

# THERMODYNAMICS

## INTRODUCTION

Thermodynamics is the branch of chemistry that deals with energy changes occurring during various physical & chemical processes. It also deals with the transformation between different forms of energy.

### Basic Terms Used In Thermodynamics

**System** : The part of universe under thermodynamics investigation is called system.

**Surrounding** : Anything out side the system is called surrounding.

**Universe = System + Surroundings**

## TYPES OF SYSTEM

**Depending on Exchange of Energy Between Sstem and Surroundings System can be Classified as:**

- (i) **Open System** : A system which can exchange both energy and matter with surrounding.
- (ii) **Closed System** : A system which can exchange only energy with surrounding.
- (iii) **Isolated System** : A system which cannot exchange matter or energy with surrounding.

**Depending on the Components of System Involved it can also be Classified as:**

**Homogeneous System** : System consisting of single phase. e.g. Pure solid, a pure liquid a solution, or a mixture of gases(gases always form homogeneous mixture)

**Heterogenous System** : A system consisting of more than one **phase**.

Ex. System of two immiscible liquids, two or more solids, a liquid in contact with its vapour etc. are example of heterogenous system.

**Boundary** : Anything which separates system and surrounding is called boundary. Across boundary energy and mass are transferred between system and surrounding.

A boundary can be real or hypothetical.

### Types of Wall or Boundary

**Rigid Wall** : The wall is immovable.

**Non Rigid Wall** : The wall is movable .

**Adiabatic Wall** : No heat exchange across the wall i.e.  $q = 0$ .

**Diathermic Wall** : The heat can be exchanged across the wall i.e.  $q \neq 0$ .

## State Variables & State of a System

**State Variables** : To define a thermodynamics states of a system, we have to specify the values of certain measurable quantities. These are called thermodynamic variable or state variable.

A system can be completely defined by four variables namely pressure, temperature, volume and composition. A system is said to be in a certain definite state when all of its properties have definite value.

**State of System** :We specify the state of a system - say, a sample of material - by specifying the values of all the variables describing the system.

If the system is a sample of a pure substance this would mean specifying the values of the Temperature(T),Pressure(P), Volume(V)and the number of moles of the substance(n).

*“When the values of state variables changes the state of system also changes i.e. state of a system depends on the value of state variables and if their value changes the state of system also changes”*



While mole, mass, heat capacity are extensive properties, concentration, density and specific heat capacity are intensive properties.

Extensive Properties	Intensive Properties
Volume	Molar Volume
Number of moles	Density
Mass	Refractive Index
Free Energy (G)	Surface Tension
Entropy (S)	Viscosity
Enthalpy (H)	Free Energy per mole
Internal Energy (E & U)	Specific Heat
Heat Capacity	Pressure
	Temperature
	Boiling Point, Freezing Point

### THERMODYNAMIC EQUILIBRIUM

Thermodynamic generally deals the equilibrium state of the system in which the state variable are uniform and constant throughout the whole system.

For a system to be in thermodynamic equilibrium all the following three types of equilibrium must co-exist.

(i) **Mechanical Equilibrium**

When there is no macroscopic movement within the system itself or of the system with respect to surroundings, the system is said to be in a state of mechanical equilibrium.

(ii) **Chemical Equilibrium**

When the system consists of more than one substance and the composition of the system does not vary with time, the system is said to be in chemical equilibrium. The chemical composition of a system at equilibrium must be uniform and there should be no **net** chemical reaction taking place.

(iii) **Thermal Equilibrium**

When the temperature throughout the entire system is the same as that of the surroundings then the system is said to be in thermal equilibrium.

**Ex.** Which is the intensive property :-

- (A) temperature      (B) viscosity      (C) density      (D) all

**Ans.** (D)

**Ex.** A thermodynamic state function is :-

- (A) one which obeys all the law of thermodynamics  
 (B) a quantity which is used in measuring thermal changes  
 (C) one which is used in thermo chemistry  
 (D) a quantity whose value depends only on the state of system

**Ans.** (D)

**Ex.** A system is changed from state A to state B by one path and from B to A by another path. If  $DE_1$  and  $DE_2$  are the corresponding changes in internal energy, then :-

- (A)  $DE_2 + E_2 = +ve$       (B)  $DE_1 + DE_2 = -ve$       (C)  $DE_1 + DE_2 = 0$       (D) none of the above

**Ans.** (C)

## THERMODYNAMIC PROCESS

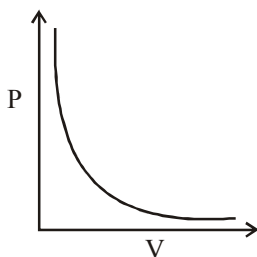
The path followed to change the state of a system is called a process.

### Path of a Process

The exact sequence of steps through which system changes state is called path of a process. e.g. reversible or irreversible path

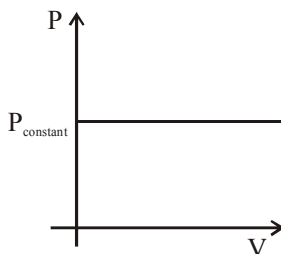
### Some Thermodynamic Processes

- (1) **Isothermal Process** : A process in which temperature of the system remains constant is called isothermal process

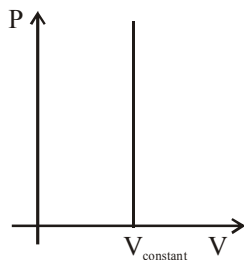


- (2) **Isobaric Process** : A process in which pressure of the system remains constant is called isobaric process. Temperature and volume of the system may change.

**Ex.** All the reactions or processes taking place in open vessel like boiling of water in open vessel, burning of charcoal, melting of wax take place at constant pressure (1 atm.)

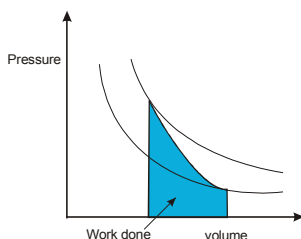


- (3) **Isochoric Process** : The process for which volume of the system remains constant is called isochoric process i.e., Heating of gas in closed vessel.



- (4) **Adiabatic Process** : A process in which no heat exchange takes place is called adiabatic process. Adiabatic process occurs in isolated systems.

i.e.  $q=0$



- (5) **Cyclic Process** : If a system after completing a series of different process returns to its initial state then overall process is called cyclic process.

*“The overall change in value of a state function during the complete cycle is zero”*

Ex.  $\Delta H=0, \Delta E=0, \Delta P.E.=0$

## HEAT AND WORK

Heat and work both are mode of energy transfer between system and surrounding.

Heat flows due to temperature gradient while work is done due to imbalance of generalized force.

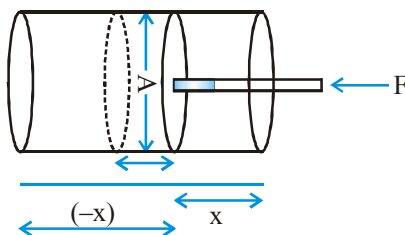
### Sign Convention

Heat absorbed by the system is **+ive**.

Heat released by the system is **-ive**

Work is classified into two broad categorioies as :

- (1) **PV Work** – This type of work is done when change in volume occurs under the influence of external pressure. Consider a cylinder(cross section area A) fitted with a frictionless piston, which enclosed n mole of an ideal gas. Let an external force F pushes the piston inside producing displacement dx in piston.



small change in volume of gas ( $dV$ ) =  $A \cdot dx$

Small work done  $dw = F \cdot dx$

$$\begin{aligned} \text{Also} \quad P &= \frac{F}{A} \\ F &= PA \\ dW &= PA \cdot dx \end{aligned}$$

$$\Rightarrow \therefore dV = -A \cdot dx \quad \text{(-ive sign indicates work is done by the system i.e. gas is expanding against } P_{\text{ext}})$$

$$\Rightarrow dW = -P_{\text{ext}} \cdot dV$$

$$\Rightarrow w = -\int P_{\text{external}} dV$$

### Sign Convention

Work done by the system is **-ive**.

Work done on the system is **+ive**

## KEY POINTS

- (1) During expansion  $dV$  is +ive and hence sign of  $w$  is -ive i.e. work is done by the system and hence Expansion Work is always negative.
- (2) During compression,  $dV$  is -ive which gives +ive value of  $w$  i.e. work is done on the system and hence Compression work is always positive.

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(2) **Non-PV Work** - Following are some examples of Non-PV work.

Stretching	Tension ( $\gamma$ ), length (l)	$w = -\int \gamma dl$	$N\ m = J$
Surface expansion	Surface tension ( $\gamma$ mm), area ( $\sigma$ )	$w = -\iint \gamma d\sigma$	$(N\ m^{-1}) (m^2) = J$
Electrical	Electrical potential ( $\phi$ ),	$w = q \times V$	$V \times C = J$

**Ex.** Find the work done, when one mole of ideal gas in 10 litre container at 1 atm. is allowed to enter a vacuated bulb of capacity 100 litre.

**Ans.** (a)  $W = -P\Delta V$

But since gas enters the vacuum bulb and pressure in vacuum is zero.

$$W = 0$$

**Ex.** If 1 mole of gas expands from 1 litre to 5 litre against constant atmospheric pressure then calculate the work done.

**Ans.** (b)  $W = -P\Delta V = -1(5 - 1) = -4$  litre-atm.

### INTERNAL ENERGY (U OR E)

Consider a system of mass 'M' is moving in gravitational field with velocity v. The total energy of system (in earth frame of reference) is given as :

$$E = K + V + U : (K = \text{kinetic energy, } V = \text{potential energy, } U = \text{internal energy})$$

A thermodynamic system is studied generally at rest so  $K = 0$ . If effect of gravitation field (or other fields are ignored) is also ignored then we left with  $E = U$ .

So, **“In absence of an external field (no external potential energy), when the system is at rest (no external kinetic energy) the total energy of the system is called its internal energy”**

The internal energy of the gas confined in a container is defined relative to a coordinate system fixed on the container. Viewed at a microscopic (atomic) level, the internal energy can take on a number of forms such as.

- The kinetic energy of the molecules ;
- The potential energy of the constituents of the system ; for example, a crystal consisting of dipolar molecules will experience a change in its potential energy as an electric field is applied to the system ;
- The internal energy stored in the form of molecular vibrations and rotations;
- The internal energy stored in the form of chemical bonds that can be released through a chemical reaction.

***The total of all these forms of energy for the system of interest is given the symbol U and is called the internal energy.***

Hence total internal energy of a system can be written as

$$U = U_{\text{translational}} + U_{\text{rotational}} + U_{\text{vibrational}} + U_{\text{intermolecular}} + U_{\text{electronic}} + U_{\text{relativistic}}$$

out of these  $U_{\text{relativistic}}$  and  $U_{\text{electronic}}$  is unaffected by ordinary heating. So basically the kinetic energy terms and  $U_{\text{intermolecular}}$  accommodate the heat provided to the system. Hence heat capacity of a sample depends upon these four terms.

For an ideal gas,  $U_{\text{intermolecular}}$  is equal to zero, because of absence of intermolecular force of attraction in ideal gas.  $U_{\text{intermolecular}}$  have large and negative value in solids and liquids.

