, a system undergoes a change in state in an infinite number of infinitesimal steps and requires infinite time to complete the process.
- In a reversible process, the system can be restored to its original state by traversing the same sequence of states in reverse order. As a result, surroundings are also restored to their original state.
- At any stage in a reversible transformation, the system does not depart from equilibrium by more than an infinitesimal amount.
- Since a reversible process requires infinite length of time, reversible processes are not real processes. It has conceptual interest only.

(vii) **Irreversible process:** A process that occurs rapidly or spontaneously such that the system does not remain in equilibrium throughout the transformation is called an irreversible process.

- After undergoing a change, both the system and surroundings does not restore their original states. Expansion of a gas against zero pressure, dissolution of a solute in a solvent, flow of liquid from higher to lower levels are examples of irreversible processes.
- In an irreversible process, the system can’t be restored to its original state by traversing the same sequence of states in reverse order.
- During an irreversible process, the system's properties, such as pressure, volume, and temperature, are not uniform throughout, meaning that the system departs from the state of equilibrium.
- All irreversible processes require finite length of time and hence are real processes.

Zeroth law of thermodynamics:

The law can be stated as:

“Two systems that are both in thermal equilibrium with a third system are in thermal equilibrium with each other.”

Let us consider three systems A, B and C arranged as shown below:

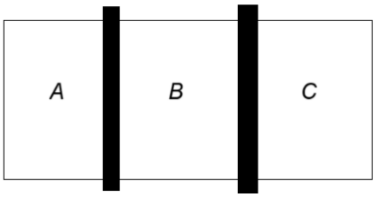
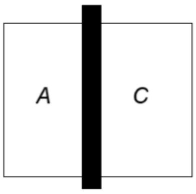


Fig (a)



Fig(b)

Systems A and B are in thermal contact and systems B and C are in thermal contact. This composite system is allowed sufficient time to come to thermal equilibrium. Then, A comes in thermal equilibrium with B and C comes in thermal equilibrium with B. Now we remove A and C from their thermal contact with B and place them in thermal contact with each other. We then observe that no changes in properties of A and C occur with time i.e. A and C are also in thermal equilibrium.

Zeroth law defines temperature. There must be some thermodynamic property which is common to two systems in thermal equilibrium. This property is called temperature. By definition, two systems in thermal equilibrium will have the same temperature. Two systems not in thermal equilibrium will have different temperatures.

Thermodynamic functions and their differentials:

State functions: Thermodynamic properties of a system that depend on the current state of the system and are independent of its previous history of the state are called **state functions**. Such properties can be regarded as functions of variables, such as P and T, that define the current state of the system. e.g. Internal energy (U), enthalpy (H) and heat capacity are examples of state functions.

Path functions: Thermodynamic properties of a system that depend on the path taken by the system to reach the current state are called path functions. Examples of path functions are the work (w) that is done during the change of a state and the energy transferred as heat (q). The energy transferred as work or heat is related to the path being taken during the change of a state, not the state itself.

If a system undergoes a change from state I to state II by a process, then the change in a state function depends only on the initial and final states of the system and not on the path taken by the system in going from I to II. Therefore, for a state function Z, the change in Z in the process is given by

$$\Delta Z = Z_{II} - Z_I$$

Here Z_{II}, Z_I are the values of the properties at the specified states.

Since a path function depends on the path taken during the change of state, the value of a path property will be different for different paths in going from state I to state II.

Exact and Inexact Differential:

If a system is taken along a path, U change from U_i to U_f and overall change is given by

$$\Delta U = \int_i^f dU = U_f - U_i$$

The value of ΔU depends on the initial and final state of the system but is independent of the path between them. This path independence of the integral is expressed by saying that dU is an **exact differential**.

An **exact differential** is an infinitesimal quantity which, when integrated, gives a result that is independent of the path between the initial and final states of the system.

An **inexact differential** is an infinitesimally small quantity that, when integrated, gives a result that depends on the path between the initial and final states. When a system is heated, total energy transferred as heat is the sum of all individual contributions at each point of the path.

$$q = \int_{i,path}^{f} dq$$

q depends on the path selected; this path dependence is expressed by saying that dq is an inexact differential. Similarly, dw is also an inexact differential.

Differentials of a state functions are exact differentials; differentials of path functions are inexact differentials.

The cyclic integral of an exact differential is zero for a cyclic process i.e. if A is any state function, ΔA must be zero for any cyclic process.

$$\oint dA = 0$$

Conversely, if

$$\oint dA = 0$$

then A must be a state function.

Properties of a state function:

If $Z = f(x, y)$ is a state function then -

(i) dZ is an exact differential given by

$$dZ = \left(\frac{\delta z}{\delta x}\right)_y dx + \left(\frac{\delta z}{\delta y}\right)_x dy$$

(ii) For a cyclic process $\oint dZ = 0$

(iii) It obeys the Euler's theorem of exactness:

$$\frac{\delta^2 z}{\delta x \delta y} = \frac{\delta^2 z}{\delta y \delta x}$$

(iv) Change in Z in a process is given by

$$\Delta Z = Z_{II} - Z_I$$

Z_{II}, Z_I are the values of the state function at final and initial states, respectively.

Test for exactness:

If f is a function of x and y, then total differential or complete differential of f is given by

$$df = \left(\frac{\delta f}{\delta x}\right)_y dx + \left(\frac{\delta f}{\delta y}\right)_x dy$$

df is an exact differential if

$$\left(\frac{\delta}{\delta y}\left(\frac{\delta f}{\delta x}\right)_y\right)_x = \left(\frac{\delta}{\delta x}\left(\frac{\delta f}{\delta y}\right)_x\right)_y$$

Or simply,

$$\frac{\delta^2 f}{\delta y \delta x} = \frac{\delta^2 f}{\delta x \delta y}$$

If df is exact, its integral between specified limits is independent of the path.

$\boldsymbol{Q.1}$. Check whether dP is an exact differential or not.

Sol^n: Let us consider a system containing an ideal gas. Pressure of the gas is a function of T, V.

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

Total differential is given by

$$dp = \left(\frac{\delta p}{\delta T}\right)_V dT + \left(\frac{\delta P}{\delta V}\right)_T dV$$

If we consider n mole of the gas, $PV = nRT$

$$\text{or } p = \frac{nRT}{V}$$

So,

$$\left(\frac{\delta p}{\delta T}\right)_V = \frac{nR}{V}$$

and

$$\frac{\delta^2 p}{\delta V \delta T} = -\frac{nR}{V^2} \dots\dots\dots\dots (1)$$

$$\left(\frac{\delta p}{\delta V}\right)_T = -\frac{nRT}{V^2}$$

and

$$\frac{\delta^2 p}{\delta T \delta V} = -\frac{nR}{V^2} \dots\dots\dots\dots (2)$$

From equations (1) and (2),

$$\frac{\delta^2 p}{\delta V \delta T} = \frac{\delta^2 p}{\delta T \delta V} = -\frac{nR}{V^2}$$

Hence dP is an exact differential.

$\boldsymbol{Q.2}$. For the same system, show that dT is an exact differential.

