



# Thermodynamics & Thermochemistry

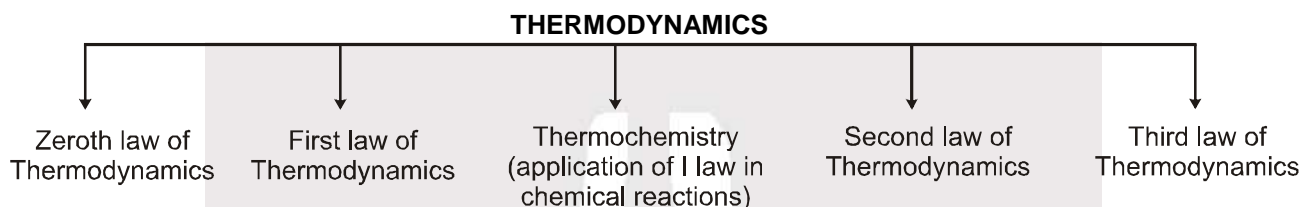
## 1. THERMODYNAMICS

### Thermodynamics I<sup>st</sup> Law

#### Section (A) : Basic definitions

##### Introduction:

**Thermodynamics:** The branch of science which deals with different forms of energy & their interconversion.



##### Application of thermodynamics:

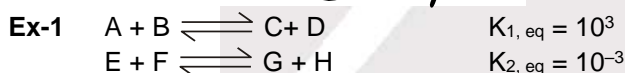
##### In chemistry using thermodynamics

- We can predict feasibility of the reaction that is if two substances are mixed then the reaction between them will take place or not.
- If reaction does take place then what are the energy changes involved during the reaction.
- If in a chemical reaction, equilibrium is going to get attained then what will be the equilibrium concentrations of different reactants & products, can be calculated with thermodynamics.

##### Limitations of thermodynamics:

- Laws of thermodynamics are applicable to matter in bulk or on system as a whole, these can not be applied on individual particles (temperature, pressure, enthalpy etc have meanings only for system as a whole).
- Using thermodynamics we cannot calculate the time taken for completion of a reaction or for attainment of chemical equilibrium.

### Solved Examples



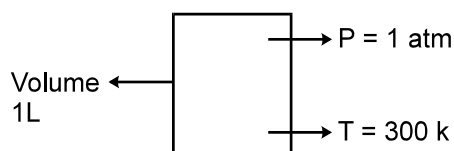
Which of these reaction will attain equilibrium earlier ?

**Sol.** We cannot predict, because value of equilibrium constant has no relation with time taken to attain equilibrium.

- ❖ More the equilibrium constant  $K$ , more will be the concentration of products at equilibrium state.
- ❖ Smaller the equilibrium constant  $K$ , lesser will be the concentration of products at equilibrium state.

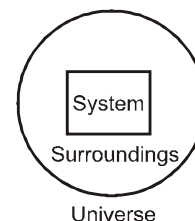
#### Terms to be used in thermodynamics:

- **System** : Part of the universe which is under study for energy changes.



**Ex.** Air in a room, water in a bottle, any living body.

- **Surrounding** : Rest of the universe.
- **Universe** : Universe = System + Surroundings

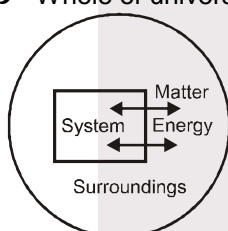




- **Boundary** : Anything which separates system & surroundings is called boundary.
  - Boundary can be real or imaginary.
  - Boundary can be flexible or rigid  
e.g. air in a flexible balloon (flexible boundary) while air in a room (fixed boundary).
  - Boundary can be adiabatic (non-conducting;  $\Delta q = 0$ ) or diathermic (conducting;  $\Delta q \neq 0$ ;  $\Delta T = 0$ ).

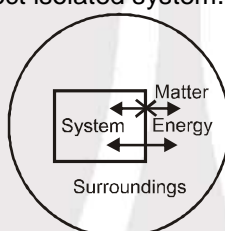
### Types of system :

- **Open system**: System which can exchange energy & matter both with the surroundings.  
e.g. : Living systems( any living organism) are open systems, air in an open room; water flow in pipe.
- **Closed system**: System which can exchange only energy but cannot exchange matter with the surroundings is called closed system.  
e.g. : any matter in a closed container ; Heating of water in closed container.
- **Isolated system**: System which cannot exchange energy and matter both with the surroundings.  
e.g. : Water in thermos flask.(Though not a perfectly isolated system but can be taken as, for small interval of time as the energy exchanges are negligible) ; Hot tea in thermos (few time).
  - Whole of universe is a perfect isolated system.



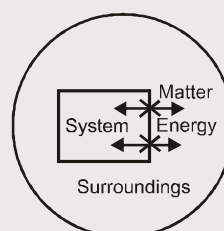
Universe

#### Open System



Universe

#### Close System



Universe

#### Isolated system

- **State of a system:**

- It means the condition in which the system is present.
- It can be specified/defined by measuring/ specifying some observable/measurable properties of the system like pressure, volume, temperature, amount of substance, elasticity, heat capacity etc.  
e.g. For an ideal gaseous system state of the system can be defined by specifying volume, temperature and pressure.
- We may have to specify more properties of the system depending on the complexity of the system.

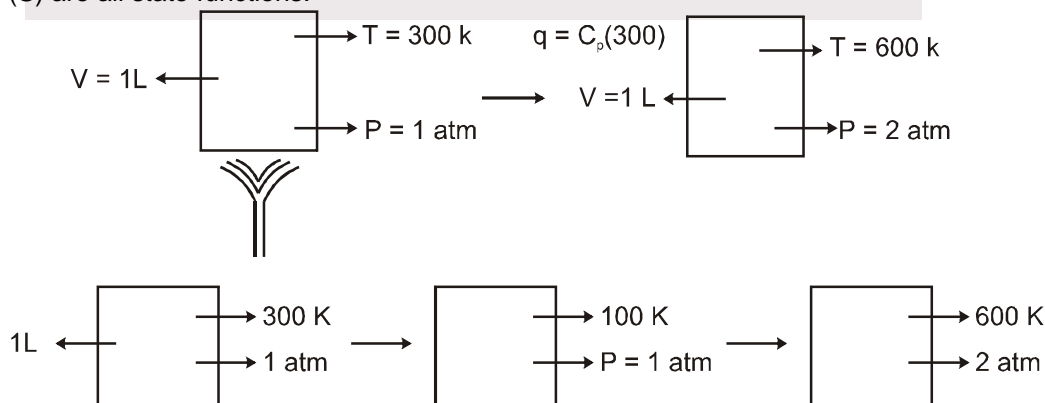
#### State function (State variables) :

- Property of a system which is dependent only on the state of the system i.e. it is a point function
- It is independent of the path adopted to attain a particular state.  
e.g. In Mechanics, Displacement of any object will a state function but distance travelled by the object will be a path function.

For any thermodynamic system,

Temperature, Pressure, Volume, Total internal energy (E or U), Enthalpy(H), Gibbs free energy (G), Entropy (S) are all state functions.

e.g.



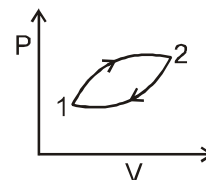


In the above example the final temperature, pressure, and the volume will be same in both the above ways but the work involved and the heat exchanged during the processes will be different.

- For a cyclic process the change in state functions must be zero.

$$\oint dx = 0$$

- State variables can be extensive or intensive.
- Change in state function are not state function.  
Eq.  $\Delta T$ ,  $\Delta V$ ,  $\Delta P$ ,  $\Delta H$ ,  $\Delta G$ ,  $\Delta V$ , etc are not state function.



- **Path function :**

- Quantities which are dependent on the path/way the system has achieved a particular state. e.g. Heat, work, Heat capacities (Molar heat capacities, specific heat capacities etc.).
- These quantities are define when there is a process going on.
- These can not have any definite (particular) value in any particular state of the system.

- **Types of properties**

- **Extensive properties :**

- Functions or properties of the system which are dependent on mass or on size of the system are called Extensive Properties.
- Extensive functions are additive in nature (The addition of the volumes of the two parts equals the volume of the whole of the room.)  
e.g. Volume, Mass, Total heat capacity, Total internal energy (E), Enthalpy(H), Gibbs Free Energy(G), Entropy(S) ; moles etc.

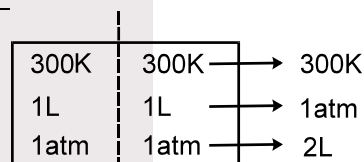
- **Intensive properties :**

- Functions or properties which are not mass dependent or size dependent are called intensive function.
- Intensive properties are not additive in nature.  
eg. Temperature, pressure, molar heat capacity, specific heat capacity, density, concentration, vapour pressure; B.P. ; F.P. ; Viscosity ; pH etc.