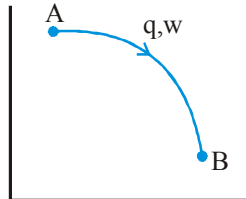
For an ideal gas  $U$  is only function of temperature e.g.  $U = F(T) + \text{Constant}$

Due to absence of pressure or volume terms in ideal gas internal energy,  $U$  is independent of pressure and volume of ideal gas.

- Internal Energy is an extensive Property and is a state function.

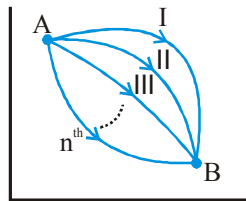
If a system is present in particular thermodynamic state say 'A' it has fixed amount of internal energy  $U_A$ . Suppose by a process the system is taken from state A to state B then

$$\Delta U = U_B - U_A$$



Since  $U$  is state function. This implies between any two fixed state, there can be infinite process or path, but  $\Delta U$  in all process will remain the same. (Property of a function of state)

Consider a system taken from state A to B by  $n^{\text{th}}$  different paths.



i.e.  $\Delta U_1 = \Delta U_2 = \Delta U_3 \dots\dots\dots$

For a given system, Internal Energy can be represented as a function of volume and temperature  $U = f(T, V)$  and the overall change in I.E. can be calculated mathematically as :

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

- For isochoric process :  $dV = 0$

$$dU = \left( \frac{\partial U}{\partial T} \right)_V \cdot dT$$

$$dU = C_v \cdot dT$$

Overall change in I.E.  $\Delta U = \int C_v \cdot dT$

- For an ideal gas

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

$$dU = C_v \cdot dT$$

$$\Delta U = \int C_v \cdot dT$$

- For a real gas  $\left(\frac{\partial U}{\partial V}\right)_T$  is **Positive** when attractive forces dominates (in both compression & expansion) and

$\left(\frac{\partial U}{\partial V}\right)_T$  is **Negative** when repulsive forces dominates (in both compression & expansion).

### KEY POINTS

Note that heat and work involve in all the process are different but  $\Delta U$  is same. This mean heat and work are indefinite quantities while  $\Delta U$  is a definite quantity.

### FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is based on energy conservation principle i.e

"Total energy of universe remain constant."

Let us consider a system whose internal energy is  $U_1$ . If the system is supplied with heat  $q$ , the internal energy of the system increases to  $U_1 + q$ . If work ( $w$ ) is now done on the system, the internal energy in the final state of the system,  $U_2$  is given by

$$U_2 = U_1 + q + w$$

or  $U_2 - U_1 = q + w$

$$\Delta U = q + w,$$

According to IUPAC, heat, added to the system and work done on the system are assigned positive values as both these **Modes** increase the internal energy of the system.

**Ex.** A system expands from 5 L to 10 L against a constant external pressure of 2 atm. If it absorbs 800 J of energy in the process. Calculate the change in its internal energy.

**Sol.**

$$\Delta u = q + w$$

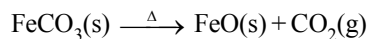
$$w = - (v_2 - v_1)$$

$$= -2(10 - 5)$$

$$= -10 \text{ atm} \cdot \text{L} \times 101.3 \text{ J} = -1013 \text{ J}$$

$$\Delta U = -213 \text{ J}$$

**Ex.**  $\text{FeCO}_3(\text{s})$  decomposes at constant pressure as  $\text{FeO}(\text{s}) + \text{CO}_2(\text{g})$



at  $25^\circ\text{C}$ , the heat absorbed during the reaction is 80 kJ.

Calculate  $\Delta H$  &  $\Delta V$  for the reaction.

**Sol.**

$$\text{FeCO}_3(\text{s}) \longrightarrow \text{FeO}(\text{s}) + \text{CO}_2(\text{g})$$

$$\Delta H = q_p = 80 \text{ kJ}$$

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

$$80 \text{ kJ} = \Delta U + \frac{[1 \times 8.314 \times 298]}{1000} \text{ kJ}$$

$$\Delta U = 77.522 \text{ kJ}$$



**ENTHALPY(H)**

Chemical reactions are generally carried out at constant pressure (atmospheric pressure) so it has been found useful to define a new state function *Enthalpy* (H) as :

$$H = U + PV$$

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

at constant pressure

$$\Delta H = \Delta U + P \Delta V \dots\dots(1)$$

From First Law  $\Delta U = q + w = q - PdV$

$$q = \Delta U + PdV = \Delta H \dots\dots(2)$$

combining with first law.

$$\Delta H = q_p$$

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

- For a given system

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

$$dH = \left( \frac{\partial H}{\partial T} \right)_P \cdot dT + \left( \frac{\partial H}{\partial P} \right)_T \cdot dP$$

- For isobaric process :  $dP = 0$

$$dH = \left( \frac{\partial H}{\partial T} \right)_P \cdot dT$$

$$dH = C_p \cdot dT$$

$$\Delta H = \int C_p \cdot dT$$

- For an ideal gas

$$\left( \frac{\partial H}{\partial P} \right)_T = 0$$

$$dH = C_p \cdot dT$$

$$\Delta H = \int C_p \cdot dT$$

**RELATIONSHIP BETWEEN  $\Delta H$  &  $\Delta U$**

The difference between  $\Delta H$  &  $\Delta U$  becomes significant only when gases are involved (insignificant in solids and liquids)

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

If substance is not undergoing chemical reaction or phase change.

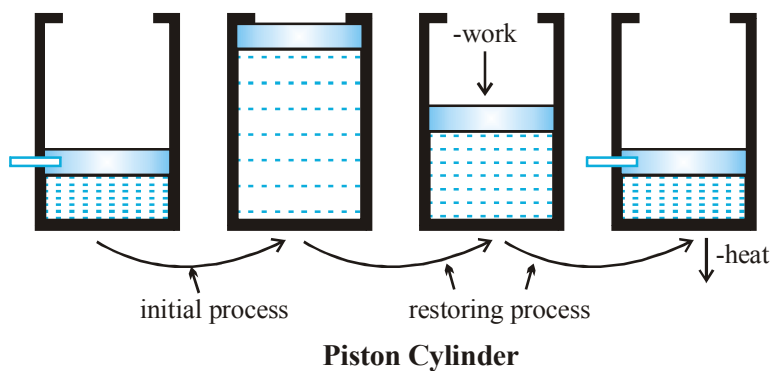
$$\Delta H = \Delta U + nR\Delta T$$

In case of chemical reaction

$$\Delta H = \Delta U + (\Delta n_g)RT$$

### Reversible Process

- These are very slow processes and do not go for completion or take very long time.
- In a reversible process the driving force is greater than the opposing force by a very small value (infinitesimally small value).
- The reversible process is carried out in such a manner that if at any moment opposing force is increased by a small amount the direction of process can be reversed
- A reversible process is also called “**quasi static**” process. A quasi static process is the one in which system remain infinitesimally closer to the state of equilibrium through out the process.

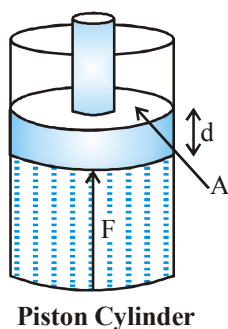


### KEY POINTS

- During a reversible process, the system and surrounding remain in equilibrium throughout the process.
- The reversible processes are idealized processes which cannot be actually carried out, but nevertheless they are very important because they help in calculation of change in state function in the process. In other words the reversible processes are hypothetical processes.

### Irreversible Process

- These are very fast processes and are completed in a short interval of time.
- In an irreversible process the driving force is much greater than the opposing force and therefore the process is completed very fast.

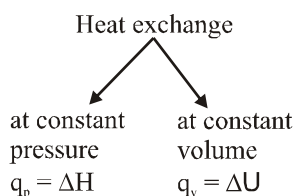


All natural processes are example of irreversible process.

S. No.	Reversible Process	Irreversible Process
1	These are slow processes.	These are instantaneous or sudden processes.
2	Driving force is infinitesimally small.	Driving force is large and finite.
3	It is an ideal process.	It is a real process.
4	It takes infinite time for completion of process.	It takes finite time for completion of the process.
5	It is an imaginary process and can not be realised in	It is a natural process and occurs in particular direction under given set of conditions.
6	Throughout the process, the system remain infinitesimally closer to state of equilibrium.	The system is far removed from state of equilibrium and exact path of process can be drawn.

### Heat Exchange at Constant Volume and Constant Pressure ( $q_p$ and $q_v$ )

Heat exchange can be divided into two parts :



Hence heat exchanged at constant pressure and volume are important **Definite quantities**

### Heat Capacity

The heat capacity of a system may be defined as the amount of heat required to raise the temperature of the system by one degree.

If  $\delta q$  is the small quantity of heat added to the system, let the temperature of the system rises by  $dT$ , then heat capacity  $C$  of the system is given by

$$C = \frac{dq}{dT} \quad \dots(i)$$

In case of gases we have two types of heat capacity i.e. heat capacity at constant volume and heat capacity at constant pressure.

### Heat Capacity at Constant Volume( $C_v$ )

Molar heat capacity at constant volume is defined by the relation

$$C_v = \frac{dq_v}{dT} \quad \dots(ii)$$

For first law of thermodynamics

$$dU = dq - dw$$

But

$$dw = P dV$$

$\therefore$

$$dU = dq - P dV \quad \dots(iii)$$

At constant volume

$$dU = dq_v$$

$\therefore$  Heat capacity at constant volume  $C_v$  is given by

$$C_v = \frac{dq_v}{dT} = \left( \frac{\partial U}{\partial T} \right)_v$$

or

$$C_v = \left( \frac{\partial U}{\partial T} \right)_v \quad \dots(iv)$$

It may be defined as the rate of change of internal energy with temperature at constant volume.

### Heat Capacity at Constant Pressure( $C_p$ )

When pressure is maintained constant, equation (i) takes the form

$$C_p = \frac{\delta q_p}{dT} \quad \dots(v)$$

From first law of thermodynamics

At constant pressure

$$\delta q_p = (dU + PdV) = dH$$

$$[\because H = U + PV \text{ At constant P, } dH = dU + PdV]$$

$$\therefore \delta q_p = dH \quad \dots(vi)$$

Heat capacity at constant pressure  $C_p$  is given by

$$C_p = \frac{\delta d_p}{dT} = \left( \frac{\partial H}{\partial T} \right)_p$$

or 
$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad \dots(vii)$$

It is the rate of change of enthalpy with temperature at constant pressure.

Hence heat capacity of a system at constant volume  $C_v$  is equal to the increase in internal energy of the system per degree rise of temperature at constant volume. Similarly heat capacity at constant pressure  $C_p$  is numerically equally to the increase in enthalpy of the system per degree rise of temperature.

For one mole of gas  $C_p - C_v = R$

For 'n' moles of gas  $C_p - C_v = nR$

- Ex.** Calculate the work done when 1 mol of zinc dissolves in hydrochloric acid at 273 K in :  
 (a) an open beaker  
 (b) a closed beaker at 300 K.

- Sol.** (a) From one mole of zinc, the no. of moles of  $H_2$  gas evolved = 1  
 Hence volume of hydrogen gas evolved = 22.4 litre (when  $P = 1$  atm and  $T = 273$  K)  
 $\therefore w = -P\Delta V = -1 \times 22.4$  litre atm

$$= -22.4 \times \frac{8.314}{0.082} \text{ J} = -2271.14 \text{ J} \quad \text{Ans.}$$

- (b) For a closed system  $P_{\text{ext}} = 0.$ , therefore,  $w = 0.$

- Ex.** Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at  $25^\circ\text{C}$  from 15 to 50 litres.