The cyclic rule: If three variables are related by some functional dependence $Z = f(x, y)$, then the partial derivatives satisfy the rule**:**

$$\left(\frac{\delta x}{\delta y}\right)_Z \left(\frac{\delta y}{\delta Z}\right)_x \left(\frac{\delta Z}{\delta x}\right)_y = -1$$

This is known as cyclic rule. For example, p, V and T are such variables and $p = f(T, V)$, so

$$\left(\frac{\delta p}{\delta T}\right)_V \left(\frac{\delta T}{\delta V}\right)_p \left(\frac{\delta V}{\delta p}\right)_T = -1$$

Work(w)

When an object moves through a distance dx up on application of a measurable force F_x exerted by part of the surroundings then surroundings has done work $dw = -F_x.dx$ on the system. F_x may be mechanical, electrical, gravitational or magnetic force and may act on and displace the entire system or only a part of the system. Accordingly, we have –

(i) Mechanical or pressure-volume work, $w = -p_{ext}\,\Delta V$
where ΔV is the change in volume of the system during an irreversible expansion.

(ii) Gravitational work, $w = mgh$. Here a body of mass m has been raised through a height h against the gravitational force.

(iii) Electrical work, $w = QV$ where V is the potential difference and Q is the quantity of electricity.

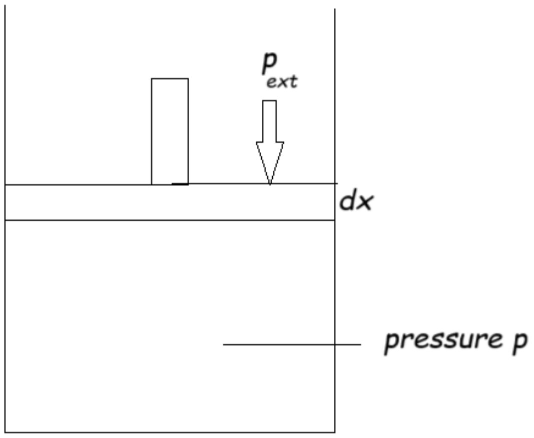
A process that **does** work is one that could be used to bring about a change in the height of a weight somewhere in the surroundings. e.g., in the process of expansion of a gas work is done by the system on the surroundings. A chemical reaction that drives an electric current through a resistance is also an example of process that does work.

Few important points to be noted:

- When work is done on a system, its energy (capacity to do work) is increased. When work is done by the system on its surroundings, energy of the system decreases.
- When work is done **by** the system **on** the surroundings, work is **negative**.
- When work is done **on** the system **by** the surroundings, work is **positive**.

Expansion Work (Mechanical work or PV work): If a system alters its volume against an opposing pressure, a work effect is produced in the surroundings. Such work effect is called expansion work.

Let us consider a system consisting of a quantity of gas enclosed in a cylinder fitted with a piston. The motion of the piston is quasi-static i.e., the surroundings remain in internal equilibrium. The piston is massless, frictionless and have area A.



If the external pressure is P_{ext}, then force on the outer face of the piston is $F = P_{ext}A$

From the definition, work required to move an object by a distance dx against an opposing force F is

$$dw = -F.dx$$

$$= -P_{ext}.A.dx$$

But $A.dx$ is the volume change in the course of expansion. Hence,

$$dw = -P_{ext}\, dV$$

Therefore, the work done when the system expands through dV against a constant pressure P_{ext} is

$$dw = -P_{ext}\, dV$$

Internal Energy (U)

Energy is defined as the capacity to do work.

When work is done on a system (other than an isolated system) (e.g. by compressing a gas), its capacity to do work is increased and thus energy of the system is increased. When the system does work (e.g. when the gas expands), its energy is reduced because it can do less work than before. Energy of a system or a system's capacity to do work may change by heat as well. As a result of temperature difference between a system and its surroundings, the energy of the system changes. In this case, energy transfer takes place in the form of heat.

In general, total energy of a system is given by

$$E = K + V + U$$

Where K = kinetic energy of the system

V = potential energy of the system due to presence of fields that act on the system.

U = internal energy of the system.

In thermodynamics, the system will be at rest and external fields will not be present - effect of gravity on systems will be ignored. Hence, $K = 0$ and $V = 0$. Therefore, in thermodynamics total energy of a system is called its internal energy, U.

Internal energy, U consists of

(i) translational energy of the molecules of a system
(ii) rotational energy of the molecules
(iii) vibrational energy of the molecules
(iv) electronic energy
(v) relativistic rest-mass energy $m_{rest}c^2$ of the electrons and nuclei
(vi) potential energy of interaction between the molecules.

Thus, Internal energy,

$$U = U_{trans} + U_{rot} + U_{vib} + U_{el} + U_{intermol} + U_{rest}$$

The internal energy is a state function in the sense that its value depends only on the current state of the system and is independent of how the state has been prepared. It is a function of the properties that determine the current state of the system:

$$U = f(n, P, T, \ldots)$$

When a system changes from initial state i to final state f, the change in internal energy is given by

$$\Delta U = U_f - U_i$$

Internal energy is an extensive property, however, molar internal energy U_m is an intensive property.

Heat (q)

In thermodynamics, heat is defined as a quantity that flows across the boundary of a system during a change in its state in virtue of a difference in temperature between the system and its surroundings and flows from a point of higher temperature to a point of lower temperature.

Few important points to be noted:

- Heat appears only at the boundary of the system.
- Heat appears only during a change in state.
- Heat is manifested by an effect in the surroundings.

Like work, heat, q is not a state function, its value depends on the path which is followed for carrying out the change in state of a system.

Energy of a system changes as a result of 'energy transfer' in the form of heat due to a temperature difference between it and surroundings. Heat and work are equivalent ways of changing a system's internal energy.

Molecular Interpretation heat and work

In molecular terms, heat is the transfer of energy that makes use of chaotic molecular motion. The chaotic motion of molecules is called thermal motion. When a system heats its surroundings, molecules of the system stimulate the thermal motion in the surroundings.

In molecular terms, work is the transfer of energy that makes use of organized motion. When a system does work it causes molecules, atoms or electrons in its surroundings to move in an organized way.

Distinction of work and heat can be made only at the surroundings.

Because, both of them flowing from surroundings creates thermal motion in the system.

Work is identified as energy transfer, making use of the organized motion of atoms in the surroundings, and heat is identified as energy transfer making use of thermal motion in the surroundings.

First law of Thermodynamics:

Mathematical formulation:

The first law of thermodynamics asserts that there exists an extensive state function U called the internal energy such that for any process in a closed system

$$\Delta U = q + w \quad \ldots\ldots\ldots\ldots(1)$$

where ΔU is the internal energy change undergone by the system in the process,

q is the heat flow into the system during the process,

w is the work done on the system during the process.

The change in internal energy ΔU of the system is accompanied by a change in energy of the surroundings equal to $-\Delta U$, so the total internal energy change of system plus surroundings remains constant. For any process,

$$\Delta U_{syst} + \Delta U_{surr} = 0$$

For an infinitesimal process, equation (1) becomes

$$dU = dq + dw \quad \ldots\ldots\ldots\ldots\ldots(2)$$

where dU is the infinitesimal change in system's energy in a process with infinitesimal heat dq flowing into the system and infinitesimal work dw done on the system.