### How to identify extensive or intensive properties

If a system in a particular state is divided into two equal or unequal parts, the properties which have value equal to the original value of that property for the whole of the system is called an **Intensive property**.

While the properties which have values different from the values for whole of the system are called **Extensive Properties**.

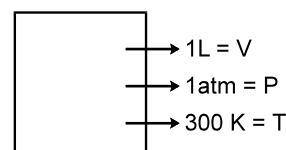


Room is divided into two equal halves

- For example consider air in a room at temp of 300K, 1 atm pressure. Now, if the room is divided by some boundary (imaginary or real) into two parts (equal or unequal) then in these two parts:
  - The temperature, pressure, density of the gas, concentration of gaseous molecules etc. will have the same value as that of for whole of the system. (intensive)
  - While the volume of two parts, mass of gas in two parts, total energy of the gaseous molecules in the two parts, entropy the two parts etc. will be different from the values of these properties as for the whole of the system initially. (extensive)

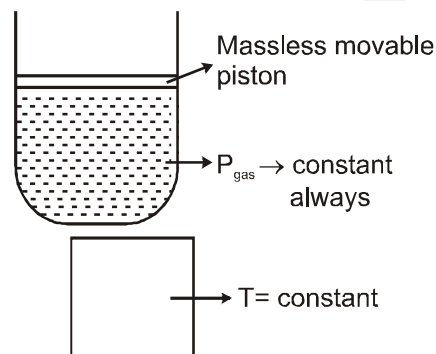
- **Thermodynamic equilibrium:**

- When there is no change in any observable or measurable property of a system with time then the system is said to be in thermodynamic equilibrium.
- Thermodynamic equilibrium consist of three types of equilibrium.
  - (a) Mechanical equilibrium
  - (b) Thermal equilibrium
  - (c) Chemical equilibrium





- Mechanical equilibrium:**  
 There should not be any pressure gradient with time or with space (for any ideal gaseous system, for a liquid system there can be pressure gradient with space as pressure at the bottom of the container in which a liquid is filled will be greater than the pressure at the surface of the liquid.) in the system.
- Thermal equilibrium:** There should not be any temperature gradient (difference). Temperature may have different values at different places/locations in a system but it should remain constant with time.
- Chemical equilibrium:** There should not be any concentration gradient of any of the species in the system.



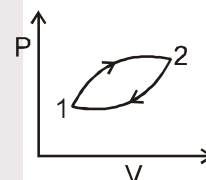
## Section (B) : Thermodynamics processes & graph

### Types of thermodynamic process on basis of state/conditions

**Thermodynamic process :** Any method/process by which system can change its state from one state of thermodynamic equilibrium to another state of thermodynamic equilibrium.

There can be infinite type of thermodynamic processes, out of these the following are important ones:

- Isothermal process :**  $T = \text{constant}$   
 $T_i = T_f$   
 $\Delta T = 0$
- Isochoric process :**  $V = \text{constant}$   
 $V_i = V_f$   
 $\Delta V = 0$
- Isobaric process :**  $P = \text{constant}$   
 $P_i = P_f$   
 $\Delta P = 0$
- Adiabatic process :**  $q = \text{constant}$   
 or heat exchange with the surrounding = 0 (zero)
- Cyclic Process :** A system undergoes a series of changes and comes back to the initial state.  
 $\Delta V = 0$   
 $\Delta H = 0$



### Types of thermodynamics processes on basis of the way the processes are carried out :

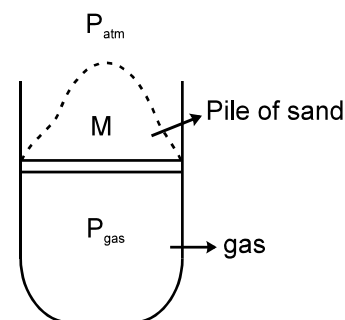
#### Reversible process :

The process that can be reversed by a very small change is known as reversible process.

- If a process is carried out in such a manner so that the system is always in thermodynamic equilibrium at every stage of the process.
- If the process is carried out such that the difference in driving force and opposing force is infinitesimally small so that process takes place at infinitesimally slow rate.

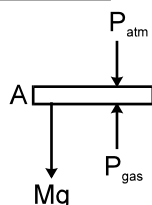
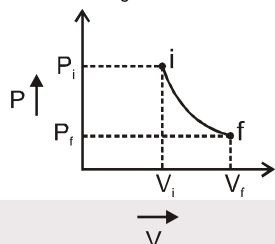
$$F_{\text{driving}} - F_{\text{opposing}} = \Delta F \text{ and } \Delta F \rightarrow 0$$

- An ideal reversible process will take infinite time to get completed.
- It is carried out infinitesimally slowly.
- Strictly speaking there is no ideal reversible process in universe. To get an idea of a reversible process we can consider the following system an ideal gas is enclosed in a container and a massless piston is put on the gas on which a pile of sand is placed having particles of negligible mass. To carry out a reversible expansion we will slowly decrease the mass of the sand let's say by removing the particles one by one, so the expansion of the gas will take place at infinitesimally small rate and we can always assume the system to be in thermodynamic equilibrium. So, the expansion will be of reversible type.





FBD of piston

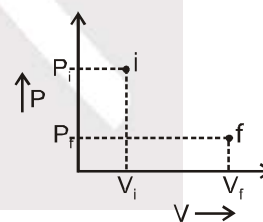
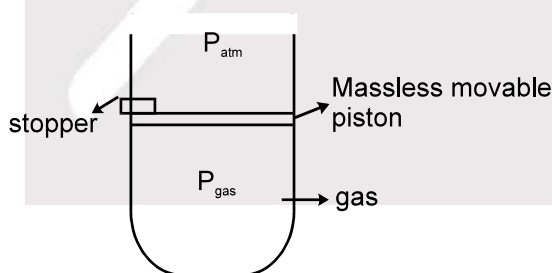

 For piston to be in equilibrium :  $P_{\text{gas}} = P_{\text{atm}} + Mg/A$ 


**Sign :** i – f : expansion  
 f – i : compression

● **Irreversible process:** The process can not be reversed by a small change is known as irreversible.

- If a process is carried out in such a manner so that the system is in thermodynamic equilibrium.
  - (I) Only at initial & final state of the process but not at the intermediate stages.
  - (II) System may be in thermodynamic equilibrium state at some finite number of intermediate stages only - for example - n step irreversible expansion of a gas.
- If during the process there is a finite difference in driving force and opposing force so that process takes place with a finite rate;  $F_{\text{driving}} - F_{\text{opposing}} = \Delta F$ .
- Irreversible processes will get completed in finite time.
- At intermediate stages of the irreversible process, different state function such as pressure, temperature etc. are not defined.
- All real process are irreversible.

Consider the above system. If the stopper placed over the piston is removed, then the piston will move with almost infinite acceleration and will keep moving to a position where the pressure of the gas becomes equal to the external pressure. Since the process will get completed in finite time and there was a finite difference between the driving force and the opposing force so, process is irreversible. During the process, the pressure of the gas can not be defined as it will be having different values at different locations.



**Sign :** i – f : expansion  
 f – i : compression

● **Modes of energy exchange:**

These are two ways by which a system can interact or can exchange energy with its surroundings.

(i) Heat & (ii) Work

Heat & Work both are forms of energy.

**Heat:** When the energy transfer across a boundary as a result of temperature difference between system & surroundings is known as heat.

● **Modes of heat transfer:** Conduction (solids); Convection (fluids); Radiation (vacuum)

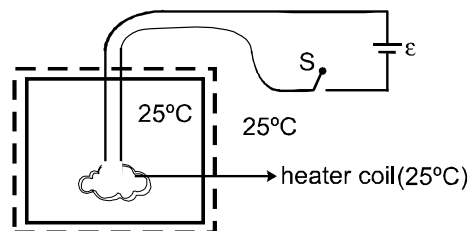
**Work:** Energy transfer which is not heat or which is not because of temperature difference is called work.



**Work can be of many types:** Mechanical work, Electrical work, Magnetic work, Gravitational work etc.

○ **The same energy transfer can be called work or can also be called heat depending on choice of the system.**

To understand this, consider a system shown below in which water is taken in a closed container at 25°C, the surroundings is also at temperature of 25°C and there is a heater coil in the dipped in the water which is connected to a battery through a switch S. Heater coil is also at 25°C initially. Now, there are two ways in which system can be chosen.



**I-System:** All contents of the container (water + Heater coil).

When switch is turned on there will be increment in the temperature of the system. Since the temperature of the surroundings was equal to temperature of the system so, heat can not flow but still there is increment in the energy of the system and hence, there is temperature increment. This must be because of electrical work done by the battery on the system not because of the heat transfer as initially temperatures were equal.

**II-System:** Water only is our system. Heater coil will be part of the surroundings.

In this case when switch is turned on the temperature of the heater coil will increase first so there will be a temperature difference between system & surroundings. Hence, this energy transfer will be called heat.