- Sol.** We have,  $W = -2.303 n RT \log \frac{V_2}{V_1} = -2.303 \times 2 \times 2 \times 298 \times \log \frac{50}{15} = -1436$  calories.

- Ex.** If a gas at a pressure of 10 atm at 300 K expands against a constant external pressure of 2 atm from a vol. of 10 litres to 20 litres find work done ? [Isothermal process]

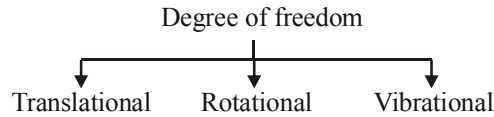
- Sol.** Process is irreversible

$$w = - \int_{10}^{20} 2 dv = -2[20 - 10] = -20 \text{ L.atm}$$

1 litre atm = 101.3 J

### Degree of Freedom and Equipartition Principle

**Degree of Freedom** is defined as the total number of modes on which a molecule of an ideal gas exchange energy during collisions. If a molecule contains only one atom (as in a monatomic gas), it has three degrees of freedom corresponding to translational motion in the three independent spatial directions X, Y and Z.

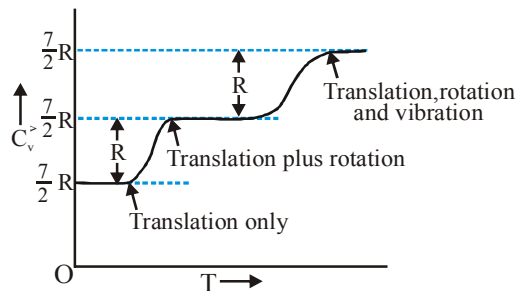


Type	Molecule	trans (f <sub>t</sub> )	rot (f <sub>r</sub> )	vib (f <sub>v</sub> )	Total (3N)
Monoatomic	He	3	0	0	3
Diatomic	N <sub>2</sub>	3	2	1	6
Triatomic linear	CO <sub>2</sub>	3	2	4	9
non-linear	H <sub>2</sub> O	3	3	3	9

vibrational degree of freedom can be calculated by the following method

$$f_v = 3N - (f_t + f_r)$$

Table shows that the observed values of  $\bar{C}_v$  for diatomic molecules deviate greatly from the predicted values, The fact that the value of  $5 \text{ cal deg}^{-1} \text{ mol}^{-1}$  (which is close to  $5R/2$ ) is most common for simple diatomic molecules shows that vibration degrees of freedom are active only at very high temperature. The following graph shows



Variation of heat capacity at constant volume of a diatomic gas due to excitation of rotational and vibrational levels.

variation of  $C_v$  with temperature highlighting the fact that with increase in temperature the vibration modes of motion also contribute to the heat capacity

According to Law of equipartition of energy (i) each translation and rotational degree of freedom in a molecule contributes  $\frac{1}{2}RT$  to the thermal energy of one mole of a gas, and (ii) each vibrational degree of freedom in a molecule contributes  $RT$  to the thermal energy of one mole of a gas.

### Isochoric and Isobaric Process

An isochoric process, also called a constant-volume process, an isovolumetric process, or an isometric process, is a thermodynamic process during which the volume of the closed system undergoing such a process remains constant.

Volume is constant throughout the process.

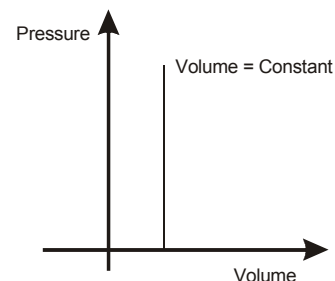
$$dV = 0$$

$$W = \int -P.dV = 0$$

from first law of thermodynamics

$$\Delta U = q + W$$

$$\Delta U = q_v = nC_v\Delta T$$



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An isobaric process is a thermodynamic process in which the pressure stays constant:  $\Delta P = 0$ . The term derives from the Greek iso- (equal) and baros (weight). The heat transferred to the system does work, but also changes the internal energy of the system. ... Since pressure is constant, this means that.

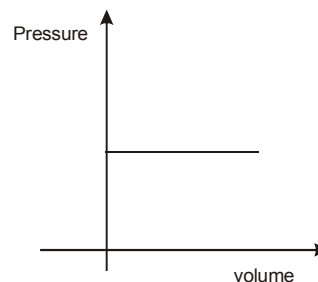
Pressure is constant

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

from first law of thermodynamics

$$\Delta U = q + W$$

$$\begin{aligned} \text{at constant } P, \quad \Delta U &= q_p - P(V_2 - V_1) \\ q_p &= \Delta U + P(V_2 - V_1) = \Delta H \end{aligned}$$



### Relationship Between $C_p$ and $C_v$ for Ideal Gas

Hence transfer of heat at constant volume brings about a change in the internal energy of the system whereas that at constant pressure brings about a change in the enthalpy of the system.

from the first law  $dH = dU + d(PV)$  for a differential change in state

if only ideal gas is involved  $PV = nRT$   $dU = nC_v dT$  and  $dH = nC_p dT$

substituting these results we get

$$nC_p dT = nC_v dT + nRdT$$

$$C_p = C_v + R \text{ valid only for ideal gas}$$

relationship between  $C_p$  and  $C_v$  for real gases, liquid and solids is beyond the scope of JEE syllabus.

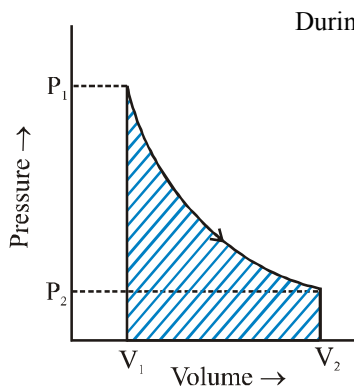
**Isothermal processes can be further classified into two types – Reversible & Irreversible.**

### Analysis of Different Thermodynamic Processes

#### ISOTHERMAL PROCESS

##### Reversible Isothermal Process

If the gas is expanded from initial volume  $V_1$  to final volume  $V_2$  by gradually changing external pressure infinite steps, process is called reversible isothermal process.



During reversible process :

$$P_{\text{ext}} = P_{\text{int}} \pm dP$$

$$\Rightarrow P_{\text{ext}} = P_{\text{int}} = \frac{nRT}{V} \text{ for an ideal gas}$$

$$\text{because } P_{\text{int}} = P_{\text{ideal}} = \frac{nRT}{V}$$

$$dw_{\text{rev, isothermal}} = -PdV$$

$$\int dw = -\int \frac{nRT}{V} dV$$

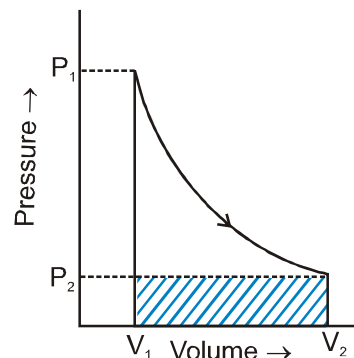
##### Work done in reversible isothermal expansion

$$w = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

**Irreversible Isothermal Expansion** : If external pressure over the piston is abruptly changed from the equilibrium value, the mechanical equilibrium of system is disturbed and piston rushes out :

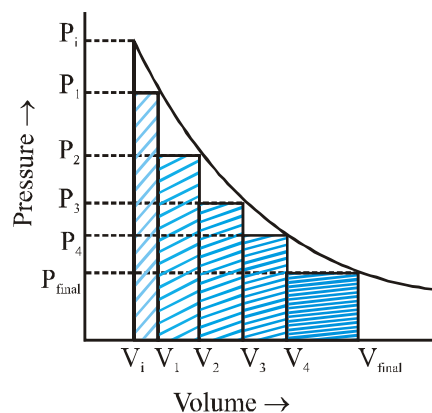
This type of P.V. work is irreversible P.V. work.

∴  $P_{\text{ext}}$  remains constant throughout the process, work done is calculated by  $W_{\text{irr}} = -P_{\text{ext}} \cdot \Delta V$



**Many Steps Irreversible Isothermal Expansion and Compression**

(Comparison) consider an irreversible expansion of an ideal gas from initial pressure of  $P_i$  to final pressure of  $P_f$  in four steps. The gas is allowed to expand against constant external pressure of  $P_1, P_2, P_3$  and  $P_4$  and finally  $P_f$ . Hence the system passes on to final state through four equilibrium states. The work done in the process is shown graphically. The area under the isotherm is the magnitude of reversible work. Clearly the magnitude of reversible work of expansion is greater than irreversible work. As the number of intermediate steps in irreversible expansion is increased, the magnitude of work increases, and as number of steps tend to infinity,  $w_{\text{irr}}$  tends to  $w_{\text{rev}}$ . The graphical comparison of irreversible and reversible work is shown in fig. Here, system is taken from initial state to the final state in four steps and isotherm represent magnitude of reversible work. Clearly,  $w_{\text{reversible}}$  is less than  $w_{\text{irreversible}}$ . Once again as the number of steps in irreversible compression increases, work required to compress the ideal gas decreases, and as number of steps tends to infinity, the  $w_{\text{rev}} = w_{\text{irr}}$ .



**Ex.** 5 mole of an ideal gas are expanded isothermally from pressure of 10 atm to 1 atm at 300 K. Calculate work done in the process. Find work done when process is carried out reversibly (in cal.)

**Sol.** (a)  $W_{\text{irr}} = -1 \text{ nrT} \left( 1 - \frac{1}{10} \right) = \frac{-\text{nrT} \cdot 9}{10}$

$W_{\text{irr}} = - 2700 \text{ Cal}$

(b)  $W_{\text{rev}} = - 2.303 \times 5 \times 2 \times 300 \log 10$   
 $= - 6909 \text{ Cal}$

**Free Expansion of Ideal Gas:** When ideal gas is allowed to expand against zero external pressure, the process is called free expansion.  $W=0$  for free expansion. During the free expansion, the ideal gas do not lose any energy, and hence temperature of ideal gas remain constant. Hence, free expansion of ideal gas is an example of isothermal, adiabatic irreversible process.

However if a real gas is allowed to expand in vacuum, the gas may be cooled or heated up depending upon temperature of the real gas. The temperature above which a gas heats up upon expansion is called inversion temperature. The inversion temperature is strictly not in JEE syllabus

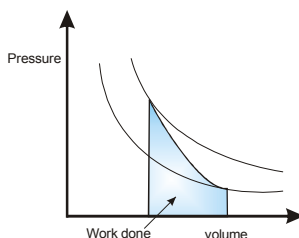
**Stoppered Expansion (Kind of an Irreversible Expansion)** : In this expansion, the gas is allowed to expand against constant external pressure but the piston is stopped at certain volume when system gradually attains equilibrium. In this type of expansion, the  $P_{\text{external}}$  and  $P_{\text{final}}$  are different. The stoppered expansion will help you realize that there can be infinite irreversible path's connection for any two given state at same temperature. (the same can be said about reversible paths)

the work done during stoppered expansion can be given by

$$w = -P_{\text{ext}} \left( \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right) \quad \text{where } P_{\text{ext}} \text{ and } P_f \text{ are different}$$

### ADIABATIC PROCESS

In thermodynamics, an adiabatic process is one that occurs without transfer of heat or matter between a thermodynamic system and its surroundings. In an adiabatic process, energy is transferred only as work.