It is found experimentally that if a system is isolated from its surroundings, then no change in internal energy takes place.

$$\Delta U = 0\ (isolated\ system)$$

The first law of thermodynamics is a statement of this observation:

$$First\ law: "The\ internal\ energy\ of\ an\ isolated\ system\ is\ constant."$$

Cyclic process and the first law: For a system undergoing a cyclic process

$$\Delta U = 0$$

$$\therefore\ q = -w \quad \ldots\ldots(3)$$

The heat absorbed by a system from the surroundings is exactly equal to the work done by the system on the surroundings. Equation (3) establishes the impossibility of a perpetual motion of a machine of the first kind. A perpetual motion machine is a machine that does work without consumption of fuel or some other source of energy.

Significance:

The first law of thermodynamics is the law of conservation of energy. Fundamental implication of first law is that although energy may be transformed from one form into another, it can neither be created nor destroyed. Whenever energy of a particular form disappears, an exactly equivalent amount of another form must be produced. According to first law, the total energy of a system and its surroundings is constant i.e. the energy of the universe is conserved. Gain or loss in energy of the system is exactly compensated by loss or gain in energy of the surroundings.

Limitations of first law:

- The first law of thermodynamics does not place any restriction on the conversion of energy from one form to another; it simply requires that the total quantity of energy be the same before and after the conversion.
- It is always possible to convert any kind of energy into an equal quantity of thermal energy manifested by an increase in temperature of some sample of matter. But, only a limited number of the kinds of energy can be completely converted into work. e.g., the mechanical energy produced by an electric motor. However, the thermal energy of a steam boiler or the chemical energy of a compound can only be partly converted into work. This limitation about conversion of energy can't be predicted in terms of the first law. This leads to postulation of second law of thermodynamics.

Internal energy change in a constant-volume process:

In general, the change in internal energy of a system is

$$dU = dq + dw$$

$$= dq + dw_e + dw_{exp}$$

where dw_e is work in addition to the work of expansion dw_{exp}.

For a system kept at constant volume, $dV = 0$

So, $dw_{exp=0}$

If the system is incapable of doing any other kind of work, $dw_e = 0$.

Under these conditions,

$$dU = dq_V$$

For a measurable change,

$$\Delta U = q_V$$

where q_V is the heat absorbed at constant volume.

Enthalpy(H)

Enthalpy is defined as

$$H = U + PV$$

- Because U, P and V are state functions, H is also a state function.
- As is true of any state function, the change in enthalpy between any pair of initial and final state is independent of path between them.
- dH is an exact differential.

Change in enthalpy at constant pressure:

For a general change in the state of the system,

$$U \text{ changes to } U + dU$$

$$P \text{ changes to } P + dP$$

$$V \text{ changes to } V + dV$$

So, H changes (from $U + PV$) to

$$H + dH = (U + dU) + (P + dP)(V + dV)$$

$$\Rightarrow H + dH = U + dU + PV + PdV + VdP + dPdV$$

[The last term $dPdV$ is the product of two infinitesimally small quantities and can be neglected.]

$$\Rightarrow H + dH = (U + PV) + dU + PdV + VdP$$

$$\Rightarrow H + dH = H + dU + PdV + VdP \ (\therefore U + PV = H)$$

$$\Rightarrow dH = dU + PdV + VdP$$

If we now substitute the first law, $dU = dq + dw$, we get

$$dH = dq + dw + PdV + VdP$$

If the system is in mechanical equilibrium with its surroundings at a pressure p and does only expansion work, then $dw = -pdV$, then

$$dH = dq + VdP$$

If heating occurs at constant pressure, $dp = 0$

$$\therefore dH = dq_p$$

For a measurable change

$$\Delta H = q_p$$

Thus, when a system is subjected to a constant pressure and only expansion work can occur, the change in enthalpy is equal to the energy supplied as heat.

Relations between ΔH and ΔU:

For any change of state at constant pressure P,

$$\Delta H = H_2 - H_2$$

$$= (U_2 + PV_2) - (U_1 + PV_1)$$

$$= (U_2 - U_1) + P(V_2 - V_1)$$

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

At constant pressure

$$\therefore \Delta H = q_p$$

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

For any general change of state, enthalpy change is

$$\Delta H = H_2 - H_2$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= (U_2 - U_1) + (P_2V_2 - P_1V_1)$$

$$or\ \Delta H = \Delta U + \Delta(PV)$$

For solids and liquids at moderate pressures, the term $\Delta(PV)$ is negligible and $\Delta H \approx \Delta U$.

- It is usually justifiable to ignore the difference between the enthalpy and internal energy of condensed phases, except at very high pressure when $\Delta(PV)$ is no longer negligible.

Perfect gas and enthalpy change:

Enthalpy of a perfect gas is

$$H = U + PV = U + nRT$$

At constant T and p, change of enthalpy during a reaction that produces or consumes gas is

$$\Delta H = H_2 - H_2$$

$$= (U_2 + n_1RT) - (U_1 + n_2RT)$$

$$= (U_2 - U_1) + RT(n_2 - n_1)$$

$$or\ \Delta H = \Delta U + RT \times \Delta n_g$$

where Δn_g is change in the number of moles gaseous species while going from reactants to products in the reaction.

Heat capacities:

The heat capacity, C of a closed system for a finite process is defined as:

$$C = \frac{q}{\Delta T}$$

where q is the heat flowing into the system

ΔT is the temperature change of the system in the process.

The heat capacity, C of a closed system for an infinitesimal process is defined as:

$$C = \frac{dq}{dT}$$

where dq is the heat flowing into the system

and dT is the temperature change of the system in the process.

For a constant-pressure process,

$$dq_p = dH \qquad \therefore\ C_p = \frac{dq_p}{dT} = \left(\frac{\delta H}{\delta T}\right)_p$$

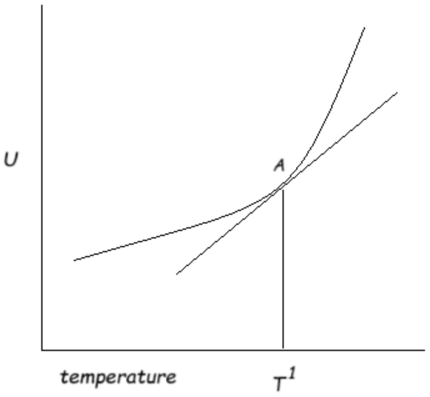
C_p is called heat capacity at constant pressure. C_p is an extensive property. The molar heat capacity at constant pressure, $C_{p,m}$ is the heat capacity per mole of material, it is an intensive property.