### ● IUPAC Sign convention about Heat and Work

Any energy given to system is taken positive so heat given to system = positive

heat taken out from system = Negative

Work done on the system = Positive

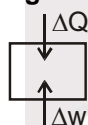
Work done by the system = Negative

The sign convention is different from physics, but the meaning always comes out to be same only in equation we have to use a different sign convention for work.

So if in any problem,  $w = -10 \text{ J}$

It means system has done work of 10 Joule on surroundings.

**According to Chemistry :**



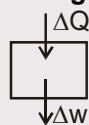
$$\Delta U = \Delta Q + \Delta W$$

IUPAC convention of Heat

1. Heat given to the system = +ve

3. Work done on the system = +ve

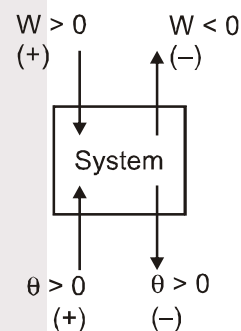
**According to Physics :**



$$\Delta U = \Delta Q - \Delta W$$

2. Heat coming out of the system = -ve

4. Work done by the system = -ve



### Section (C) : Work calculation

#### WORK DONE (w) :

Energy that is transmitted from one system to another in such a way that difference of temperature is not directly involved is known as work. It is a **path function**.

This definition is consistent with our understanding of work as  $dw = Fdx$ . The force  $F$  can arise from electrical, magnetic, gravitational & other sources.

**Units :** Heat & work both are forms of energy. Hence, their units are units of energy. i.e. SI system: Joules (J). Much data is available in the old units of calories (cal) as well.

$P \times V = (\text{litre} \cdot \text{atmosphere})$  term which has unit of energy. It is useful to remember the conversion

1 litre. atm = 101.3 Joules = 24.206 cal





- For irreversible processes, state parameters such as P, T etc cannot be defined. Hence, work cannot be estimated using  $P_{\text{gas}}$ . But by the work energy theorem

$$W_{\text{gas}} = -W_{\text{ext}} + \Delta K_{\text{piston}}$$

When the piston comes to rest again  $\Delta K_{\text{piston}} = 0$

$$\therefore W_{\text{gas}} = -W_{\text{ext}} = -\int P_{\text{ext}} dv$$

as the external pressure is always defined hence, for all processes work can be calculated using

$$W_{\text{gas}} = -W_{\text{ext}} = -\int P_{\text{ext}} \cdot dv = -P_{\text{ext}} \Delta V$$

## ● Calculation of work for different type of process on an ideal gas.

### 1. ISOTHERMAL PROCESS :

(A) **Isothermal expansion:** There are many ways in which a gas can be expanded isothermally.

(a) **Isothermal reversible expansion :**

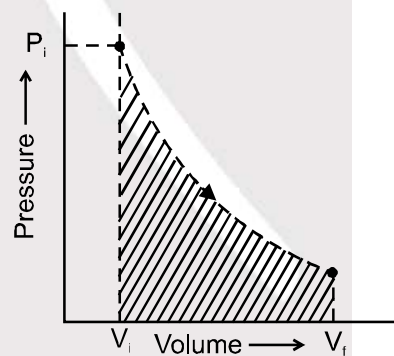
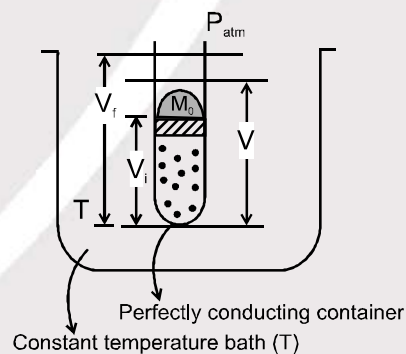
$$P_{\text{ext}} = P_0 + \frac{mg}{A} = P_{\text{gas}} = P \text{ (always)}$$

In reversible process,  $P_{\text{ext}} = P_{\text{gas}}$  (thermodynamic equilibrium always)

Since process is isothermal ;  $P = \frac{nRT}{V}$

$$W = -\int_{V_i}^{V_f} P_{\text{ext}} dV = -\int_{V_i}^{V_f} P dV \Rightarrow W = -\int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$W = -nRT \ln \left( \frac{V_f}{V_i} \right)$$



**PV diagram Representation**

Work = Area under the P-V diagram

In expansion work is done by system on the surroundings and  $V_f > V_i$

$$W = -ve$$

(b) **Irreversible isothermal expansion :**

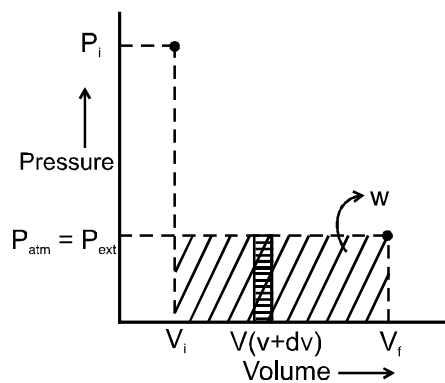
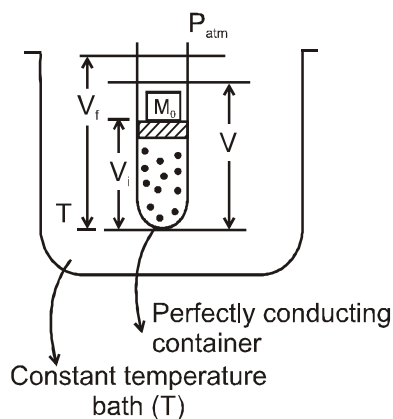
(i) **Single step isothermal expansion**

We are assuming expansion against atmospheric pressure which need not be the case in a given problem.

A mass equal to  $m_0$  is placed on piston initially to maintain equilibrium.

Initially,  $P_i = P_{\text{gas}} = P_{\text{atm}} + m_0 g/A$




**PV diagram Representation**

For expansion to take place,  $m_0$  mass is suddenly removed so gas expands against constant external pressure of  $P_{atm}$

In this case, the pressure of the gas will not be defined as the sudden expansion has taken place so all the molecules of sample will not get the information of expansion simultaneously, there will be a time gap and hence, there will be a **state of turbulence**.

From some intermediate state of volume ' $V$ ', the work done is slight expansion from

$$V \longrightarrow (V + dV)$$

$$dw = -P_{ext} \cdot dV \quad (\text{IUPAC sign convention})$$

$$\text{So, } W = \int dw = - \int_{V_i}^{V_f} P_{ext} \cdot dV = -P_{ext} (V_f - V_i)$$

Only initial and final states can be located (as at intermediate stages pressure of the gas is not defined)

### (ii) Two step isothermal expansion:

**Mass  $M_0$  is divided into two mass (may be equal or unequal)**

$$M_0 = (m_1 + m_2)$$

Now, if  $m_1$  only is removed, then the expansion of gas will take place against constant external pressure

$$P_{ext_1} = (P_{atm} + m_2g/A)$$

and this expansion will take place only upto volume  $V_1$  such that

$$P_{ext_1} \cdot V_1 = P_i V_i \quad (\text{isothermal})$$

Now, if second mass  $m_2$  is also removed then expansion

$V_1 \longrightarrow V_f$  will take place against constant pressure

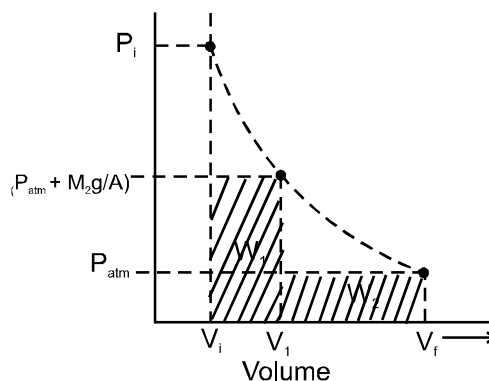
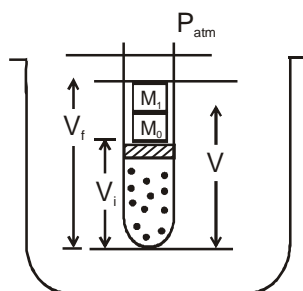
$$\text{So, } P_{ext_2} = P_{atm}$$

$$\text{work done is expansion } V_i \longrightarrow V_1 ; \quad W_1 = -(P_{atm} + M_2g/A) (V_i - V_1)$$

$$\& \text{ work done is expansion } V_1 \longrightarrow V_f ; \quad W_2 = -P_{atm} (V_f - V_1)$$

$$\text{Total work} = W_1 + W_2$$



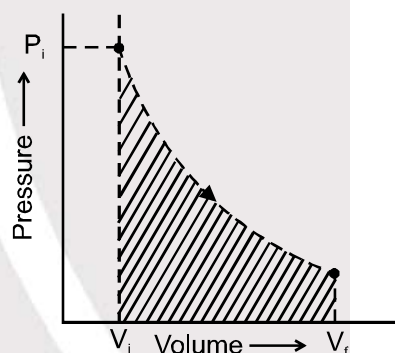
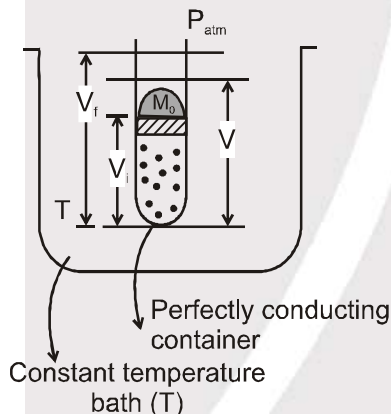


**PV Diagram representation**

• Work done in this irreversible expansion is greater than work done by gas during the single stage expansion of gas and so on for three step expansion we divide the mass  $m_0$  into three masses  $m_1, m_2$  and  $m_3$  and remove these step by step and so on.