**Reversible Adiabatic Process** : In an adiabatic process, no loss or gain of heat takes place i.e.,  $dq = 0$ .

From first law, we have,

$$dq = dU + dw$$

Since  $dq = 0$

$$\therefore dU = -dw$$

For an ideal gas,

$$dU = C_v dT$$

$$\therefore C_v dT = -dw = -pdV$$

$$\text{or, } C_v dT = -(nRT/V)dV$$

$$\text{or, } C_v dT/T + nR dV/V = 0$$

Integrating the above equation between  $T_1$  and  $T_2$  and  $V_1$  and  $V_2$ , the initial and final temperature and volumes, we have,

$$\int_{T_1}^{T_2} C_v \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V} = 0$$

$$\text{or } C_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 0$$

$$C_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1} \Rightarrow \ln \frac{V_2}{V_1} = \ln \left( \frac{T_2}{T_1} \right)^{-\frac{C_v}{nR}}$$

$$\ln \frac{V_2}{V_1} = \ln \left( \frac{T_2}{T_1} \right)^{-1} \quad (\because C_v = \frac{nR}{\gamma-1})$$



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

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{T_1}{T_2}\right) \quad \dots\dots(1)$$

or  $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$   
 $T V^{\gamma-1} = \text{constant}$

For an ideal gas,

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

or  $\frac{T_1}{T_2} = \frac{P_1 V_1}{P_2 V_2} \quad \dots\dots(2)$

∴ from equation (1) & (2) we have

$$P_1 V_1^\gamma = P_2 V_2^\gamma = \text{constant}$$

In general, for a reversible adiabatic expansion

$P V^\gamma = \text{constant}$                       Applicable only on a  
 $T V^{\gamma-1} = \text{constant}$                       reversible adiabatic process  
 $T P^{1-\frac{\gamma}{\gamma}} = \text{constant}$

∵  $q = 0$

⇒  $W = \Delta U = nC_v (T_2 - T_1)$

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

$$= \frac{nRT_2 - nRT_1}{\gamma - 1}$$

$$= \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

**Irreversible Adiabatic Process :** Suppose an ideal gas is confined in a adiabatic container fitted with friction less piston. If the thermodynamic equilibrium of system is disturbed by changing external pressure suddenly by finite value and let the system come to equilibrium the process is irreversible adiabatic process. The work done (w) is given by

$$\Delta U = w = -P_{\text{ext}} (V_f - V_i)$$

$$\Delta U = nC_v (T_f - T_i)$$

⇒  $nC_v (T_f - T_i) = -P_{\text{ext}} (V_f - V_i)$

$$nC_v (T_f - T_i) = -P_{\text{ext}} \left( \frac{nRT_f}{P_f} - \frac{nRT_i}{P_i} \right)$$

First we have to calculate the final temperature ( $T_f$ ) from this equation.

now  $w = \Delta U = nC_v (T_2 - T_1)$

$$w = \left[ \frac{P_f V_f - P_i V_i}{\gamma - 1} \right]$$

*Handwritten notes:*  
 $C_v = \frac{nR}{\gamma - 1}$   
 $\rightarrow \left. \begin{array}{l} nRT_2 = P_2 V_2 \\ nRT_1 = P_1 V_1 \end{array} \right\}$

## CHEMISTRY FOR JEE MAIN & ADVANCED

**Ex.** Which of the following processes must violate the first law of thermodynamics? (There may be more than one answer!)

- (A)  $W > 0$ ,  $Q < 0$ , and  $\Delta E_{\text{int}} = 0$
- (B)  $W > 0$ ,  $Q < 0$ , and  $\Delta E_{\text{int}} > 0$
- (C)  $W > 0$ ,  $Q < 0$ , and  $\Delta E_{\text{int}} < 0$
- (D)  $W < 0$ ,  $Q > 0$ , and  $\Delta E_{\text{int}} < 0$
- (E)  $W > 0$ ,  $Q > 0$ , and  $\Delta E_{\text{int}} < 0$

**Sol.**

The correct option is (E).

In accordance to first law of thermodynamics, for a thermodynamic system, in which internal energy is the only type of energy the system may have, the law of conservation of energy may be expressed as

$$Q + W = \Delta E_{\text{int}}$$

Here  $Q$  is the energy transferred (as heat) between the system and environment,  $W$  is the work done on (or by) the system and  $\Delta E_{\text{int}}$  is the change in the internal energy of the system.

By convention we have chosen  $Q$  to be positive when heat is transferred into the system and  $W$  to be positive when work is done on the system.

In the option (E),  $W > 0$  and  $Q > 0$ . If we put this condition in the left hand side of the equation  $Q + W = \Delta E_{\text{int}}$ , then the right hand side of the equation must be greater than zero ( $\Delta E_{\text{int}} > 0$ ). Thus  $W > 0$ ,  $Q > 0$ , and  $\Delta E_{\text{int}} < 0$  must violate the first law of thermodynamics. Therefore option (E) is correct.

**Ex.** Consider the following processes that can be done on an ideal gas: constant volume,  $\Delta V = 0$ ; constant pressure,  $\Delta P = 0$ ; and constant temperature,  $\Delta T = 0$ .

- (a) For which process does  $W = 0$ ?
- (b) For which process does  $Q = 0$ ?
- (c) For which of these process does  $W + Q = 0$ ?
- (d) For which of these process does  $\Delta E_{\text{int}} = Q$ ?
- (e) For which of these process does  $\Delta E_{\text{int}} = W$ ?

- (A)  $\Delta V = 0$                       (B)  $\Delta P = 0$                       (C)  $\Delta T = 0$                       (D) None of these

**Sol.**

(A) The correct option is (A)  $\Delta V = 0$ .

The change in work done  $\Delta W$  is defined as,

$$\Delta W = P\Delta V$$

Therefore  $W = 0$  for the process where  $\Delta V = 0$ . From the above observation we conclude that, option (A) is correct.

(B) The correct option is (D) None of these.

In adiabatic process the exchange of heat with surrounding is zero ( $Q=0$ ). In this process, the change of volume, pressure and temperature occurs. Therefore option (D) is correct.

(C) The correct option is (C)  $\Delta T = 0$ .

For a thermodynamic system, in which internal energy is the only type of energy the system may have, the law of conservation of energy may be expressed as,

$$Q + W = \Delta E_{\text{int}}$$

Where  $Q$  is the energy transferred (as heat) between the system and its environment,  $W$  is the work done on or by the system and  $\Delta E_{\text{int}}$  is the change in the internal energy of the system.

As  $W + Q = 0$ , it signifies that  $\Delta E_{\text{int}} = 0$  and it is possible only when  $\Delta T = 0$ . Therefore option (C) is correct.

(D) The correct option is (A)  $\Delta V = 0$ .

For a thermodynamic system, in which internal energy is the only type of energy the system may have, the law of conservation of energy may be expressed as,

$$Q + W = \Delta E_{int}$$

Here Q is the energy transferred (as heat) between the system and its environment, W is the work done on or by the system and  $\Delta E_{int}$  is the change in the internal energy of the system.

As  $\Delta E_{int} = Q$ , it signifies that  $W=0$ .

The change in work done  $\Delta W$  is defined as,

$$\Delta W = P\Delta V$$

Therefore  $W = 0$  for the process where  $\Delta V = 0$ . From the above observation we conclude that, option (A) is correct.

(E) The correct option is (D) None of these.

For a thermodynamic system, in which internal energy is the only type of energy the system may have, the law of conservation of energy may be expressed as,

$$Q + W = \Delta E_{int}$$

Here Q is the energy transferred (as heat) between the system and its environment, W is the work done on or by the system and  $\Delta E_{int}$  is the change in the internal energy of the system.

As  $\Delta E_{int} = W$ , it signifies that  $Q=0$ .

In adiabatic process the exchange of heat with surrounding is zero ( $Q=0$ ). In this process, the change of volume, pressure and temperature occurs. Therefore option (D) is correct.

### Comparison of Isothermal and Adiabatic Process

Starting from same state, if system is allowed to expand to same final pressure,

$$|w_{rev, isothermal}| > |w_{rev, adiabatic}|.$$

In reversible isothermal process, heat is entering from surrounding, while in adiabatic process, work is done on the expansion of internal energy of system.

Starting from same initial state, if system is compressed to same final pressure,  $w_{rev, adia} > w_{rev, iso}$ . During adiabatic compression, the work done is getting stored in the system, and temperature of system increases, the gas become less and less compressible, and greater work is required to compress the system.

### POLYTROPIC PROCESS

A process described by  $PV^x = C$  is called polytropic process, where x is a real number.

Work done for polytropic process :

$$dw = - PdV$$

Let us suppose an ideal gas is undergoing polytropic process

$$dw = - PdV$$

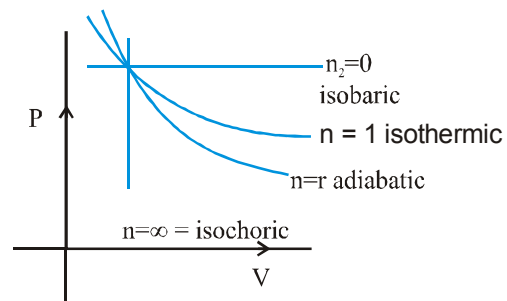
$$W = \int dw = \int_{V_1}^{V_2} \frac{C}{V^n} dV$$

$$\Rightarrow w = \left[ \frac{-C}{(-n+1)} \cdot \frac{1}{V^{n-1}} \right]_{V_1}^{V_2}$$

$$= \frac{C}{(n-1)} \left( \frac{1}{V_2^{n-1}} - \frac{1}{V_1^{n-1}} \right)$$

$$w = \frac{C}{(n-1)} \left( \frac{P_2 V_2 - P_1 V_1}{C} \right)$$

$$w = \left( \frac{P_2 V_2 - P_1 V_1}{n-1} \right)$$



**Heat Capacity ( $C_m$ ) For Polytropic Process**

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

from first law

$$dq = dU + PdV \quad \dots\dots\dots(i)$$

$$C = \frac{dq}{dT} = \frac{nC_v dT}{dT} + \frac{nRT}{V} \cdot \frac{dV}{dT}$$

$$C = nC_v + \frac{nRT}{V} \cdot \left( \frac{dV}{dT} \right) \quad \dots\dots\dots(ii)$$

$$PV^n = k$$

$$\frac{nRT}{V} \times V^n = K$$

$$T \cdot V^{n-1} = \text{constant}$$

On differentiating we get

$$\frac{dV}{dT} = - \left( \frac{V}{T} \right) \left( \frac{1}{n-1} \right) \quad \dots\dots\dots(iii)$$

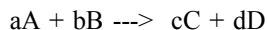
substituting (iii) in equation (ii)

$$C = n_g C_v + \frac{n_g R}{1-n}$$

from 1 mole gas

$$\boxed{C = C_v + \frac{R}{1-n}}$$

**Relationship Between  $\Delta_r H$  And  $\Delta_r U$  in Chemical Reactions :** For a general chemical reaction given by



$$\therefore H = U + PV$$

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

if P is constant then

$$\Delta_r H = \Delta_r U + P(\Delta V)$$

$$\Delta_r H = \Delta_r U + P(V_f - V_i) \quad \dots\dots\dots(2)$$

(a) If all the reactant and products are ideal gases  $V_c, V_d, V_a$  and  $V_b$  all are equal to molar volume of ideal gas e.g.  $V = RT/P$  which on substitution in previous equation gives

$$\Delta_r H = \Delta_r U + (d + c - a - b)RT$$

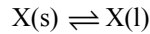
$\Delta_r H = \Delta_r U + \Delta n_g RT \quad \dots\dots\dots(3)$  Where  $\Delta n_g$  is difference of stoichiometric coefficient of gaseous products and gaseous reactants.