For a constant-volume process,

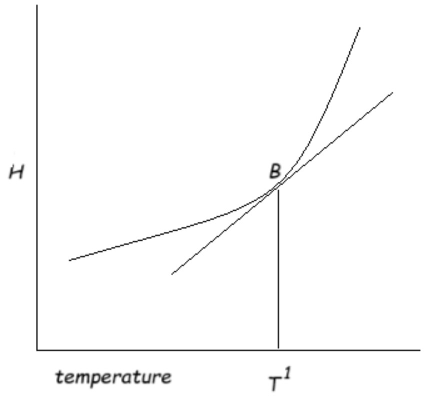
$$dq_V = dU \qquad \therefore\ C_V = \frac{dq_V}{dT} = \left(\frac{\delta U}{\delta T}\right)_V$$

C_V is called heat capacity at constant volume. C_V is an extensive property. The molar heat capacity at constant volume, $C_{V,m}$, is an intensive property.

If we plot internal energy against temperature at constant volume or enthalpy against temperature at constant pressure, then the slope of each curve at any temperature gives the $C_p\ or\ C_V$ of the system at that temperature.



Fig(a)



Fig(b)

In Fig(a), the slope of the tangent at A gives C_V at the temperature T_1.

In Fig(b), the slope of the tangent at B gives C_p at the temperature T_1.

In general, heat capacities depend on temperature and approaches zero at very low temperatures. For small range of temperature at and above room temperature, heat capacities can be treated almost independent of temperature.

Relation between C_p and C_v:

The heat capacity at constant pressure (C_p) is always greater than that at constant volume (C_V). This happens because, when heat is supplied at constant pressure, the system not only increases its internal energy but also does work to expand against the external pressure. In contrast, at constant volume no expansion work is done, so all the heat goes into raising the internal energy. As a result, the temperature rises more quickly at constant volume. To achieve the same temperature, increase at constant pressure, more heat must be supplied. Therefore, $C_p > C_V$.

For a perfect gas:

Using definitions,

$$\therefore\ C_p - C_V = \left(\frac{\delta H}{\delta T}\right)_p - \left(\frac{\delta U}{\delta T}\right)_V$$

From the definition of enthalpy,

$$H = U + PV = U + nRT$$

$$\left(\frac{\delta H}{\delta T}\right)_p = \left(\frac{\delta U}{\delta T}\right)_p + nR$$

$$\therefore\ C_p - C_V = \left(\frac{\delta U}{\delta T}\right)_p + nR - \left(\frac{\delta U}{\delta T}\right)_V$$

For an ideal gas

$$C_V = \left(\frac{\delta U}{\delta T}\right)_V = \left(\frac{\delta U}{\delta T}\right)_p$$

$$\therefore\ C_p - C_V = nR$$

For one mole of a perfect gas,

$$\therefore\ C_{p,m} - C_{V,m} = R$$

(2) The general case:

From definition,

$$C_p - C_V = \left(\frac{\delta H}{\delta T}\right)_p - \left(\frac{\delta U}{\delta T}\right)_V \text{ ………………..(1)}$$

From definition of enthalpy, $H = U + pV$,

$$\therefore \left(\frac{\delta H}{\delta T}\right)_p = \left(\frac{\delta U}{\delta T}\right)_p + p\left(\frac{\delta V}{\delta T}\right)_p \text{………………….(2)}$$

From (1) and (2), $\therefore\ C_p - C_V = \left(\frac{\delta U}{\delta T}\right)_p + p\left(\frac{\delta V}{\delta T}\right)_p - \left(\frac{\delta U}{\delta T}\right)_V$………….(3)

Since, U is a state function and $U = f(T, V)$, its perfect differential,

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

Differentiating with T at constant pressure,

$$\left(\frac{\delta U}{\delta T}\right)_p = \left(\frac{\delta U}{\delta T}\right)_V + \left(\frac{\delta U}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_p \text{………………….(4)}$$

(3) & (4) ⇒ $C_p - C_V = \left(\frac{\delta U}{\delta T}\right)_V + \left(\frac{\delta U}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_p + p\left(\frac{\delta V}{\delta T}\right)_p - \left(\frac{\delta U}{\delta T}\right)_V$

$$= \left(\frac{\delta U}{\delta V}\right)_T \left(\frac{\delta V}{\delta T}\right)_p + p\left(\frac{\delta V}{\delta T}\right)_p$$

$$\Rightarrow\ C_p - C_V = \left(\frac{\delta V}{\delta T}\right)_p \left[\left(\frac{\delta U}{\delta V}\right)_T + p\right] \text{………………….(5)}$$

This equation is general and is applicable to all substances, solids, liquids and gases.

The term $\left(\frac{\delta U}{\delta V}\right)_T$ represents the change in internal energy with changes in volume at constant temperature and is known as the **internal pressure, $\boldsymbol{\pi_T}$**.

For perfect gases, $\pi_T = \left(\frac{\delta U}{\delta V}\right)_T = 0$

Hence, equation (5) becomes,

$$C_p - C_V = p\left(\frac{\delta V}{\delta T}\right)_p$$

For ideal gas $pV = nRT$,

$$\therefore \left(\frac{\delta V}{\delta T}\right)_p = \frac{nR}{p}$$

$$\Rightarrow \; C_p - C_V = p \times \frac{nR}{p}$$

$$\Rightarrow \; C_p - C_V = nR$$

∴ For perfect gases,

$$C_{p,m} - C_{V,m} = R$$

Thermodynamics of Ideal Gases: Expansion Processes

1. Reversible Isothermal Expansion of an Ideal Gas

Let us consider n mole of an ideal gas which is expanded isothermally and reversibly from V_1 to V_2 . For an isothermal process, the temperature of the system remains constant throughout the expansion. For an ideal gas, internal energy depends only on temperature, i.e.,

$$U = f(T).$$

This means that:

$$\Delta U = 0$$

Enthalpy is defined by:

$$H = U + PV$$
$$\therefore \Delta H = \Delta U + \Delta(PV)$$

For an ideal gas, $PV = nRT$,

$$\therefore \Delta H = \Delta U + \Delta(nRT)$$
$$= 0 + 0$$
$$= 0$$

(For isothermal processes, $\Delta U = 0$ and $\Delta T = 0$).

According to the first law:

$$\Delta U = q + w$$
$$\Rightarrow 0 = q + w$$
$$\Rightarrow q = -w$$

This shows that in an isothermal expansion, work is done at the cost of the heat absorbed. Work (w) and heat (q) are path functions, so their magnitudes depend on whether the expansion is reversible or irreversible.

Work during a Reversible Isothermal Expansion

For a reversible expansion, the external pressure is matched to the internal pressure at each step ($p_{ext} = p$). For each step:

$$dw = -p_{ext}dV = -pdV$$

The total work for a reversible expansion from volume V_1 to V_2 is given by:

$$w_{rev} = -\int_{V_1}^{V_2} p\,dV$$

Using the ideal gas law, $P = nRT/V$:

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

Since T is constant:

$$w_{rev} = -nRT\int_{V_1}^{V_2} \frac{dV}{V} = -nRT[lnV_2 - lnV_1] = -nRTln\frac{V_2}{V_1}$$

Here $w_{rev} < 0$ because $V_2 > V_1$ i.e. $ln\frac{V_2}{V_1} > 0$. In this case the system has done work on the surroundings.