**(iii) For  $n$  step expansion and  $n \rightarrow \infty$**

If  $n \rightarrow \infty$ ; Irreversible process becomes reversible process



**PV Diagram representation**

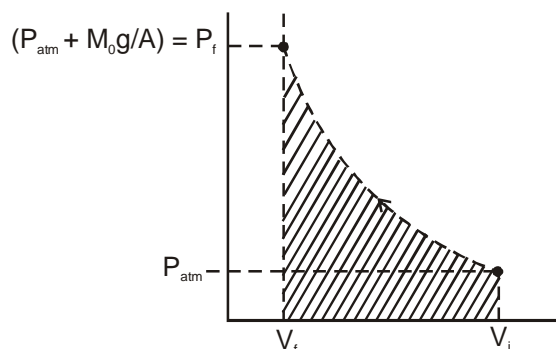
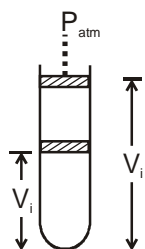
**(B) Isothermal compression of ideal gas :**

**(a) Reversible isothermal compression of an ideal gas**

This can be achieved by placing particles of sand one by one at a very slow take in the assembly which keeps the temperature of gas constant in this case the expression of work done will be exactly similar to as obtained in case of reversible expansion of gas

$$W = -nRT \ln(V_f/V_i)$$

This will automatically come out to be +ve as  $V_f < V_i$



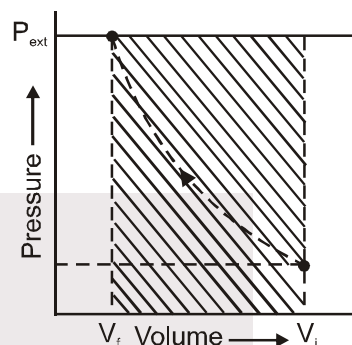
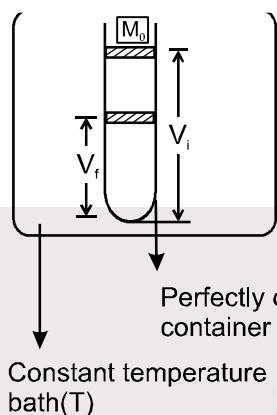

**(b) Irreversible isothermal compression of an ideal gas**
**(i) Single step compression :**

To compress gas a mass  $m_0$  is suddenly placed on massless piston

$$dw = -P_{\text{ext}} \cdot dv = -(P_{\text{atm}} + m_0g/A) dv$$

so, to calculate total work done on the gas

$$W = \int dw = -\int_{V_i}^{V_f} P_{\text{ext}} \cdot dv ; \quad W = -P_{\text{ext}} (V_f - V_i)$$

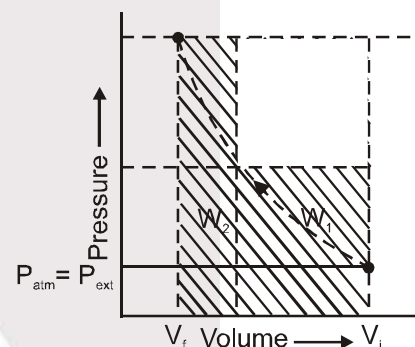

**(ii) Two step compression :**

Place mass  $m_0$  in two fragments ( $m_1+m_2$ ) the graphical representation will make the calculation of work done. If  $m_1$  is placed first, then the first compression has taken place against external pressure of  $(P_{\text{atm}} + m_1g/A)$

$$\text{So, } W_1 = -(P_{\text{atm}} + m_1g/A) (V_1 - V_i)$$

$$\text{Similarly, } W_2 = -(P_{\text{atm}} + m_0g/A) (V_f - V_1)$$

**Note :** If process takes place in  $n$  steps and  $n \rightarrow \infty$  then process will be like reversible compression.


**Conclusion :**

**Whenever work is done on the gas then it will be minimum in case of reversible process.**

That's why different machines/engines are designed to work reversibly so maximum output can be obtained but minimum input is given to it.

- { output – work done by engine/machine/system
- { input – work done by system as a surrounding

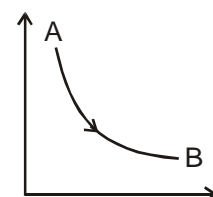
- **If expansion/compression takes place against constant external pressure then it is irreversible.**
- **If there is sudden change then the process is irreversible.**

**Reversible and irreversible isothermal process.**

- Except the infinite stage compression/expansion, all are irreversible.
- We can redefine reversible and irreversible as follows:

**Reversible process:** If a process operates in such a fashion that when it is reversed back both the system as well as surroundings are restored to their initial position w.r.t. both work and heat, is known as reversible process.

If for the process  $A \rightarrow B$  work =  $w$ , heat =  $Q$  then if for the process  $B \rightarrow A$ , work =  $-w$ , heat =  $-Q$  then the process is reversible.



- If the external pressure is constant in isothermally process, process is irreversible.



## Solved Examples

**Ex-2.** Calculate the work performed when 2 moles of hydrogen expand isothermally and reversibly at 25°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-3.** 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

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

$$1 \text{ litre atm} = 101.3 \text{ J}$$

### 2. ISOCHORIC PROCESS :

Since  $dv = 0$

So,  $w = 0$  (for both reversible and irreversible process)

### 3. ISOBARIC PROCESS :

Since  $P = \text{constt.} = P_{\text{ext}}$

So,  $w = -P_{\text{ext}} (V_f - V_i)$  (for both reversible and irreversible process)

## Section (D) : Heat & Internal energy

### Calculation of $\Delta E$ :

#### Internal Energy (E, also denoted by U) :

Every system having some quantity of matter is associated with a definite amount of energy, called internal energy.

- It is the sum of all forms of energies present in the system.

$$E = E_{\text{Translational}} + E_{\text{Rotational}} + E_{\text{Vibrational}} + E_{\text{bonding}} + \dots$$

$$\Delta E = E_{\text{Final}} - E_{\text{Initial}}$$

#### ● Thermodynamic definition of an ideal gas :

- For a gas the internal energy is directly proportional to its absolute temperature then the gas is termed as an ideal gas.

$$\text{so } \left( \frac{\partial E}{\partial V} \right)_T = 0, \left( \frac{\partial E}{\partial P} \right)_T = 0$$

$\Delta E = q_v$ , heat supplied to a gas at constant volume, since all the heat supplied goes to increase the internal energy of the gas.

- It is an extensive property & a state function. It is exclusively a function of temperature.

If  $\Delta T = 0$  ;  $\Delta E = 0$  as well.

- With change in temperature only kinetic energy changes.

#### ● Degree of freedom : The total no of modes on which a molecule of an ideal gas can exchange energy during collisions is known as its degrees of freedom.

Translational degree of freedom = 3 (for all type of gases.)

Rotational degree of freedom

= 0	–	monoatomic gases
= 2	–	diatomic or linear polyatomic gases
= 3	–	non-linear polyatomic gases.

If "f" is initial degree of freedom for that gas.

f = 3	for monoatomic
= 5	for diatomic or linear polyatomic
= 6	for non - linear polyatomic



- **Law of equipartition of energy :**

Energy equal to  $\frac{1}{2} kT$  is associated with each degree of freedom per ideal gas molecule

Where k is Boltzmann constant

$$E/\text{molecule} = f \times \frac{1}{2} kT \quad \Rightarrow \quad E/\text{mole} = \frac{f}{2} RT \quad \text{when } (R = k \times N_A)$$

∴ For n moles,

$$E = \frac{f}{2} nRT \text{ only for ideal gas.} \quad \Rightarrow \quad \Delta E = \frac{f}{2} nR\Delta T$$

- **Calculation of Heat (q)**

- Heat is a path function and is generally calculated indirectly using 1<sup>st</sup> law of thermodynamics.
- First calculate  $\Delta E$  and W & then q or heat can be calculated if heat capacity of any process is given to us.