(b) In case of liquid and solids present in chemical equations, their molar volumes can be ignored in comparison to molar volume of ideal gases and hence do not count stoichiometric coefficient of solid and liquids in  $\Delta n_g$ .

(c) In case of non ideal behaviour of gases, equation (2) should be used.

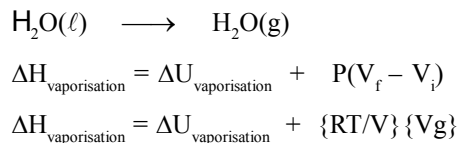
**Change in Internal Energy And Enthalpy in Phase Transition** : At certain temperature under one atmospheric pressure, one phase changes into other phase by taking certain amount of Heat. The temperature at which this happens is called transition temperature and heat absorbed during the process is called Enthalpy of phase transition. Heat absorbed during transition is exchanged at constant pressure and temperature and it is significant to know that the process is reversible.

**Fusion** : Solid ice at 273K and 1 atm pressure reversibly changes into liquid water. Reversibly, isothermally and isobarically, absorbing heat known as latent heat of fusion or enthalpy of fusion.



**Vaporisation** : Water at 373K and 1 atm pressure changes into its vapors absorbing heat known as latent heat of vaporisation. The latent heat of vaporisation is heat exchanged isothermally, isobarically and reversibly to convert water into its vapour at boiling point.

Internal energy change of phase transitions involving gas phase has no practical significance because it is not possible to carry out  $\Delta U$  of phase transition directly through an experiment. However  $\Delta U$  of phase transition can be determined theoretically from experimentally obtained value of  $\Delta H$  of phase transition.



ignoring volume of liquid as compared to molar volume of gas

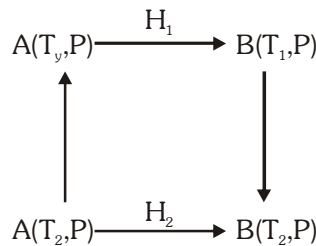
$$\Rightarrow \Delta H_{\text{vap.}} = \Delta U_{\text{vap.}} + RT$$

where R is gas constant and T absolute temperature for condensed phase transitions like solid liquid transitions

$$\Delta H_{\text{vap.}} \approx \Delta U_{\text{vap.}}$$

**Variation of Enthalpy with Temperature (KIRCHHOFF'S EQUATION)**: The enthalpy of chemical reactions and phase transition do vary with temperature. Although the variation in  $\Delta H$  with temperature is usually small compared to the value of  $\Delta H$  itself,

consider a reaction  $A \longrightarrow B$  at temperature  $T_1$  and pressure P



$$\Rightarrow \Delta H_2 - \Delta H_1 = \Delta_r C_p (T_2 - T_1) \quad \text{If } \Delta_r C_p \text{ is independent of 'temperature'}$$

$$\text{where } \Delta_r C_p = \sum n_p x(C_p)_{\text{products}} - \sum n_r x(C_p)_{\text{reactants}}$$

$n_p \rightarrow$  stoichiometric coefficients of products

$n_r \rightarrow$  stoichiometric coefficients of reactants

## CHEMISTRY FOR JEE MAIN & ADVANCED

**Ex.** Calculate the maximum work done when pressure on 10 g of hydrogen is reduced from 20 atm to 1 atm at a constant temperature of 273 K. The gas behaves ideally. Will there be any change in internal energy? Also, calculate 'q'.

**Sol.** We have,

$$W = -2.303 nRT \log \frac{P_1}{P_2}$$

$$n = \text{number of moles of hydrogen} = \frac{\text{wt. in grams}}{\text{mol. wt.}} = \frac{10}{2} = 5 \text{ moles.}$$

$$\text{Thus, } W = -2.303 \times 5 \times 2 \times 273 \times \log \frac{20}{1} = -8180 \text{ calories.}$$

further, the change in state of the system at constant temperature will not change internal energy i.e.,  $\Delta E = 0$ .

Again,  $q = \Delta E - W = 0 - (-8180) = 8180$  calories.

**Ex.** A liquid of volume of 100 L and at the external pressure of 10 atm—Lt the liquid is confined inside an adiabatic bath. External pressure of the liquid is suddenly increased to 100 atm and the liquid gets compressed by 1 L against this pressure then find,

(i) work (ii)  $\Delta U$  (iii)  $\Delta H$

**Sol.** Work done =  $-100 \times -1 = 100$  L. atm

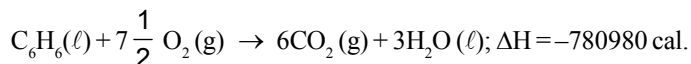
$$\Delta q = 0 \quad \Delta w = \Delta U$$

$$\Rightarrow 100 = \Delta U$$

$$\begin{aligned} \Delta H &= \Delta U + (P_1 V_2 - P_1 V_1) \\ &= 100 + (100 \times 99 - 100 \times 10) \\ &= 100 + 100 \times 89 = 9000 \text{ lit atm.} \end{aligned}$$

$$1 \text{ L. atm} = 101.3 \text{ Joule.}$$

**Ex.** For the combustion of 1 mole of liquid benzene at 25°C, the heat of reaction at constant pressure is given by,



What would be the heat of re action at constant volume?

**Sol.** We have,  $\Delta H = \Delta E + \Delta n_g RT$

$$\text{Here, } \Delta n_g = 6 - 7.5 = -1.5.$$

$$\text{Thus, } \Delta E = \Delta H + \Delta n_g RT = -780980 - (-1.5) \times 2 \times 298 = -780090 \text{ calories.}$$

**Ex.** Calculate q, W,  $\Delta E$  and  $\Delta H$  when 100 gm of  $\text{CaCO}_3$  is converted into its aragonite form given density of calcite = 2 g/cc and density of aragonite = 2.5 g/cc

**Sol.**  $\text{CaCO}_3 \rightleftharpoons \text{CaCO}_3$   
 Calcite Aragonite  $\Delta H = 2 \text{ kJ/mole}$

Generally for solid  $\longrightarrow$  Solid

solid  $\longrightarrow$  Liquid

solid  $\longrightarrow$  Liquid

transitions  $W \ll q$  So,  $\Delta E \simeq q = \Delta H$

while for gaseous conversion for example

Solid  $\longrightarrow$  gas

Liquid  $\longrightarrow$  gas

$q = \Delta H \neq \Delta E$ , as W will be significant

**Spontaneous Process** is the time-evolution of a system in which it releases free energy and moves to a lower, more thermodynamically stable energy state.

**A Non Spontaneous Reaction** is a chemical reaction in which the standard change in free energy is positive and energy is absorbed.

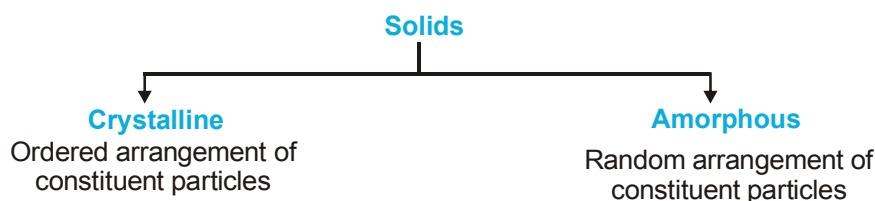
#### Example of Natural Processes

- (i) Water flowing down hill
- (ii) Heat flowing from hot body towards cold body on its own
- (iii) mixing of two gases.
- (iv) Rusting of iron
- (v) Evaporation of water at room temperature.
- (vi) Formation of  $\text{NH}_3(\text{g})$  from  $\text{N}_2(\text{g})$  and  $\text{H}_2(\text{g})$  gas in a closed container.
- (vii) Expansion of ideal gas in vacuum
- (viii) Burning of coal in  $\text{O}_2$

Every natural process leads to production of disorder. (During irreversible process system moves from ordered state to disordered state).

#### ENTROPY (S)

It is the measure of degree of randomness of a system. More random is the system, higher will be its entropy.



For same amount of substance,

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

$$S_{\text{crystalline}} < S_{\text{amorphous}}$$

As number of atoms in a molecule increases, it becomes more complex and hence entropy increases.

Ex.  $\text{NO} < \text{NO}_2 < \text{N}_2\text{O}_3 < \text{N}_2\text{O}_5$

**Ex.** Raw Egg  $\xrightarrow{\text{boil}}$  boiled egg

Weather the entropy of the system will increase or decrease ?

**Sol.** As raw egg contains proteins, entropy will increase due to breaking of H – bond.

Proteins molecules which were associated by H – bonding will be free and thus their will be more free protein molecules in boiled eggs as compared to raw eggs.

Thus entropy will increase.

Entropy is an **extensive property** and is a state function. Therefore we can **only calculate change in entropy**.

$$\text{Change in Entropy } (\Delta S) = S_{\text{final}} - S_{\text{initial}}$$

**THE SECOND LAW OF THERMODYNAMICS**

There are two types of processes reversible process or quasi static process in which system remains in equilibrium with surrounding through out the process.

However reversible processes can not take place on it's own – and are not natural process. Reversible process do not lead to production of disorder.

On the other hand most of the processes taking place around us is example of irreversible process. Irreversible process also natural processes or spontaneous processes.

The second law of thermodynamics predict's direction of natural change. It do so with the help of state function 'S' - called entropy of system. But for predicting direction of natural change another quantity  $S_{\text{surrounding}}$  is also needed.  $S_{\text{surrounding}}$  which is called entropy of surrounding is a path dependent quantity.

$$\begin{aligned} dS_{\text{system}} &= \frac{dq_{\text{rev}}}{T} \\ dS_{\text{surr}} &= -\frac{dq}{T} \end{aligned}$$

Since  $S_{\text{system}}$  is state function - If a system make transition from state A to state B - by infinite paths in few of them may be reversible and other may be irreversible.  $\Delta S_{\text{AB}}$  will be same irrespective of path (A direct consequence of  $S_{\text{system}}$  being a state function).

However, If same transition from A to B is done by different irreversible path's,  $\Delta S_{\text{surrounding}}$  will be different in all processes. However if transition from A → B take place by many reversible path's,  $\Delta S_{\text{surr}}$  along each path will be same because

$$-\sum_{A \rightarrow B}^{\text{path 1}} \frac{dq_{\text{rev}}}{T} = -\Delta S_{\text{system}} = -\sum_{A \rightarrow B}^{\text{path 2}} \frac{dq_{\text{rev}}}{T}$$

⇒  $\Delta S_{\text{surr}} (\text{path 1}) = -\Delta S_{\text{system}} = -\Delta S_{\text{surr}} (\text{path 2})$

	$\Delta S_{\text{system}}$	$\Delta S_{\text{surrounding}}$
reversible process	$\int_A^B \frac{dq_{\text{rev}}}{T}$	$-\int_A^B \frac{dq_{\text{rev}}}{T}$
Irreversible process	$\int_A^B \frac{dq_{\text{rev}}}{T}$	$\int_A^B \frac{dq_{\text{irrev}}}{T} = -\left(\frac{q_{\text{irrev}}}{T}\right)_{A \rightarrow B}$

**Entropy change of system and surrounding in reversible and irrversible process**

Note that  $\Delta S_{\text{surr}} = -\frac{q_{\text{actual}}}{T}$

The central concept of entropy is given briefly, because JEE syllabus deals with consequence of second law rather than it's derivation.