This equation can also be written in terms of pressure. At constant temperature,

$$p_1V_1 = p_2V_2$$
$$\Rightarrow \frac{V_2}{V_1} = \frac{p_1}{p_2}$$
$$w_{rev} = -nRTln\frac{V_2}{V_1} = -nRTln\frac{p_1}{p_2}$$

2. Irreversible Isothermal Expansion of an Ideal Gas

Two types of irreversible expansions are possible:

- free expansion
- expansion against a constant external pressure.

Free Expansion:

Free expansion means expansion against a vacuum, i.e., $p_{ext} = 0$.

$$w_{irr} = \int dw = -\int p_{ext}\, dV = 0$$

Since U and H are state functions, ΔU and ΔH are the same as in a reversible process. For an isothermal process:

$$\Delta U = 0$$
$$\Delta H = 0$$

From the first law:

$$\Delta U = q_{irr} + w_{irr}$$
$$\Rightarrow 0 = q_{irrev} + 0$$
$$\Rightarrow q_{irrev} = 0$$

Expansion against a Constant External Pressure:

$$w_{irr} = \int_{V_1}^{V_2} dw = -\int_{V_1}^{V_2} p_{ext}\, dV = -p_{ext}\int_{V_1}^{V_2} dV = -\, p_{ext}(V_2 - V_1)$$

Since U and H are state functions, ΔU and ΔH are the same as in a reversible process. For an isothermal irreversible process:

$$\Delta U = 0$$

$$\Delta H = 0$$

From the first law of thermodynamics:

$$\Delta U = q_{irr} + w_{irr}$$

$$\Rightarrow 0 = q_{irrev} + w_{irr}$$

$$\Rightarrow q_{irrev} = -w_{irr} = p_{ext}(V_2 - V_1)$$

Comparison of work done in Reversible and Irreversible process

The work obtained in a reversible expansion is more than that in an irreversible expansion.

$$|\, w_{rev}\,| - |\, w_{irr}\,| > 0$$

For isothermal reversible expansion of n mole of an ideal gas from volume V_1 to V_2 at temperature T, work done is given by

$$w_{rev} = -nRT ln\frac{V_2}{V_1}$$

$$= -nRT ln\left[1 - \left(1 - \frac{p_1}{p_2}\right)\right]$$

Expanding $ln\left[1 - \left(1 - \frac{p_1}{p_2}\right)\right]$ as the logarithmic series (Maclaurin (power) series)

$$ln(1 - x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \frac{x^4}{4} - \ldots\ldots\ldots\ldots \quad \text{for } |x| < 1$$

and neglecting the higher terms

$$w_{rev} = -nRT\left(\frac{p_1}{p_2} - 1\right)$$

Now for isothermal irreversible expansion of an ideal gas against a constant pressure p_2.

$$w_{irr} = -p_2(V_2 - V_1)$$

$$= -p_2\left(\frac{nRT}{p_2} - \frac{nRT}{p_1}\right)$$

$$= -nRT\left(1 - \frac{p_2}{p_1}\right)$$

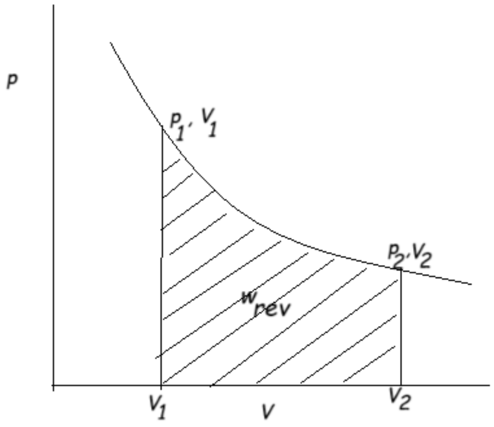
The difference is:

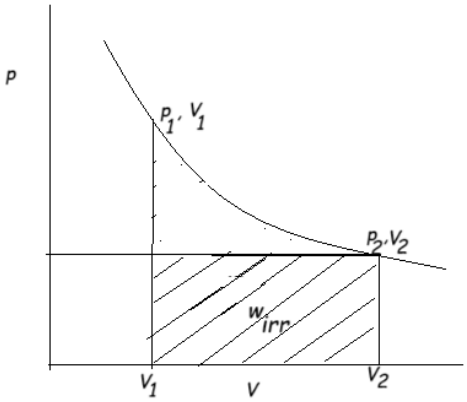
$$\begin{aligned} \mid w_{rev} \mid - \mid w_{irr} \mid &= nRT\left(\frac{p_1}{p_2}-1\right) - nRT\left(1-\frac{p_2}{p_1}\right) \\ &= nRT\left[\frac{p_1}{p_2}-1-1+\frac{p_2}{p_1}\right] \\ &= nRT\left[\frac{p_1^2 - 2p_1p_2+p_2^2}{p_1p_2}\right] \\ &= nRT\,\frac{(p_1-p_2)^2}{p_1p_2} \\ &= +ve\ quantity \end{aligned}$$

Since $(p_1 - p_2)^2$ is always positive.

$$\therefore |w_{rev}| > |w_{irr}|$$

Therefore, the work done in a reversible process is more than that in an irreversible expansion.





Why is work done in a reversible process maximum?

- When a gas expands, it pushes against the external pressure (p_{ext}) and does work.
- The formula for a small amount of work is:

$$dw = -p_{ext}dV$$

- For maximum work, the external pressure should be as large as possible, because work = pressure × volume change.
- But if p_{ext} is larger than the internal pressure (p), the gas cannot expand.
- If p_{ext} is much smaller than p, the gas expands suddenly, but the pressure difference is wasted and less work is obtained.
- The only way to get the maximum work is to let the gas expand step by step, so that at every stage: p_{ext} is infinitesimally less than p. Such a process, where expansion happens through in many infinitesimally small steps, is called a reversible process.

3. Reversible Adiabatic Expansion in a Perfect Gas

Let us consider adiabatic reversible expansion of an ideal gas from the state (p_1, V_1, T_1) to (p_2, V_2, T_2).

For an adiabatic process,

$$dq = 0.$$

For a reversible process in a system with only P-V work:

$$dw = -pdV \quad \text{……………………}(1)$$

Again, for a perfect gas:

$$C_V = \left(\frac{\delta U}{\delta T}\right)_V$$

$$\Rightarrow dU = C_V dT \text{ ……………………}(2)$$

Therefore, the first law becomes:

$$dU = dq + dw$$

$$\Rightarrow dU = dw = C_V dT$$

Calculation of ΔU, w, ΔH:

$$w = \int_1^2 dw = \int_1^2 dU = \int_1^2 C_V dT$$

Assuming C_V to be constant in the range T_1 to T_2:

$$w = U_2 - U_1 = C_V \int_1^2 dT$$

$$w = \Delta U = C_V(T_2 - T_1)$$

For n moles of an ideal gas,

$$T = \frac{PV}{nR}$$

$$\therefore \Delta U = C_V\left(\frac{p_2V_2}{nR} - \frac{p_1V_1}{nR}\right)$$

$$\Rightarrow \Delta U = \frac{C_V}{n}\left(\frac{p_2V_2 - p_1V_1}{R}\right)$$

$$\Rightarrow \Delta U = C_{V,m}\left(\frac{p_2V_2 - p_1V_1}{C_{p,m} - C_{V,m}}\right)$$

$$\Rightarrow \Delta U = \left(\frac{p_2V_2 - p_1V_1}{\frac{C_{p,m}}{C_{V,m}} - 1}\right)$$

$$\Rightarrow \Delta U = \left(\frac{p_2V_2 - p_1V_1}{\gamma - 1}\right) \qquad \left[Since \frac{C_{p,m}}{C_{V,m}} = \gamma\right]$$