- **Total Heat Capacity ( $C_T$ )**

Heat required to raise the temperature of system by 1°C under the given process is known as total heat capacity.

$$\text{Mathematically, } C_T = \frac{dq}{dT} \text{ J/}^\circ\text{C}$$

- It is extensive properties and path function.

$$\text{So, } dq = C_T dT$$

$$\text{on integrating } \boxed{q = \int C_T dT}$$

- **Molar heat capacity (C)**

Heat required to raise temperature of 1 mole of a substance by 1°C

$$\text{Mathematically, } C = \frac{dq}{ndT} \text{ J mole}^{-1} \text{ K}^{-1}$$

$$\text{So, } dq = nCdT$$

$$q = \int nCdT = nC\Delta T$$

C is intensive path function.

$C_p$  is molar heat capacity at constant pressure

$C_v$  is molar heat capacity at constant volume

$C_p$  and  $C_v$  are intensive but not a path function

- **Specific heat capacity (s) :**

Heat required to raise temperature of unit mass (generally 1 g) of a substance by 1°C.

$$S = \frac{dq}{mdT} \text{ Jg}^{-1} \text{ K}^{-1}$$

$$\text{So, } dq = msdT$$

$$q = \int dq = \int ms dT = ms\Delta T$$

S is intensive path function

$S_p$  is specific heat capacity at constant pressure

$S_v$  is specific heat capacity at constant volume

$S_p$  &  $S_v$  are intensive but not a path function

Total heat capacity, molar heat capacity & specific heat capacity of a process on a substance are related as

$$C_T = nC = ms \quad \& \quad C = Ms$$

Where m – weight of substance, M – molar mass of substance, n – no. of moles of the substance





For isothermal process  $C = \pm\infty$       For isobaric process  $C = C_p$   
 For isochoric process  $C = C_v$       For adiabatic process  $C = 0$   
 Heat capacity can have value from  $-\infty$  to  $+\infty$  depending on the process.

**Note :**

- (1) Heat capacity is a path function and different type of heat capacities are defined
- (2) Remember heat capacity of a substance is not fixed it is dependent on type of process which is being performed on that substance.

## Solved Examples

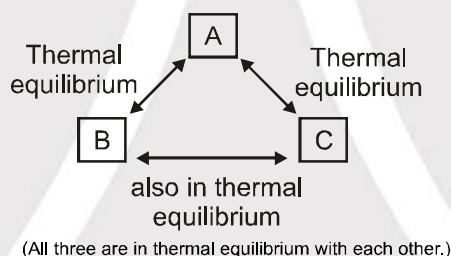
**Ex-4.** During an expansion of ideal gas the work done by gas is 100 J and the heat capacity of process is found to be  $+2 \text{ J}^\circ\text{C}$ . Find  $\Delta E$  of gas if the final temperature of gas is  $25^\circ\text{C}$  higher than its initial temperature.

**Sol.**  $\Delta E = q + W$   
 $q = 2 \times 25 = 50 \text{ J}$  &  $W = -100 \text{ J}$   
 $\Delta E = 50 - 100 = -50 \text{ J}$

### Section (E) : First law of thermodynamics

#### Zeroth Law of Thermodynamics (ZLOT) :

- If two systems are in thermal equilibrium with third system, then they are also in thermal equilibrium with each other.



#### First Law of Thermodynamics (FLOT) :

##### Law of energy conservation :

Energy of total universe is always conserved.

or

Total energy of an isolated system is always conserved.

or

Hence absolute value of E can never be calculated only change in value of E can be calculated for a particular process.

##### Mathematical form of First Law of thermodynamics.

If a system is initially in a particular state in which its total internal energy is  $E_1$ . Now  $q$  amount of heat is given to it and  $w$  amount of work is done on it so that in new state its total internal energy becomes  $E_2$ . Then according to 1<sup>st</sup> Law of thermodynamics.

$$E_2 = E_1 + q + w$$

$$\text{so } \Delta E = (E_2 - E_1) = q + w$$

##### Application of First Law

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

Since

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

$$\Delta U = \Delta Q - P\Delta V$$




**Section (F) : Adiabatic, isothermal, polytropic & free expansion processes**
**4. Adiabatic process :**

$dQ = 0$  (no heat changed b/w system and surrounding)  
 $dU = dQ + dW$

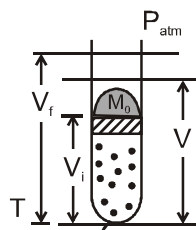
$$\Rightarrow nC_v dT = -PdV \quad \Rightarrow \int nC_v dT = \int -\frac{nRT}{V} \cdot dV$$

$$\Rightarrow \int_{T_1}^{T_2} \frac{C_v \cdot dT}{T} = - \int_{V_1}^{V_2} \frac{R}{V} \cdot dV \quad \Rightarrow C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

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

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

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



Perfectly non-conducting container

- This is only valid when the quantity  $PV^\gamma$  or  $TV^{\gamma-1}$  is constant only for a quasi-static or reversible process.
- For irreversible adiabatic process these equations are not applicable.

**Operation of adiabatic process**
**(a) Reversible Adiabatic**

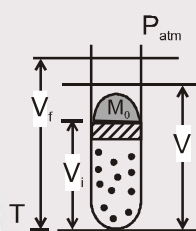
- Operation wise adiabatic process and isothermal process are similar hence all the criteria that is used for judging an isothermal irreversible processes are applicable to adiabatic process.
- Also, volume in case of isothermal is more than that of adiabatic at constant pressure and no of moles,  $V \propto T$

$$w = - \int P_{\text{ext}} \cdot dv, \text{ but } P_{\text{ext}} = P_{\text{int}} = \frac{K}{V^\gamma}$$

$$\therefore w = - \int \frac{K}{V^\gamma} \cdot dv,$$

$$\Rightarrow W = -K \left[ \frac{V_2^{-\gamma+1} - V_1^{-\gamma+1}}{(1-\gamma)} \right] = \frac{P_2 V_2^\gamma \cdot V_2^{1-\gamma} - P_1 V_1^\gamma \cdot V_1^{1-\gamma}}{\gamma-1}$$

$$\Rightarrow \text{Work done} = \frac{P_2 V_2 - P_1 V_1}{\gamma-1} \quad (\text{as } K = P_2 V_2^\gamma = P_1 V_1^\gamma)$$



Perfectly non-conducting container

**(b) Irreversible Adiabatic**
**Adiabatic irreversible expansion -**

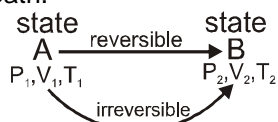
$$W = \int -P_{\text{ext}} \cdot dv = -P_{\text{ext}} (V_2 - V_1)$$

$$\text{and } \int du = \int dw$$

$$\therefore W = \Delta u$$

$$W = nC_v (T_2 - T_1) = \frac{nR(T_2 - T_1)}{\gamma-1} = \frac{P_2 V_2 - P_1 V_1}{\gamma-1}$$

**Note:** If two states A and B are connected by a reversible path then they can never be connected by an irreversible path.

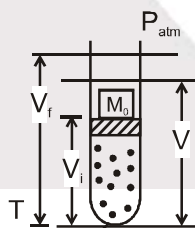


If the two states are linked by an adiabatic reversible and irreversible path then

$$W_{\text{rev.}} = \Delta U_{\text{rev.}}$$

But as  $u$  is a state function

$$\therefore \Delta U_{\text{rev.}} = \Delta U_{\text{irrev.}} \Rightarrow W_{\text{irrev.}} = W_{\text{rev.}}$$



Perfectly non-conducting container





as work is a path function.  
If we assume that

$$W_{\text{irrev.}} = W_{\text{rev.}} \Rightarrow \text{It implies that}$$

$$\Delta U_{\text{rev.}} \neq \Delta U_{\text{irrev.}} \text{ Which again is a contradiction as } U \text{ is a state function.}$$

- Two states A and B can never lie both on a reversible as well as irreversible adiabatic path.
- There lies only one unique adiabatic path linkage between two states A and B.