**Prediction of Spontaneity of Process :** If total entropy change in a process is positive the process must be spontaneous.

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \text{ for spontaneous change.}$$

The second law of thermodynamics was developed during course of development of cyclic engines. Second law was discovered while studying efficiency of steam engines. In 1824 a french engineer Sodi carnot pointed out that for a cyclic heat engine to produce continuous mechanical works, it must exchange heat with two bodies at different temperature without a cold body to discard heat, the engine can-not function continuously.



**2<sup>nd</sup> Law Statement**

It is impossible for a system to undergo cyclic process whose sole effects are the flow of heat from a heat reservoir and the performance of an equivalent amount of work by the system on surrounding.

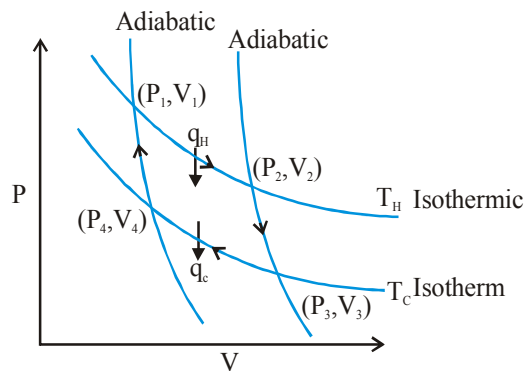
The key term in above statement is cyclic engine. If the first part of it's operation when engine do work heat is absorbed and expansion on take place in second part, it must return to it's original state and to contract, it must loose heat to a cold object (sink).

In other words energy taken from source in one cycle can not be completely converted into work.

**Efficiency of Carnot Engine.**

Carnot has devised an engine based on reverssible steps. The efficiency of carnot engine is maximum, because it is based on reversible cycle. A Carnot engine completes a cycle in four steps.

The Carnot cycle



Reversible isothermal expansion from  $P_1, V_1$  to  $P_2, V_2$  at temp  $T_H$

Reversible adiabatic expansion from  $P_2, V_2$  at temp  $T_H$  to  $P_3, V_3$  at temp  $T_C$

Reversible isothermal compression from  $P_3, V_3$  to  $P_4, V_4$  at temp  $T_H$

Reversible isothermal compression from  $P_4, V_4$  to  $P_1, V_1$  at temp  $T_C$

A carnot engine rejects minimum heat to the surrounding in its operation and maximum part of heat taken form source is converted into work. Hence efficiency of carnot engine is given by

$$\eta = \frac{\text{(Net work done by engine in one cycle)}}{\text{Net heat absorbed from source}}$$

$$\eta = \frac{-w_{\text{net}}}{q_H} \quad \text{where } w_{\text{net}} \text{ is net work done on the engine(system) in one cycle.}$$

It can be easily shown that  $-w_{\text{net}} = q_H + q_C = w_{\text{net}}$

$$q_H + q_C = nRT_H \ln \frac{V_2}{V_1} + nRT_C \ln \frac{V_4}{V_3}$$

also 
$$\left\{ \begin{matrix} T_C V_4^{\gamma-1} = T_H V_1^{\gamma-1} \\ T_C V_3^{\gamma-1} = T_H V_2^{\gamma-1} \end{matrix} \right\} \Rightarrow \left\{ \begin{matrix} \frac{V_4}{V_3} = \frac{V_1}{V_2} \end{matrix} \right\}$$

because of reversible adiabatic process  
substituting these result's

$$\boxed{\eta = \frac{T_H - T_C}{T_H} = \frac{q_H + q_C}{q_H}}$$

- Efficiency of Carnot engine only depends upon temperature of source and sink and independent of choice of working substance.
- Sum of the  $\frac{q_{rev}}{T}$  in a cyclic process is zero.

For the Carnot cycle  $\frac{q_H}{T_H} + \frac{q_C}{T_C} = 0 \Rightarrow$  for carnot cycle  $\sum \frac{q_{rev}}{T} = 0$

- **The result in previous article is valid for any reversible cyclic process. It can be very easily varified.**

Hence  $\oint \frac{dq_{rev}}{T} = 0 \Rightarrow$  Sum of the  $\frac{dq_{rev}}{T}$  over a cyclic path is zero.

now If  $\oint dX = 0 \Rightarrow dX$  is differential of a state function and X is state function.

$\Rightarrow dS = \frac{dq_{rev}}{T} =$  definite quantity

$\Rightarrow S_{system}$  is a state function.

### Clausius Inequality

From our experience we known if any one step in carnot engine is consciously made irreversible the efficiency of carnot engine will decrease from theoretical value

$$\eta = \frac{q_H + q_C}{q_H} = \frac{T_H - T_C}{T_H}$$

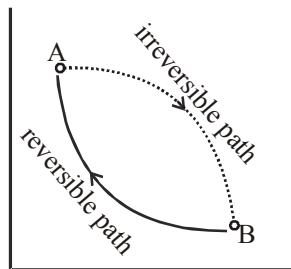
$\Rightarrow \frac{q_H}{T_H} + \frac{q_C}{T_C} < 0$

$\Rightarrow \sum \frac{q_{irr}}{T} < 0$

this mathematical statement is called **Clausius inequality**.

### Entropy Change in Isolated System (Isolated System = sys + surr)

Consider a system taken from state A to state B by an irreversible path and returned to state A by a reversible path. Since one of the step is irreversible, according to Clausius inequality, sum of q/T over the cycle must be less than zero. Hence



$$\sum_{A \rightarrow B} \frac{q_{irr}}{T} + \sum_{B \rightarrow A} \frac{q_{rev}}{T} \leq 0 \Rightarrow \sum_{A \rightarrow B} \frac{q_{irr}}{T} = - \sum_{B \rightarrow A} \frac{q_{rev}}{T}$$

But  $-\sum_{B \rightarrow A} \frac{q_{rev}}{T} = \sum_{A \rightarrow B} \frac{q_{rev}}{T}$  since the process is reversible

for infinitesimally small change

$$\left(\frac{dq}{T}\right)_{A \rightarrow B} = dS_{\text{system } A \rightarrow B}$$

$$\Rightarrow dS_{\text{system}} - \left(\frac{dq}{T}\right)_{A \rightarrow B} > 0$$

$$\Rightarrow dS_{\text{system } A \rightarrow B} + dS_{\text{sur } A \rightarrow B} > 0$$

$$\Rightarrow \Delta S_{\text{Total isolated sys}} > 0$$

- **Entropy Calculation in Process Involving Ideal Gases.**

From First law

$$dq = dU + PdV$$

$$\Rightarrow \frac{dq_{\text{rev}}}{T} = \frac{dU}{T} + \frac{PdV}{T}$$

But for ideal gas

$$\frac{dU}{T} = \frac{nC_v dT}{T} \quad \{\because dU = nC_v dT\}$$

$$\Rightarrow dS_{\text{sys}} = \frac{nC_v dT}{T} + \frac{nR}{V} dV$$

Integration gives

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \left(\frac{V_2}{V_1}\right)$$

For isothermal process

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

For adiabatic process

$$V_1 = V_2$$

$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

For isochoric process

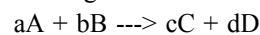
$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

For isobaric process

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

### Entropy Change in Chemical Reaction

From application of third law absolute entropy of every compound or element can be deduced for a general chemical reaction taking place at given condition



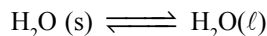
$$\Delta S = \Delta S_{\text{system}} = \text{entropy change of reaction}$$

$$= (aS_C + dS_D - aS_A - bS_B)$$

where  $S_C$ ,  $S_D$ ,  $S_A$  and  $S_B$  are molar entropy of substance A, B, C and D under given circumstance.

### Entropy Change in Phase Transition

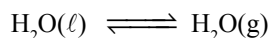
**Fusion** : When solid ice is heated below 273 K at external pressure of 1 atm its temperature slowly rises. At 273 K however, it starts melting into liquid without increase in temperature. The process is reversible phase transition from solid to liquid represented as :



Since process is reversible (you can safely assume that phase transition at constant temperature and pressure are reversible phase transitions).

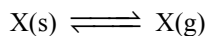
$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_f} \quad \text{entropy of fusion at Melting point.}$$

**Vapourisation** : From your day to day experience you know that under atmospheric pressure temperature of  $\text{H}_2\text{O (l)}$  can not exceed 373 K. Since at 373 K liquid  $\text{H}_2\text{O}$  undergoes phase transition.



$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

**Sublimation** : It is the process in which solid directly changes into gaseous state



$$\Delta S_{\text{sub}} = \frac{\Delta H_{\text{sub}}}{T_{\text{sub}}}$$

**Phase Transition** : Allotrope<sub>1</sub>  $\rightleftharpoons$  Allotrope<sub>2</sub>

$$\Delta S_{\text{transition}} = \frac{\Delta H_{\text{transition}}}{T_{\text{transition}}}$$

### KEY POINTS

Boiling point at 1 atm pressure is called normal boiling point. There can be infinite boiling points of liquid depending upon external pressure we are applying on boiling vessel.

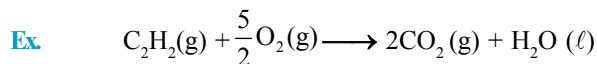
### Entropy and Criteria of Spontaneity of Chemical Process

The entropy change of chemical reaction together with entropy change of surrounding determine spontaneity of a chemical process under given set of conditions.

$\Delta S_T > 0$  the reaction will be Spontaneous.

$\Delta S_T < 0$  the reaction will be Non-Spontaneous.

$\Delta S_T = 0$  Equilibrium



- Ex.** (a) One mole of an ideal gas expands isothermally and reversibly at 25°C from a volume of 10 litres to a volume of 20 litres.
- What is the change in entropy of the gas?
  - How much work is done by the gas?
  - What is  $q$  (surroundings)?
  - What is the change in the entropy of the surroundings?
  - What is the change in the entropy of the system plus the surroundings?
- (b) Also answer the questions opening a stopcock and allowing the gas to rush into an evacuated bulb of 10 L volume.

**Sol.** (a)(i)  $\Delta S = 2.303 nR \log \frac{V_2}{V_1} = 2.303 \times 1 \times 8.314 \times \log \frac{20}{10} = 5.76 \text{ J/K.}$

(ii)  $W_{\text{rev}} = -2.303nRT \log \frac{V_2}{V_1}$   
 $= -2.303 \times 1 \times 8.314 \times 298 \times \log \frac{20}{10} = -1781 \text{ J.}$

(iii) For isothermal process,  $\Delta E = 0$  and heat is absorbed by the gas,

$$q_{\text{rev}} = \Delta E - W = 0 - (-1718) = 1718 \text{ J.}$$

$$\therefore q_{\text{rev}} = 1718 \text{ J.} \quad (\because \text{process is reversible})$$

(iv)  $\Delta S_{\text{surr}} = -\frac{1718}{298} = -5.76 \text{ J/K.}$

As entropy of the system increases by 5.76 J, the entropy of the surroundings decreases by 5.76J, since the process is carried out reversibly.