Now,

$$\Delta H = \Delta U + \Delta(PV)$$
$$\Rightarrow \Delta H = \Delta U + \Delta(nRT)$$
$$\Rightarrow \Delta H = \Delta U + nR \times \Delta T$$
$$\Rightarrow \Delta H = \Delta U + nR(T_2 - T_1)$$
$$\Rightarrow \Delta H = C_V(T_2 - T_1) + nR(T_2 - T_1)$$
$$\Rightarrow \Delta H = (T_2 - T_1)(C_V + nR)$$
$$\Rightarrow \Delta H = C_p(T_2 - T_1)$$

Relation between T and V:

Let us consider adiabatic reversible expansion of an ideal gas from the state (p_1, V_1, T_1) to (p_2, V_2, T_2).

For an adiabatic process,

$$dq = 0$$

For a reversible process in a system with only P-V work:

$$dw = -pdV \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Again, for a perfect gas:

$$C_V = \left(\frac{\delta U}{\delta T}\right)_V$$
$$\Rightarrow dU = C_V dT \ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Therefore, the first law becomes:

$$dU = dq + dw$$
$$\Rightarrow dU = dw = -pdV \ldots\ldots\ldots\ldots\ldots(3)$$

From (2) and (3), $C_V dT = -pdV$

$$\Rightarrow C_V dT = -\left(\frac{nRT}{V}\right) dV \qquad \text{[Using } pV = nRT\text{]}$$
$$\Rightarrow \frac{C_V}{n}\frac{dT}{T} = -R\frac{dV}{V}$$
$$\Rightarrow C_{V,m}\frac{dT}{T} = -R\frac{dV}{V}$$

Integrating this within the limits specified and assuming $C_{V,m}$ to be constant in the temperature range $T_1 \rightarrow T_2$,

$$C_{V,m}\int_{T_1}^{T_2}\frac{dT}{T} = -R\int_{V_1}^{V_2}\frac{dV}{V}$$
$$\Rightarrow C_{V,m} ln\frac{T_2}{T_1} = -R ln\frac{V_2}{V_1}$$

$$\Rightarrow ln\frac{T_2}{T_1} = -\frac{R}{C_{V,m}} ln\frac{V_2}{V_1}$$

$$\Rightarrow ln\frac{T_2}{T_1} = \frac{R}{C_{V,m}} ln\frac{V_1}{V_2}$$

$$\Rightarrow ln\frac{T_2}{T_1} = ln\left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{R}{C_{V,m}}} \qquad \Big| \quad \frac{R}{C_{V,m}} = \frac{C_{p,m}-C_{V,m}}{C_{V,m}} = \gamma - 1$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \text{......................(4)}$$

$$\Rightarrow T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \text{...............(5)}$$

$$\Rightarrow TV^{\gamma-1} = constant$$

Relation between P and V:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \text{......................(4)}$$

For an ideal gas,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\Rightarrow \frac{T_2}{T_1} = \frac{p_2V_2}{p_1V_1}$$

Putting this in equation (4) ,

$$\frac{p_2V_2}{p_1V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$\Rightarrow \frac{p_2}{p_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$\Rightarrow p_1V_1^{\gamma} = p_2V_2^{\gamma}$$

$$\Rightarrow pV^{\gamma} = constant$$

Comparison of Isotherms and Adiabats corresponding to the expansion of an ideal gas:

In an isothermal process according to Boyle's law

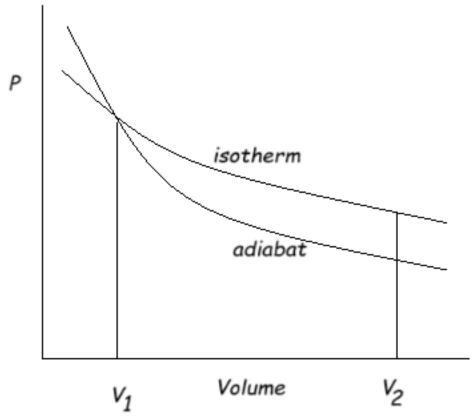
$$pV = constant$$

$$p = constant\frac{1}{V}$$

In an adiabatic process

$$pV^{\gamma} = constant$$

$$\Rightarrow p = constant\frac{1}{V^{\gamma}}$$



The pressure decreases more rapidly with an increase in volume along an adiabat than an isotherm due to the presence γ as power to V. Therefore:

$$w_{ad} < w_{iso}$$

The physical reason for this difference is that in an isothermal expansion, energy flows into the system as heat and maintains the temperature, so the pressure does not fall as much. In an adiabatic expansion, no heat can enter the system resulting in pressure drop.

4. Irreversible Adiabatic Expansion of a Perfect Gas

The irreversible work of expansion for an ideal gas in an adiabatic change against a constant external pressure p_{ext} is given by:

$$w_{irr} = -p_{ext}(V_2 - V_1)$$

If $p_{ext} = P_2$ (the final pressure of the gas):

$$w_{irr} = -p_2(V_2 - V_1)$$

For an adiabatic process, $q = 0$. From first law,

$$\Delta U = q + w_{irr}$$

$$\Rightarrow \Delta U = w_{irr} = -p_2(V_2 - V_1)$$

U is a state function, so value of ΔU is same in reversible and irreversible processes:

$$w_{irr} = \Delta U = C_V(T_2 - T_1) = nC_{V,m}(T_2 - T_1)$$

$$\Rightarrow -p_2(V_2 - V_1) = nC_{V,m}(T_2 - T_1)$$

$$\Rightarrow -p_2\left(\frac{nRT_2}{p_2} - \frac{nRT_1}{p_1}\right) = nC_{V,m}(T_2 - T_1)$$

$$\Rightarrow RT_1\frac{p_2}{p_1} - RT_2 = C_{V,m}(T_2 - T_1)$$

$$\Rightarrow RT_1\frac{p_2}{p_1} - RT_2 = C_{V,m}T_2 - C_{V,m}T_1$$

$$\Rightarrow RT_1\frac{p_2}{p_1} + C_{V,m}T_1 = RT_2 + C_{V,m}T_2$$

$$\Rightarrow T_1\left(R\frac{p_2}{p_1} + C_{V,m}\right) = T_2\left(R + C_{V,m}\right)$$