○ **Comparison of Adiabatic Expansion (single stage Vs Infinite stage)**

Single stage means irreversible process

Infinite stage means reversible process

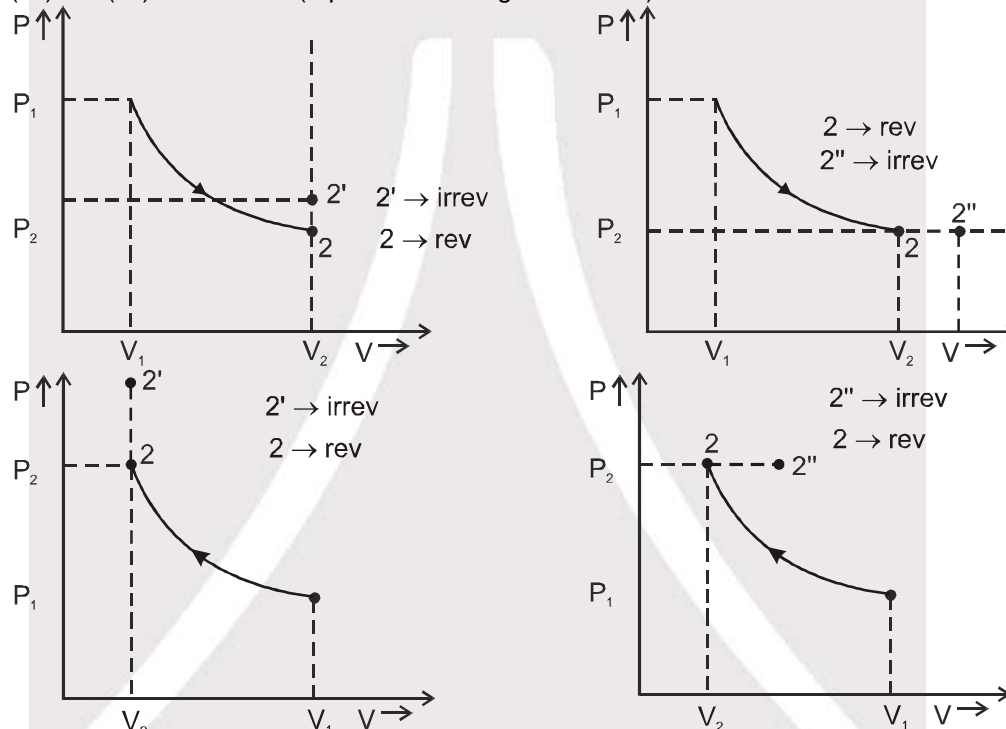
In adiabatic compression process,

$$(W_{\text{gas}})_{\text{rev}} < (W_{\text{gas}})_{\text{irrev}} \Rightarrow \Delta U_{\text{rev.}} < \Delta U_{\text{irrev.}}$$

$$\therefore (T_2)_{\text{rev.}} < (T_2)_{\text{irrev}}$$

$$(P_2)_{\text{rev.}} < (P_2)_{\text{irrev}} \quad (\text{If volume change are same})$$

$$(V_2)_{\text{rev.}} < (V_2)_{\text{irrev}} \quad (\text{If pressure change are same})$$



• **Comparison of single stage Vs two stage expansion(adiabatic).**

If the expansion is carried out in two stages then work done in two stage by the gas > work done in one stage by the gas. So,  $\Delta U_{\text{two stage}} > \Delta U_{\text{single stage}}$

$\therefore T_f$  in two stage <  $T_f$  in single stage because decrease in internal energy in two stage is > decrease in internal energy in one stage.

○ **Adiabatic Irreversible process (calculation of state parameters)**

State A  $\xrightarrow{\text{irrev}}$  State B

$$P_1, V_1, T_1 \quad P_2, V_2, T_2$$

$$W = \frac{nR(T_2 - T_1)}{\gamma - 1} = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1} = -P_{\text{ext.}} (V_2 - V_1) \quad , \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

• **Free expansion :**

Always going to be irreversible and since  $P_{\text{ext}} = 0$

$$\text{So, } dW = -P_{\text{ext.}} dV = 0$$

If no heat is supplied  $q = 0$

then  $\Delta E = 0$  So,  $\Delta T = 0$ .


**Section (G) : Enthalpy**
**Calculation of  $C_p$  and  $C_v$** 
**(a) Constant volume process (Isochoric)**

$$dU = dq + dw$$

$$\therefore dU = (dq)_v \quad (\text{Heat given at constant volume} = \text{change in internal energy})$$

$$\therefore dU = (nC_dT)_v$$

$$dU = nC_v dT$$

$C_v$  is Specific molar heat capacity at constant volume.

$$C_v = \frac{1}{n} \frac{dU}{dT} = \frac{1}{n} \frac{d(fnRT)/2}{dT} = \frac{fR}{2}$$

**(b) Constant pressure process (Isobaric) :**

$$dU = dQ + dW$$

$$dU = dQ - PdV$$

$$\Rightarrow dQ = dU + PdV \quad \dots\dots\dots (i)$$

Defining a new thermodynamic function

$H \equiv$  Enthalpy

- It is a state function and extensive property

- It is mathematically defined as :

$$H = U + PV$$

as  $dH = dU + d(PV)$

as  $P = \text{constant}$

$$dH = dU + PdV \quad \dots\dots\dots (ii)$$

from equation (i) & (ii)

$$\therefore dH = (dq)_p \quad \text{only at constant pressure.}$$

Heat given at constant pressure = Change in enthalpy

$$dH = (nC_dT)_p$$

$$dH = nC_p dT$$

- **Relation between  $C_p$  and  $C_v$  for an ideal gas**

$$H = U + PV$$

$$\therefore dH = dU + d(PV)$$

for an ideal gas

$$PV = nRT$$

$$d(PV) = d(nRT) = nRdT$$

$$nC_p dT = nC_v dT + nRdT$$

$$\Rightarrow C_p - C_v = R \quad \text{only for ideal gas} \Rightarrow \text{Mayer's Relationship}$$

**Table # 1 At Normal temperature**

S.No.	Gas	Degree of freedom	$C_{v,m} \left( \frac{fR}{2} \right)$	$C_{p,m} \left( \frac{f+2}{2} \right) R$	$\gamma = \left( \frac{f+2}{f} \right)$	Examples
1.	Monoatomic	3	$\frac{3R}{2}$	$\frac{5R}{2}$	$\frac{5}{3}$	He; Ne
2.	Diatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$	N <sub>2</sub> ; O <sub>2</sub> ; H <sub>2</sub>
3.	Linear polyatomic	5	$\frac{5R}{2}$	$\frac{7R}{2}$	$\frac{7}{5}$	CO <sub>2</sub> ; HCl
4.	Non-Linear polyatomic	6	$\frac{6R}{2}$	$\frac{8R}{2}$	$\frac{8}{6}$	H <sub>2</sub> O; NH <sub>3</sub> ; CH <sub>4</sub>

**Note :** At high temperature vibrational degree of freedom is also included.





● **Calculation of  $\Delta H$ ,  $\Delta U$ , work, heat etc.**

**Case - I** For an ideal gas undergoing a process.

the formula to be used are

$$dU = nC_v dT = \frac{f}{2} nRdT$$

$$dH = nC_p dT = \left(\frac{f}{2} + 1\right) nRdT$$

$$W = - \int P_{\text{ext.}} dV$$

$$dH = dU + d(PV)$$

$$du = dq + dw$$

### Solved Examples

**Ex-5.** 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.,  $\Delta U = 0$ .

$$\text{Again, } q = \Delta U - W = 0 - (-8180) = 8180 \text{ calories.}$$

**Case - II** For solids and liquid system :

$$dU = nC_v dT \neq \frac{f}{2} nRdT \quad (\text{as it is not an ideal gas})$$

$$dH = nC_p dT \neq \left(\frac{f}{2} + 1\right) nRT \quad (\text{as it is not an ideal gas})$$

$$W = - \int P_{\text{ext.}} dV$$

$$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$$

$$dU = dq + dw$$

### Solved Examples

**Ex-6.** 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 =  $-100 \times -1 = 100 \text{ L. atm}$

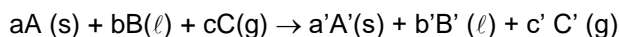
$$\Delta q = 0 \quad \Delta w = \Delta U$$

$$\Rightarrow 100 = \Delta U$$

$$\begin{aligned} \Delta H &= \Delta U + (P_2V_2 - P_1V_1) \\ &= 100 + (100 \times 99 - 100 \times 10) \\ &= 100 + 100 \times 89 = 9000 \text{ lit atm.} \end{aligned}$$

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



**Case - III****For chemical reactions :**

$$W = -\int P_{\text{ext.}} dV = \int -P_{\text{ext.}} (V_f - V_i)$$

$$= -P_{\text{ext.}} [(V_{A'}(s) + (V_{B'}(\ell) + (V_{C'}(g) - (V_A(s) + (V_B(\ell) + (V_C(g))$$

$$\therefore W = -P_{\text{ext.}} [V_{C'}(g) - V_C(g)]$$

$$= -P_{\text{ext.}} \left[ \frac{n'_c RT}{P_{\text{ext}}} - \frac{n_c RT}{P_{\text{ext}}} \right] = -\frac{P_{\text{ext.}} (n'_c - n_c) RT}{P_{\text{ext.}}}$$

$$W = -(n'_c - n_c) RT$$

$$\therefore W = -\Delta n_g RT$$

$$dU = dq + dw$$

if at constant pressure

$$dq = dH$$

$$\therefore dU = dH - pdV$$

$$dU = dH - \Delta n_g RT$$

$$\therefore dH = dU + \Delta n_g RT$$

## Solved Examples

**Ex-7.** For the combustion of 1 mole of liquid benzene at 25°C, the heat of reaction at constant pressure is

given by,  $C_6H_6(\ell) + 7\frac{1}{2} O_2(g) \rightarrow 6CO_2(g) + 3H_2O(\ell)$ ;  $\Delta H = -780980$  cal.