(v)  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0 \dots$  for reversible process

(b)(i)  $\Delta S = 5.76 \text{ J/K}$ , which is the same as above because  $S$  is a state function

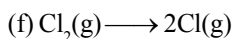
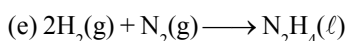
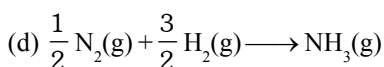
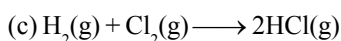
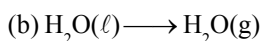
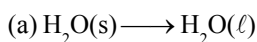
(ii)  $W = 0$  ( $\because p_{\text{ext}} = 0$ )

(iii) No heat is exchanged with the surroundings.

(iv)  $\Delta S_{\text{surr}} = 0.$

(v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increase in an irreversible process.

**Ex.** Will  $\Delta S$  be positive or negative in the following processes ? Discuss qualitatively

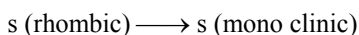


**Sol.** As we have discussed that the entropy of reaction is more if there is a change in value of  $\Delta v_g$  (the change in the stoichiometric number of gaseous species), since the entropy of gases is much larger than the entropy of the condensed phases.

## CHEMISTRY FOR JEE MAIN & ADVANCED

- ∴ for process (a)  $\Delta S$  is +ve  
 for process (b)  $\Delta S$  is +ve  
 for process (c)  $\Delta S$  is zero  
 for process (d)  $\Delta S$  is negative  
 for process (e)  $\Delta S$  is negative  
 for process (f)  $\Delta S$  is positive

**Ex.** Sulphur exists in more than one solid form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs :



Thermodynamic measurements reveal that at 101.325 kPa and 298 K,

$$\Delta_r H = 276.144 \text{ J mol}^{-1} \text{ and } \Delta_r G = 75.312 \text{ J mol}^{-1}$$

- (a) Compute  $\Delta_r S$  at 298 K  
 (b) Assume that  $\Delta_r H$  and  $\Delta_r S$  do not vary significantly with temperature, compute  $T_{\text{eq}}$ , the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

**Sol.** (a) Since

$$\Delta_r G = \Delta_r H - T\Delta_r S,$$

Therefore

$$\begin{aligned} \Delta_r S &= \frac{\Delta_r H - \Delta_r G}{T} = \frac{276.144 \text{ J mol}^{-1} - 75.312 \text{ J mol}^{-1}}{298 \text{ K}} \\ &= 0.674 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

(b) When the rhombic sulphur is in equilibrium with monoclinic sulphur, we would have

$$\Delta_r G = 0 = \Delta_r H - T_{\text{eq}} \Delta_r S$$

$$\begin{aligned} \text{Thus } T_{\text{eq}} &= \frac{\Delta_r H}{\Delta_r S} = \frac{276.144 \text{ J mol}^{-1}}{0.674 \text{ J mol}^{-1}} \\ &= 409.7 \text{ K} \end{aligned}$$

**Ex.** At 1 atm and 27°C, will the vaporisation of liquid water be spontaneous ? Given  $\Delta H = 9710 \text{ cal}$  and  $\Delta S = 26 \text{ eu}$ .

**Sol.**  $\text{H}_2\text{O}(\ell) = \text{H}_2\text{O}(\text{g})$  (P = 1 atm)

$$\Delta G = \Delta H - T\Delta S = 9710 - 26 \times 300 = +1910 \text{ cal}$$

since  $\Delta G$  is positive, at 1 atm, vaporisation is not possible. Rather the reverse process of condensation will occur.

The temperature at which the liquid and vapour will be equiv. can be obtained, by putting  $\Delta G = 0$ , i.e

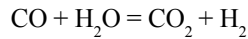
$$\Delta G = 9710 - 26T = 0$$

$$T = 373.4 \text{ }^\circ\text{C}$$

This indeed is the boiling point of water at 1 atm.

<b>Ex.</b>	Gases	$\Delta G_f^\circ$ (Cal/mole)
	CO	-32.80
	H <sub>2</sub> O	-54.69
	CO <sub>2</sub>	-94.26
	H <sub>2</sub>	0

Estimate the standard free energy change in the chemical reaction



**Sol.** Using the necessary data from the table

	CO	H <sub>2</sub> O	CO <sub>2</sub>	H <sub>2</sub>
	$\Delta G^\circ - 32.8$	-54.69	-94.26	0 kcal
$\therefore \Delta G^\circ =$	$-94.26 + 0 - (-32.8) - (-54.69)$			
	$= -6.8 \text{ kcal/mol}$			

### THIRD LAW OF THERMODYNAMICS

Third law of thermodynamics helps in determining absolute entropy of substances. It is based on an assumption that entropy of every perfectly crystalline substance is zero at zero

Kelvin. This is justified because, at absolute zero every substance is in state of lowest energy and position of every atom or molecule is defined in solid. Hence at  $T=0$   $S(T=0)=0$  Third law

If we have sufficient heat capacity data (and the data on phase changes) we could write

$$S(T) = S(T=0) + \int_0^T \frac{C_p}{T} dT \quad \dots\dots\dots(i)$$

(If there is a phase change between 0 K and T, we would have to add the entropy of the phase change.) If  $C_p$  were constant near  $T = 0$ , we would have,

$$S(T) = S(T=0) + C_p \ln \frac{T}{0},$$

Which is undefined. Fortunately, experimentally  $C_p \rightarrow 0$  as  $T \rightarrow 0$ . For nonmetals  $C_p$  is proportional to  $T^3$  at low temperature. For metals  $C_p$  is proportional to  $T^3$  at low temperatures but shifts over to being proportional to  $T$  at extremely low temperatures. (The latter happens when the atomic motion "freezes out" and the heat capacity is due to the motion of the conduction electrons in the metal.)

equation (i) could be used to calculate absolute entropies for substances if we know what the entropy is at absolute zero. Experimentally it appears that the entropy at absolute zero is the same for all substances. The third law of thermodynamics modifies this observation and sets

$$S(T=0) = 0$$

for all elements and compounds in their most stable and perfect crystalline state at absolute zero and one atmosphere pressure. (All except for helium, which is a liquid at the lowest observable temperatures at one atmosphere.)

The advantage of this law is that it allows us to use experimental data to compute the absolute entropy of a substance. For example, suppose we want to calculate the absolute entropy of liquid water at 25°C. We would need to know the  $C_p$  of ice from 0 K to 273.15 K. We also need the heat of fusion of water at its normal melting point. With all of this data, which can be obtained partly from theory and partly from experiment, we find

$$S_{\text{H}_2\text{O}}^\circ(25^\circ\text{C}) = 0 + \int_0^{273.15} \frac{C_p(s)}{T} dT + \frac{\Delta H_{\text{fus}}}{273.15} + \int_{273.15}^{298.15} \frac{C_p(l)}{T} dT.$$

Some substances may undergo several phase changes.

**GIBB'S FUNCTION**

Entropy is a universal criteria of spontaneity. This means for any process if  $\Delta S_{\text{Total}} > 0$  the process is spontaneous. Most of the chemical process take place at constant temperature and pressure. A very useful criteria of spontaneity of process at constant temperature and pressure is Gibb's function :

Gibb's function (G) is defined as

$$G = H - TS \quad \dots\dots(i)$$

Gibb's function and spontaneous process :

from 2<sup>nd</sup> law we know :

$$\frac{dq}{T} \leq dS_{\text{system}} \quad : \text{ Less than sign for if } q = q_{\text{irr}}$$

$$\Rightarrow dq \leq TdS \quad \dots\dots(ii)$$

$$dq = dV + PdV \quad \dots\dots(iii)$$

substituting value of dq from equation (iii) to equation (ii)

$$dV + PdV - TdS \leq 0$$

$$\Rightarrow d(H - TS)_{P,T} \leq 0$$

$$\because d(H - TS)_{P,T} = (dH - TdS - SdT)_{P,T}$$

$$= (dU + PdV + VdP - TdS - SdT)_{P,T} \leq 0$$

$$\Rightarrow d(H - TS)_{P,T} \leq 0$$

$$\Rightarrow d(dG)_{P,T} \leq 0$$

**Statement**

During course of every spontaneous process, Gibb's function decreases. If a process is allowed to run spontaneously, eventually it attain equilibrium. At equilibrium, the Gibb's function attains minimum value. No further decrease to the value of Gibb's function is possible at equilibrium.

**Hence at equilibrium. (dG)<sub>T,P</sub> = 0.**

$\Rightarrow$  Entropy change in spontaneous process :

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \geq 0$$

The sign  $>$  is for spontaneous process. A state of equilibrium in a close system is attained spontaneously. As system approaches equilibrium from non-equilibrium state –  $S_{\text{Total}}$  keeps on increasing and at equilibrium  $S_{\text{Total}}$  attains its maximum value.

$\Rightarrow$   $\Delta S_{\text{Total}} = 0$  at equilibrium

at this point  $S_{\text{Total}} =$  **maximum value at equilibrium in a close system**

**Spontaneous and Non Spontaneous**

Sign of $\Delta H$	Sign of $\Delta S$	Comment	Example	$\Delta H^{\circ}_{298}$	$\Delta S^{\circ}_{298}$
-	+	spontaneous at all temperature	$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $C(s) + O_2(g) \longrightarrow CO_2(g)$	-185 -394	14.1 3
-	-	spontaneous at low temperature	$H_2(g) + 1/2 O_2(g) \longrightarrow H_2O(l)$ $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$	-44 -198	-119 -187
+	+	spontaneous at high temperature	$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$ $N_2(g) + O_2(g) \longrightarrow 2NO(g)$	176 180	284 25
+	-	non spontaneous at all temperature	$3O_2 \longrightarrow 2O_3$ $2H_2O(l) + O_2(g) \longrightarrow 2H_2O_2(l)$	286 196	-137 -126



**SIGNIFICANCE OF GIBB'S FUNCTION**

(a) Decrease in Gibb's function at constant temperature and pressure is related to  $\Delta S_{\text{total}}$  (total entropy change of system and surrounding).

We known :

$$\Delta G = \Delta H - T\Delta S \quad \text{.....(i) ; at constant T and pressure}$$

also  $\Delta H = q_p$  at constant pressure

$q_p$  = heat absorbed by system at constant pressure.

$$\Rightarrow \Delta G = q_p - T\Delta S \quad \text{.....(ii)}$$

this gives  $-\frac{\Delta G}{T} = -\frac{q_p}{T} + \Delta S$

$$-\frac{q_p}{T} + \Delta S_{\text{surrounding}}$$

$$\Rightarrow -\frac{\Delta G}{T} = (\Delta S_{\text{surrounding}} + \Delta S_{\text{system}})$$

Student might get confused in

Ex :  $-\frac{q}{T} = \Delta S_{\text{surr.}}$

Ex :  $q$  = Heat absorbed by system

$-q$  = Heat absorbed by surrounding

$$\Rightarrow \boxed{-\Delta G = T(\Delta S_{\text{Total}})}$$

Note equation (ii) can be written as  $\Delta G = q - q_{\text{rev}}$ .

for spontaneous process  $(\Delta G)_{T,P} < 0$

$$\Rightarrow q - q_{\text{rev}} < 0 \Rightarrow q_{\text{rev}} > q$$

**Gibbs Function And Non PV Work**

Decrease in Gibb's function at constant temperature and pressure in a process gives an estimate or measure of maximum non-PV work which can be obtained from system in reversible, manner.