$$\Rightarrow T_1\left(R\frac{p_2}{p_1} + C_{V,m}\right) = T_2C_{p,m}$$

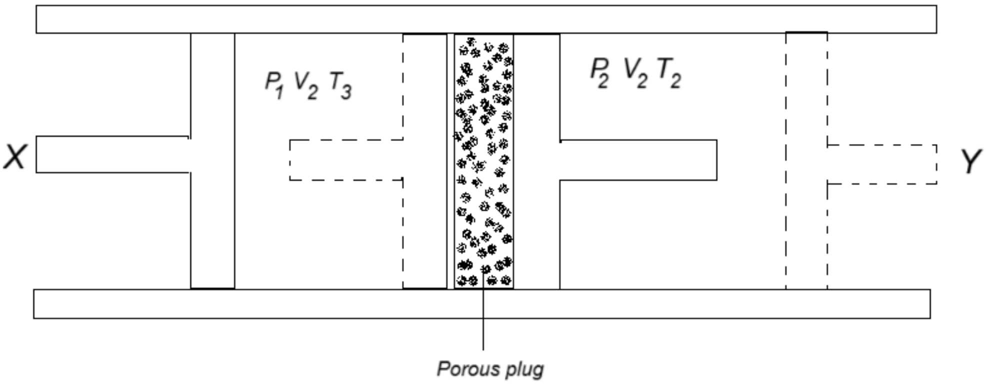
$$\Rightarrow T_2 = T_1\frac{\left(R\frac{p_2}{p_1} + C_{V,m}\right)}{C_{p,m}}$$

Joules-Thomson Effect

When a gas is made to expand adiabatically through a throttle from one constant pressure to another (high to low), there occurs a change in temperature of the gas. The cooling of a gas by adiabatic expansion is called the Joule-Thomson effect.

The experiment:

The experiment was performed in a thermally insulated tube fitted with porous plug and two pistons X and Y, as shown below:



Let us consider a fix amount of gas that passes through the plug from high-pressure side at the state (P_1,V_1,T_1). As a result of this passage the gas emerges on the low-pressure side and acquires a new state (P_2,V_2,T_2). The gas suffers isothermal compression on the left-hand side and expands isothermally on the right-hand side. As the gas expands a change in temperature is observed.

During compression, the work done on the gas is

$$w_1 = -P_1 1(0 - V_1) = P_1V_1$$

When the gas expands isothermally at T_2, the work done by the gas is

$$w_2 = -P_2(V_2 - 0) = -P_2V_2$$

∴ Final work = $w = w_1 + w_2 = P_1V_1 - P_2V_2$

Because all changes to the gas occur adiabatically $q = 0$.

From first law, $\Delta U = q + w$, we get, $\Delta U = w$

$$\Rightarrow \Delta U = U_2 - U_1 = w = P_1V_1 - P_2V_2$$

$$\Rightarrow U_2 + P_2V_2 = U_1 + P_1V_1$$

$$\Rightarrow H_1 = H_2 \ (\because H = U + PV)$$

$$\Rightarrow \Delta H = 0$$

The expansion occurs without change of enthalpy. It is an isoenthalpic process.

The Joule-Thomson Coefficient (μ): Joule-Thomson Coefficient (μ) is defined as

$$\mu = \left(\frac{\delta p}{\delta T}\right)_H \qquad \text{.........(1)}$$

i.e. μ is defined as the change in temperature per unit pressure change when a gas expands under adiabatic conditions.

Applying Euler's chain rule on *H*, *P* and *T*, we get

$$\left(\frac{\delta H}{\delta T}\right)_p \left(\frac{\delta T}{\delta p}\right)_H \left(\frac{\delta p}{\delta H}\right)_T = -1$$

$$\Rightarrow \left(\frac{\delta T}{\delta p}\right)_H = -\frac{1}{\left(\frac{\delta H}{\delta T}\right)_p} \times \left(\frac{\delta H}{\delta p}\right)_T = -\frac{1}{C_p}\left(\frac{\delta H}{\delta p}\right)_T$$

$$\Rightarrow \mu = -\frac{1}{C_p}\left(\frac{\delta H}{\delta p}\right)_T$$

$$\because H = U + PV$$

$$\therefore \left(\frac{\delta H}{\delta p}\right)_T = \left(\frac{\delta U}{\delta p}\right)_T + \left(\frac{\delta (PV)}{\delta p}\right)_T$$

$$\Rightarrow -\mu C_p = \left(\frac{\delta U}{\delta p}\right)_T + \left(\frac{\delta (PV)}{\delta p}\right)_T$$

$$\Rightarrow \mu = -\frac{1}{C_p}\left[\left(\frac{\delta U}{\delta V}\right)_T \left(\frac{\delta V}{\delta p}\right)_T + \left(\frac{\delta (PV)}{\delta p}\right)_T\right]$$

$$\Rightarrow \mu = -\frac{1}{C_p}\left(\frac{\delta U}{\delta V}\right)_T \left(\frac{\delta V}{\delta p}\right)_T - \frac{1}{C_p}\left(\frac{\delta (PV)}{\delta p}\right)_T$$

This is a general equation and applicable to all gases.

(a) For ideal gas:

$$\left(\frac{\delta U}{\delta V}\right)_T = 0 \text{ and } \left(\frac{\delta (PV)}{\delta p}\right)_T = 0$$

$$\therefore \mu = 0$$

Which means, in case of expansion of an ideal gas through a porous plug, there is no change in temperature of the gas.

The change in temperature in a Joule-Thomson experiment occurs due to the involvement of intermolecular forces. For an ideal gas μ is zero because intermolecular forces are absent in a perfect gas.

(b) For real gases: Real gases have non-zero Joule-Thomson coefficients. Depending on the nature of the gas, the pressure, and the temperature, the sign of the coefficient may be either positive or negative.

A positive sign implies that dT is negative when dp is negative. This indicates that the gas cools on expansion.

A negative sign implies that dT is positive when dp is negative. This indicates that the gas gets heated on expansion.

Gases that show a heating effect ($\mu < 0$) at one temperature show a cooling effect ($\mu > 0$) when the temperature is below a certain temperature called inversion temperature (T_i). Inversion temperature is the temperature at which a gas shows neither a heating effect nor a cooling effect. At this temperature, $\mu = 0$, for the gas.

Liquefaction of Gases

Liquefaction of gases (by Joule-Thomson Effect): When a compressed gas is allowed to expand adiabatically into a region of low pressure or vacuum, in general, a lowering of temperature is observed. This is known as Joule-Thomson effect. More precisely, above inversion temperature (T_i), a gas on expansion shows a heating effect while below it the gas cools on expansion. Most gases have fairly high inversion temperatures except H_2 and He (T_i,H_2=193K & T_i,He $= 33K$). Most gases can be cooled by Joule-Thomson effect at ordinary temperature.

A Linde Refrigerator works on the principle that, below its inversion temperature, a gas cools on expansion. The gas is recirculated many times through a pipe fitted with a throttle. When it is beneath its inversion temperature, it cools on expansion through the throttle. After recirculation of this cooling gas and for a big enough pressure drop across the throttle, the temperature falls below the condensation temperature, and the liquid forms.

Degrees of Freedom

The number of independent coordinates needed to specify each kind of motion (translation, rotation, vibration) is called the **number of degrees of freedom** for that kind of motion. Each such coordinate specifies a mode of motion, so the number of degrees of freedom is the number of modes of motion. A polyatomic molecule containing N-atoms has 3N degrees of freedom since each atom requires 3 degrees of freedom in the x, y, and z-directions to specify its position.