What would be the heat of reaction at constant volume?

**Sol.** We have,

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

Here,

$$\Delta n_g = 6 - 7.5 = -1.5.$$

Thus,

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

## Section (H) : Phase transition

### Case - IV During phase transformation.

Phase transitions generally take place at constant pressure (unless specified) and at constant temperature. So,  $\Delta T = 0$ .

But still  $\Delta H$  and  $\Delta E$  are non zero (different from process on an ideal gas)

Because during phase transitions though the kinetic energy of molecules of substance remains same but the potential energy gets modified or changed and since  $E$  is summation of all type of energies. So,  $\Delta E \neq 0$ . Also, during this phase transition  $\Delta(PV) \neq 0$

Hence,  $\Delta H \neq 0$ .

Now, to calculate heat – generally latent heats of transitions are given and since process is taking place at constant pressure. So,  $q = \Delta H$ .

To calculate  $W$ , use  $dW = -P_{\text{ext}} dV$  and then calculate  $\Delta E$  using 1<sup>st</sup> law of thermodynamics.

## Solved Examples

**Ex-8.** Calculate  $q$ ,  $W$ ,  $\Delta E$  and  $\Delta H$  when 100 g of  $CaCO_3$  is converted into its aragonite form given density of calcite = 2 g/cc and density of aragonite = 2.5 g/cc

**Sol.**



Calcite                      Aragonite       $\Delta H = 2$  kJ/mole

Generally for    solid  $\rightarrow$  Solid

                         solid  $\rightarrow$  Liquid

                         solid  $\rightarrow$  Liquid

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

while for gaseous conversion for example

                         Solid  $\rightarrow$  gas

                         Liquid  $\rightarrow$  gas

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





S.No.	Process	w	q	$\Delta U$	$\Delta H$	Molar heat capacity
1.	Isochoric	0	$nC_{v,m}(T_f - T_i)$	$q_v$	$nC_{p,m}(T_f - T_i)$	$C_{v,m}$
2.	Isobaric	$-P_{\text{ext}}(V_2 - V_1)$	$nC_{p,m}(T_f - T_i)$	$q + w$	$nC_{p,m}(T_f - T_i)$	$C_{p,m}$
3.	Isothermal	$W_{\text{rev}} = -nRT \ln\left(\frac{V_f}{V_i}\right)$ $W_{\text{irrev}} = -P_{\text{ext}}(V_f - V_i)$	$-w$	0	0	$\pm \infty$
4.	Adidatic	$\frac{P_f V_f - P_i V_i}{\alpha - 1}$	0	w	0	0
5.	Polytropic	$\frac{P_f V_f - P_i V_i}{(n-1)}$	$\Delta U - w$	$nC_{v,m}(T_2 - T_1)$	$nC_{p,m}(T_2 - T_1)$	$C_{v,m} + \frac{R}{1-\gamma}$

## Thermodynamics II<sup>nd</sup> & III<sup>rd</sup> Law

### Section (A) : Introduction about entropy

#### ● II<sup>nd</sup> Law of thermodynamics :

**Requirement : I<sup>st</sup> law insufficient to Explain**

Neutralization, Melting of ice  $> 0^\circ$

Combustion, Freezing of water  $< 0^\circ$

Fall of water, Boiling of water  $> 100^\circ \text{C}$

Cooling of a hot body, Free expansion of a gas, mixing of gases.

**Spontaneous /Natural /Irreversible Processes :**

If a system moves along in a direction on its own and system, surrounding interactions without the help of any external agency, then that direction is known as spontaneous direction and the process is known as a spontaneous process.

**Limitation :**

First law cannot predict the direction of any process. But in nature a process is found to have a specific direction at certain conditions.

1. Energy can be the factor : To achieve stability

\* All exothermic processes are spontaneous.

\* All endothermic processes are non spontaneous.

**Exceptions**

\* melting of ice (above  $0^\circ\text{C}$ ) although  $\Delta H > 0$ ,  $\Delta E > 0$

\* Vaporization of water (above  $100^\circ\text{C}$ )  $\Delta H > 0$ ,  $\Delta E > 0$

\* Spreading of ink in water  $\Delta H = 0$ ,  $\Delta E = 0$

\* Mixing of two gases

\* Endothermic solution of salt  $\Delta H > 0$ ,  $\Delta E > 0$

2. It is observed that nature tries to distribute energy and matter uniformly (randomization)

**Second law of thermodynamics :**

Entropy of the universe is constantly increasing.

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \text{ for a spontaneous process.}$$

Where (**S**) = entropy is the measure of randomness or disorder. It is a state function and extensive property.

Mathematically

$$ds = \frac{dq_{\text{rev}}}{T} \text{ or } \Delta S = \int \frac{dq_{\text{rev}}}{T}, \quad \frac{dq}{T} \text{ is state function only for reversible process}$$

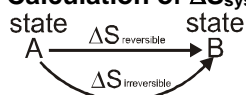
$$dS \propto dq_{\text{rev}}, \quad dS \propto \frac{1}{T}$$

At Higher T - entropy is already high. Therefore, heat addition will not introduce much change in the entropy.



## Section (B) : Entropy Calculation

- **Calculation of  $\Delta S_{\text{system}}$**

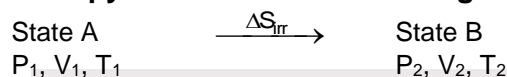


As 'S' is a state function. Hence 'ΔS' will also be a state function.

$$\therefore \Delta S_{\text{irrev}} = \Delta S_{\text{rev}}$$

$$\Delta S = \int_A^B \frac{dq_{\text{rev}}}{T} \text{ reversible path}$$

- **Entropy calculation for an ideal gas undergo in a process.**



As 'S' is a state function. So, ΔS will not depend upon path

$$\Delta S_{\text{irrev}} = \Delta S_{\text{rev, system}} = \int_A^B \frac{dq_{\text{rev}}}{T} \text{ rev path.}$$

from the first law

$$dU = dQ + dw$$

$$dQ = dU - dw$$

for reversible path

$$dq = dq_{\text{rev}}$$

$$dq_{\text{rev}} = dU + P_{\text{gas}} dV \quad \{P_{\text{ext}} = P_{\text{gas}} \text{ reversible}\}$$

$$\Delta S_{\text{rev, system}} = \int_A^B \frac{dU + P_{\text{gas}} dV}{T}$$

for an ideal gas

$$\frac{P_{\text{gas}}}{T} = \frac{nR}{V} \quad \& \quad du = nc_v dT$$

$$\therefore \Delta S_{\text{sys}} = \int_{T_1}^{T_2} \frac{nc_v dT}{T} + \int_{V_1}^{V_2} \frac{nR dV}{V}$$

$$\therefore \Delta S_{\text{system}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

- **Calculation of  $\Delta S_{\text{surrounding}}$**  : As the surrounding is an infinite heat reservoir hence, no. amount of heat given to the surrounding can cause turbulence in it, hence all heat exchanges with surroundings are considered to be reversible.

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{surrounding}}}{T}$$

For surrounding T is constant

$$\therefore \Delta S_{\text{surr}} = \frac{1}{T} \int dq_{\text{surr}} = \frac{q_{\text{surrounding}}}{T}$$

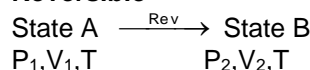
**But according to the law of conservation of energy**

$$q_{\text{surr}} = -q_{\text{system}}$$

$$\therefore \Delta S_{\text{surr}} = \frac{-q_{\text{system}}}{T}$$

- **Isothermal process :**

(a) **Reversible**







$$\Delta S_{\text{system}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

Since  $T_1 = T_2$

$$\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surrounding}} = -\frac{q_{\text{system}}}{T}$$

$du = dq + dw$  (since  $T_1 = T_2$  . So,  $du = 0$ )

$\therefore dq = -dw$

$$\therefore q = -w \text{ as } w = -nRT \ln \frac{V_2}{V_1}$$

$$q = nRT \ln \frac{V_2}{V_1}$$

$$\therefore \Delta S_{\text{sys.}} = \frac{-nRT \ln \frac{V_2}{V_1}}{T} = -nR \ln \frac{V_2}{V_1}$$

$$\begin{aligned} \Delta S_{\text{universe}} &= \Delta S_{\text{system}} + \Delta S_{\text{surr}} \\ &= nR \ln \frac{V_2}{V_1} - nR \ln \frac{V_2}{V_1} = 0 \end{aligned}$$

**(b) Irreversible**

State A  $\xrightarrow{\text{irrev}}$  State B  
 $P_1, V_1, T$                        $P_2, V_2, T$

$$\Delta S_{\text{system}} = nR \ln \frac{V_2}{V_1}$$

$$\Delta S_{\text{surrounding}} = -\frac{q_{\text{system}}}{T}$$

$q_{\text{system}}$  is calculated using FLOT

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

$$\therefore \Delta S_{\text{surrounding}} = \frac{-P_{\text{ext}}(V_2 - V_1)}{T}$$

$$\begin{aligned} \Delta S_{\text{universe}} &= nR \ln \frac{V_2}{V_1} - \frac{P_{\text{ext}}(V_2 - V_1)}{T} \\ &= \frac{1}{T} \left[ \left( nRT \ln \frac{V_2}{V_1} \right) - P_{\text{ext}} (V_2 - V_1) \right] = \frac{1}{T} [W_{\text{irrev}} - W_{\text{rev}}] > 0 \end{aligned}$$

As irreversible work of gas is more than reversible work.