The example of non-PV work is electrical work done by chemical battery.

Expansion of soap bubble at for a closed system capable of doing non-PV work apart from PV work first law can be written as

$$dU = dq - PdV = dw_{\text{non-PV}}$$

$- dw_{\text{non-PV}}$  = non-PV work done by the system.

$$dG = d(H - TS)$$

$$= dH - TdS - SdT$$

$$dG = dU + PdV + VdP - TdS - SdT$$

$$dG = dq - PdV - w_{\text{non,PV}} + PdV + VdP - TdS - SdT$$

for a reversible change at cont. T and P

$$dG = dq_{\text{rev.}} - dw_{\text{non}} + VdP - TdS - SdT$$

since  $dq_{\text{rev}} = TdS$

$$\Rightarrow -(dG)_{T,P} = dw_{\text{non-PV}}$$

- Non-PV work is work done due to chemical energy transformation or due to composition change and decrease in Gibb's function in a isothermal and isobaric process provide a measure of chemical energy stored in bonds and intermolecular interaction energy of molecules.

### Gibbs Free Energy Change at Constant Temperature

In order to derive an equation which will enable us to calculate the Gibbs free energy change of an isothermal process but with varying pressure, we may conveniently start with the equation,

$$G = E + PV - TS$$

Differentiating the above equation, we get

$$dG = dE + PdV + VdP - TdS - SdT$$

According to first law of thermodynamics,

$$dQ = dE + PdV$$

$$\therefore dG = dQ + VdP - TdS - SdT$$

Further since  $\frac{dQ}{T} = dS$ , we can replace  $dQ$  by  $TdS$ .

$$\therefore dG = VdP - SdT$$

At constant temperature,  $dT = 0$

$$\therefore dG = VdP$$

or 
$$\left(\frac{dG}{dP}\right)_T = V$$

Thus Gibb's function of every substance increases on increasing pressure, but this increase is maximum for gases, compared to solids or liquids since gases have maximum molar volume. On integrating equation  $dG = VdP$  for very minute changes from state 1 to 2, we have

$$\Delta G = G_2 - G_1 = \int_1^2 VdP$$

In case of one mole of a perfect gas,

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

$$\therefore \Delta G = RT \int_1^2 \frac{dP}{P} = RT \ln \frac{P_2}{P_1}$$

For  $n$  moles of a perfect gas, the free energy change is

$$\Delta G = nRT \ln \frac{P_2}{P_1}$$

### Gibbs Free Energy Change at Constant Pressure

From equation which is

$$dG = VdP - SdT \quad (\text{Only for pure substances})$$

when pressure is constant,  $dP = 0$

$$\therefore dG = -SdT$$

or 
$$\left(\frac{dG}{dT}\right)_P = -S$$

thus Gibb's function of every substance decreases with temperature, but this decrease is maximum for gases since they have maximum state of disorder. Hence on increasing temperature, gas phase gain maximum stability compared to solid or liquid phase.

### For Chemical Reaction

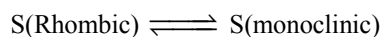
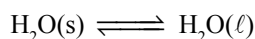
$$\boxed{d(\Delta_r G) = \Delta_r V(dp) - \Delta_r S(dT)}$$

at constant temperature, If  $\Delta_r V \simeq \text{constant}$

$$\Rightarrow \int_1^2 d(\Delta_r C_p) = \Delta_r V \int_1^2 dp$$

$$\Rightarrow \boxed{\Delta_r C_{p_2} - \Delta_r C_{p_1} = \Delta_r V(P_2 - P_1)}$$

only for condensed phase : equilibrium like



### GIBBS FREE ENERGY CHANGE IN CHEMICAL REACTIONS

Gibbs free energy changes have a direct relationship with the tendency of the system to proceed to a state of equilibrium. In view of this fact, it is desirable to have a knowledge of the free energy of chemical compounds so that the Gibbs free energy change of a possible reaction could be easily calculated. Standard free energies have been used for this case. A zero value of the Gibbs free energy is assigned to the free energies of the stable form of the elements at 25°C and 1 atm. pressure.

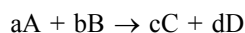
With this as reference point, free energies of compounds have been calculated which are called standard Gibbs free energies of formation. The difference in the Gibbs free energy of products and reactants in their standard states (at 25°C and 1 bar pressure) is denoted as  $\Delta G^\circ$ .

In standard enthalpy and entropy values are available,  $\Delta G^\circ$  can be written from equation as,

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

### GIBB'S FREE ENERGY IN CHEMICAL REACTIONS FROM GIBB'S FREE ENERGY OFFORMATION OF COMPOUNDS

Consider a chemical reaction,



The standard Gibb's free energy change  $\Delta G^\circ$  can be computed on the basis discussed above (i.e., by assigning zero value to the Gibbs free energy of the stable form of elements at 25°C and 1 bar pressure). With this as reference, the standard Gibbs free energy of the products and reactants can be determined. The standard Gibbs free energy change for the overall reaction can be evaluated as :

$$\begin{aligned} \Delta G^\circ &= \sum G_{f(\text{products})}^\circ - \sum G_{f(\text{reactants})}^\circ \\ &= (cG_c^\circ + dG_D^\circ) - (aG_A^\circ + bG_B^\circ) \end{aligned}$$

A negative sign of  $\Delta G^\circ$  will show that the reaction will proceed spontaneously.

note that  $\Delta G^\circ$  can be defined at any temperature, at standard pressure of 1 bar

### Reversible Phase Transitions and Gibb's Free Energy Change

During reversible phase transition which occurs at transition temperatures, Gibb's function change become zero, impling the fact that these processes are reversible processes.

at 373K and 1 atm pressure  $\Delta G = 0$  for  $H_2O(l) \rightarrow H_2O(g)$

at 273K and 1atm pressure  $\Delta G = 0$  for  $H_2O(s) \rightarrow H_2O(l)$

Gibb's energy and equilibrium constant, an important topic taken up in chemical equilibrium.

Application of Gibb's function in decribing variation of vapour pressure, boiling and melting point with temperature is taken up in chemical equilibrium and liquid solutions variation of G/T with temperature , has important implication in pridicting feasibitily of process at different temperatures. This gives Famous Gibb's Helmholtz equation taken up in electrochemistry.

### Topics of Thermodynamics taken up in Later Chapters

#### Application of

- Gibb's function and non-PV work is taken in electrochemistry.
- Gibb's free energy and phase equilibrium taken in liquid solution.
- Gibb's function and position of equilibrium and relationship between  $\Delta G^\circ$  and  $K_{eq}$  taken up in chemical equilibrium.
- Variation of  $\frac{G}{T}$  with temperature also called Gibb's helmholtz equation taken in electrochemistry.

**Ex.**  $K_a$  for  $CH_3COOH$  at  $25^\circ C$  is  $1.754 \times 10^{-5}$  . At  $50^\circ C$ ,  $K_a$  is  $1.633 \times 10^{-5}$  What are  $\Delta H^\circ$  and  $\Delta S^\circ$  for the ionisation of  $CH_3COOH$ ?

**Sol.**  $(\Delta G^\circ)_{298} = -2.303RT \log K = -2.303 \times 8.314 \times 298 \times \log(1.754 \times 10^{-5})$   
 $= 27194 \text{ J.}$

$(\Delta G^\circ)_{323} = 2.303 \times 8.314 \times 323 \times \log(1.633 \times 10^{-5})$   
 $= 29605 \text{ J.}$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$27194 = \Delta H^\circ - 298 \Delta S^\circ$$

$$29605 = \Delta H^\circ - 323 \Delta S^\circ$$

$$\therefore \Delta H^\circ = -1.55 \text{ kJ/mol}$$

$$\Delta S^\circ = -96.44 \text{ J/mol.K}$$

# tips

## First law of Thermodynamics

For a finite change :  $q = \Delta E - w = \Delta E - P\Delta V$

where  $q$  is heat given to system,  $\Delta E$  is change in internal energy and  $-w$  is work done by the system.

$$dq = dE - dw = dE - PdV$$

## Work Done in an Irreversible Process

$$w = -P_{\text{ext}} \times \Delta V = -P_{\text{ext}} \times (V_2 - V_1) = -P_{\text{ext}} \times R \left[ \frac{P_1 T_2 - P_2 T_1}{P_1 P_2} \right]$$

$P_{\text{ext}}$  is the pressure against which volume changes from  $V_1$  to  $V_2$

## Work Done in Reversible Process, i.e., Maximum Work

### Isothermal Conditions

$$w_{\text{rev}} = -2.303 nRT \log_{10} (V_2/V_1)$$

$$w_{\text{rev}} = -2.303 nRT \log_{10} (P_1/P_2)$$

$w_{\text{rev}}$  is maximum work done.

### Adiabatic Conditions

$$w_{\text{rev}} = [nR/(\gamma - 1)] [T_2 - T_1]$$

$\gamma$  is poisson's ratio.

Also for adiabatic process, following conditions hold good :

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

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

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

## Heat Capacities

At constant pressure  $C_p = (\delta H/\delta T)_p$

$C_p$  is molar heat capacity at constant pressure.

At constant volume  $C_v = (\delta E/\delta T)_v$

$C_v$  is molar heat capacity at constant volume.

$$C_p \times c_p \times M \text{ and } C_v = c_v \times M$$

and  $C_p - C_v = R/M$

$$C_p/C_v = c_p/c_v = \gamma \quad (\text{The poisson's ratio})$$

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$c_p$  and  $c_v$  are specific heats at constant pressure and volume respectively.

### Entropy

$$\Delta S = \sum S_{\text{products}} - \sum S_{\text{reactants}}$$

$$\Delta S = q_{\text{rev}}/T = 2.303 nR \log_{10} (V_2/V_1) = 2.303 nR \log_{10} (P_1/P_2)$$

$$\Delta S_{\text{fusion}} = \Delta H_{\text{fusion}}/T$$

$$\Delta S_{\text{vap}} = \Delta H_{\text{vap}}/T$$

$\Delta S$  is entropy change.

### Free Energy

$$G = H - TS$$

$$\Delta G = \Delta H - T\Delta S \text{ and } \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\text{In standard state})$$

At equilibrium,  $\Delta G = 0$

$$-\Delta G^\circ = RT \ln K_p \text{ (or } K_c)$$

$$= 2.303 RT \log_{10} K_p \text{ (or } K_c)$$

$\Delta G$  is free energy change and  $\Delta G^\circ$  is standard free energy change.  $K_c$  and  $K_p$  are equilibrium constants in terms of concentration and pressure respectively.

### Unit Conversion

$$1 \text{ cal} = 4.1868 \text{ J} = 4.1868 \times 10^7 \text{ erg.}$$

$$1 \text{ J} = 10^7 \text{ ergs}$$

$$1 \text{ eV} = 1.602 \times 10^{-19} = 1.602 \times 10^{-12} \text{ ergs.}$$

$$1 \text{ MeV} = 10^6 \text{ eV}$$

order :  $1 \text{ cal} > 1 \text{ J} > 1 \text{ erg} > 1 \text{ eV}$ .