Vibrational Degrees of Freedom

If we subtract the translational and rotational degrees of freedom from the total 3N degrees of freedom, we are left with:

- 3N−6 vibrational degrees of freedom for non-linear molecules.
- 3N−5 vibrational degrees of freedom for linear molecules.

A vibrational degree of freedom is also known as a normal mode of vibration or a fundamental mode of vibration.

Degrees of freedom	Linear	Non-Linear
Translational	3	3
Rotational	2	3
Vibrational	3N−5	3N−6
Total	3N	3N

Principle of Equipartition of Energy

This principle is stated as:

"Each quadratic term in the molecular energy expression contributes $\frac{1}{2}kT$ to the average energy per molecule."

The molecular energy is the sum of translational, rotational, vibrational, and electronic energies:

$$\epsilon_{total} = \epsilon_{tr} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{el}.$$

Translational, Rotational, and Vibrational Energy

Translational Energy: The translational energy is given by:

$$\epsilon_{tr} = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$$

Since ϵ_{tr} has three terms, each quadratic in momentum, the equipartition principle says that it contributes $3 \times \frac{1}{2}kT = \frac{3}{2}kT$ to the average kinetic energy per molecule.

Rotational Energy: The rotational energy of a molecule is given by:

$\epsilon_{rot} = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2$ (linear molecule).

$\epsilon_{rot} = \frac{1}{2}I_x\omega_x^2 + \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$ (non-linear molecule).

Where ω_x, ω_y and ω_z are angular velocities and I_x, I_y and I_z are moment of inertia about x, y and z-axes, respectively. Since each term in the above expression are quadratic in velocity, it contributes on an average $\frac{1}{2}kT$ towards average rotational energy. Thus,

The average rotational energy is

$\epsilon_{rot} = \frac{1}{2}kT + \frac{1}{2}kT = kT$ for a linear molecule and

$\epsilon_{rot} = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$ for a non-linear molecule.

Vibrational Energy: If a normal mode of vibration is assumed to be a simple harmonic oscillator, then the energy of each mode is given by:

$$\epsilon_{vib} = \frac{1}{2}\mu\left(\frac{dr}{dt}\right)^2 + \frac{1}{2}k(r - r_e)^2$$

where μ is the reduced mass, k is the force constant, r_e is the equilibrium value of the co-ordinate. Since both the terms in the above expression are quadratic in velocity or the position co-ordinate each will contribute $\frac{1}{2}kT$ towards average vibrational energy.

So, each mode contributes $2 \times \frac{1}{2}kT = kT$ towards the average vibrational energy.

Total Average Energy per molecule:

The total average energy contribution due to all modes is:

For a linear molecule:

$$\varepsilon = \epsilon_{tr} + \epsilon_{rot} + \epsilon_{vib} = \frac{3}{2}kT + kT + (3N - 5)kT$$

For a non-linear molecule:

$$\varepsilon = \epsilon_{tr} + \epsilon_{rot} + \epsilon_{vib} = \frac{3}{2}kT + \frac{3}{2}kT + (3N - 6)kT$$

The total average energy per mole:

Linear:

$$E_m = \frac{3}{2}N_AkT + N_AkT + (3N - 5)N_AkT = \frac{3}{2}RT + RT + (3N - 5)RT$$

Non-linear:

$$E_m = \frac{3}{2}N_AkT + \frac{3}{2}N_AkT + (3N - 5)N_AkT = \frac{3}{2}RT + \frac{3}{2}RT + (3N - 6)RT$$

Heat Capacity of Gases

Heat capacity of a gas is defined as the amount of heat required to increase its temperature by 1 degree. Two heat capacities are defined for the gas:

(i) Heat capacity at constant volume (C_V):

$$C_V = \left(\frac{\delta q}{\delta T}\right)_V = \left(\frac{\delta U}{\delta T}\right)_V$$

(ii) Heat capacity at constant pressure (C_p):

$$C_p = \left(\frac{\delta q}{\delta T}\right)_p = \left(\frac{\delta H}{\delta T}\right)_p$$

For one mole of an ideal gas,

$$C_{p,m} - C_{V,m} = R$$

Heat Capacity of Monatomic Gas

A monoatomic gas consists of atoms only. Atoms have only translational motion, and the number of translational degrees of freedom is 3. Thus, according to the principle of equipartition of energy, each translational degrees of freedom contribute $\frac{1}{2}kT$ to the average energy per atom.

$$\therefore \epsilon_{tr} = 3 \times \frac{1}{2}kT = \frac{3}{2}kT$$

Average energy per mole, $U_m = N_A \epsilon_{tr} = N_A \times \frac{3}{2}kT = \frac{3}{2}RT$

Now, molar heat capacity at constant volume,

$$C_{V,m} = \left(\frac{\delta U_m}{\delta T}\right)_V = \frac{3}{2}R = \frac{3}{2} \times 8.314\, JK^{-1}mol^{-1} = 12.47JK^{-1}mol^{-1}$$

$$\therefore \quad C_{p,m} = C_{V,m} + R = \frac{3}{2}R + R = \frac{5}{2}R$$

∴ Heat capacity ratio is

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

Heat Capacity of Diatomic Gas

For a linear diatomic molecule:

Number of translational degrees of freedom = 3
Number of rotational degrees of freedom = 2
Number of vibrational degrees of freedom = 3N−5=1
Average translational energy per molecule:

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

Average rotational energy per molecule:

$$\epsilon_{rot} = \frac{1}{2}kT + \frac{1}{2}kT = kT$$

Average vibrational energy per molecule:

$$\epsilon_{vib} = 1 \times kT = kT$$

Total average energy per molecule:

$$\varepsilon = \epsilon_{tr} + \epsilon_{rot} + \epsilon_{vib} = \frac{3}{2}kT + kT + kT = \frac{7}{2}kT$$

∴Total average internal energy per mole:

$$U_m = N_A\epsilon = N_A \times \frac{7}{2}kT = \frac{7}{2}RT$$

Now, molar heat capacity at constant volume,

$$C_{V,m} = \left(\frac{\delta U_m}{\delta T}\right)_V = \frac{7}{2}R$$

$$\therefore \quad C_{p,m} = C_{V,m} + R = \frac{7}{2}R + R = \frac{9}{2}R$$

∴ Heat capacity ratio is

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{\frac{9}{2}R}{\frac{7}{2}R} = \frac{9}{7} = 1.286$$

Limitations of Equipartition Principle

Heat capacity values calculated using the equipartition principle agree well with experimental values over a wide range. However, for polyatomic gases, there are two points of disagreement:

1. Theoretical heat capacity values are substantially lower than experimentally observed values.
2. Experimental values noticeably depend on temperature, whereas theoretical values are temperature independent.

The principle's failure lies in the fact that it is a law of classical physics, and for the interpretation of molecular properties, one must use quantum mechanics. At lower temperatures, contributions to heat capacity only come from translational and rotational motions. A 1° rise in temperature at low temperatures cannot increase the number of molecules in higher vibrational levels, so vibrational motion does not contribute to heat capacity. The contribution from vibrational levels only appears at high temperatures.