● **Adiabatic Process (Isoentropic process)**

**(a) Reversible Adiabatic**

State A  $\xrightarrow{\text{rev}}$  State B  
 $P_1, V_1, T_1$                        $P_2, V_2, T_2$

$$\Delta S_{\text{system}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

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

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

$$(\Delta S)_{\text{system}} = nC_V \ln \left( \frac{V_1}{V_2} \right)^{\gamma-1} + nR \ln \frac{V_2}{V_1} = 0$$



$$\Delta S_{\text{surr}} = -\frac{q_{\text{sys}}}{T} = 0 \quad (q_{\text{sys}} = 0) \quad \therefore \Delta S_{\text{universe}} = 0 + 0 = 0$$

**(b) Irreversible Adiabatic**

$$\text{State A} \xrightarrow{\text{irre}} \text{State B}$$

$$P_1, V_1, T_1 \qquad \qquad P_2, V_2, T_2$$

Using irreversible adiabatic process it is not possible to reach same state B which was reached by reversible adiabatic.

$$\Delta S_{\text{system}} = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} > 0 \quad [(T_2)_{\text{irrev}} > (T_2)_{\text{rev}}]$$

$$\Delta S_{\text{surr}} = -\frac{q_{\text{sys}}}{T} = 0 \quad \text{as } q = 0$$

For irreversible expansion the decrease in temperature will be lesser as work done is lesser hence, decrease in entropy due to fall in temperature will be lesser in case of irreversible expansion. Hence, net entropy would increase.

● **Isobaric process :**

**(a) Reversible Isobaric**

$$\text{State A} \xrightarrow{\text{rev}} \text{State B}$$

$$P, V_1, T_1 \qquad \qquad P, V_2, T_2$$

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{-dq_{\text{sys}}}{T} = -nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} = 0$$

**(b) Irreversible Isobaric**

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{nC_p dT}{T} = nC_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{rev}}}{T} = \frac{-nC_p (T_2 - T_1)}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} > 0$$

● **Isochoric Process**

**(a) Reversible Isochoric**

$$\text{State A} \xrightarrow{\text{rev}} \text{State B}$$

$$P_1, V, T_1 \qquad \qquad P_2, V, T_2$$

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{nC_V dT}{T} = nC_V \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{-dq_{\text{sys}}}{T} = -nC_V \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} = 0$$

**(b) Irreversible Isochoric**

$$\Delta S_{\text{sys}} = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} \frac{nC_V dT}{T} = nC_V \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{surrounding}} = \frac{-nC_V (T_2 - T_1)}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surrounding}} > 0$$





## Entropy Calculation for phase transformations

$$\Delta S_{\text{fusion}} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{Q}{T}$$

$$\text{For constant pressure } \Delta S_{\text{fus.}} = \frac{\Delta H_{\text{fus.}}}{T}$$

$$\text{For constant volume } \Delta S_{\text{fus.}} = \frac{\Delta U_{\text{fusion}}}{T}$$

$$\Delta S_{\text{vap}} = \int \frac{dq}{T} = \frac{1}{T} \int dq = \frac{Q}{T}$$

$$\text{For constant Pressure, } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$$

$$\text{For constant Volume, } \Delta S_{\text{vap}} = \frac{\Delta U_{\text{vap}}}{T}$$

## Entropy Calculation solid or liquid systems:

### (a) 'Cu' block kept in open atmosphere

$$\Delta S_{\text{system}} = \int_{T_1}^{T_2} \frac{msdT}{T} = m \ln \frac{T_2}{T_1}$$

$$\therefore \Delta S_{\text{surr}} = \int \frac{dq_{\text{surr}}}{T} = \frac{q_{\text{surr}}}{T_2}$$

$$\text{but } q_{\text{surr}} = -q_{\text{system}} = -ms(T_2 - T_1) = ms(T_1 - T_2)$$

$$\text{Hence, } \Delta S_{\text{surr}} = \frac{ms(T_1 - T_2)}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surr}}$$

$$\therefore \Delta S_{\text{universe}} = ms \ln \frac{T_2}{T_1} + \frac{ms(T_1 - T_2)}{T_2} > 0$$

### (b) Two copper block kept in contact in thermostat

Two blocks are of same mass

$$\Delta S_{\text{surr}} = 0 \text{ (since no heat is lost to surrounding)}$$

$$\Delta S_{\text{system}} = \Delta S_A + \Delta S_B$$

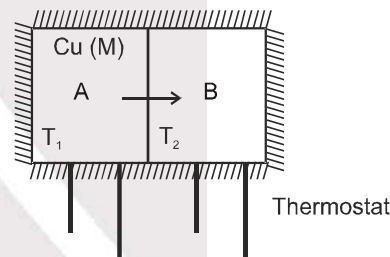
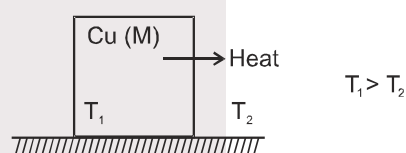
System will reach a common temperature ( $T_f$ )

and  $T_1 > T_f > T_2$

$$\begin{aligned} \Delta S_{\text{system}} &= \int_{T_1}^{T_f} \frac{dq_A}{T} + \int_{T_2}^{T_f} \frac{dq_B}{T} \\ &= \int_{T_1}^{T_f} \frac{msdT}{T} + \int_{T_2}^{T_f} \frac{msdT}{T} = ms \left[ \ln \frac{T_f}{T_1} + \ln \frac{T_f}{T_2} \right] \end{aligned}$$

$$\Delta S_{\text{system}} = ms \ln \frac{T_f^2}{T_1 T_2}$$

$$\text{Since } T_f = \frac{T_1 + T_2}{2} \quad \therefore \Delta S_{\text{system}} = ms \ln \frac{(T_1 + T_2)^2}{4T_1 T_2}$$



## Solved Examples

**Ex-9.** (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,  $\Delta U = 0$  and heat is absorbed by the gas,

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

$\therefore q_{\text{rev}} = 1718 \text{ J.}$  ( $\therefore$  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)  $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ ..... 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)  $W = 0$  ( $\therefore p_{\text{ext}} = 0$ )

(iii) No heat is exchanged with the surroundings.

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

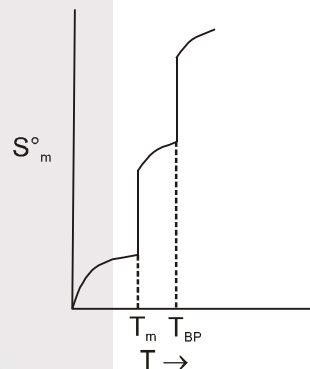
(v) The entropy of the system plus surroundings increases by 5.76 J/K, as we expect entropy to increase in an irreversible process.

### ● Third Law Of Thermodynamics :

The entropy of perfect crystals of all pure elements & compounds is zero at the absolute zero of temperature.

Thus, absolute value of entropy unlike the absolute value of enthalpy for any pure substance can be calculated at any given temperature. In standard state (298 K, 1 atm), it is standard absolute entropy  $S^\circ$ .

$$\Delta S = S_{T(K)} - S_{0(K)} = \int_0^T \frac{nCdT}{T}$$



### ● For chemical reaction



$$\Delta S_{\text{system}}^\circ = (\sum S_{\text{m}}^\circ n_i)_{\text{product}} - (\sum S_{\text{m}}^\circ n_i)_{\text{reactant}}$$

where  $S_{\text{m}}^\circ$  = standard molar entropy. It can be calculated using third law of thermodynamics.

$$\Delta S_{\text{surr}} = \frac{-Q_{\text{system}}}{T} = \frac{-\Delta H_{\text{system}}}{T}$$

\* For a perfectly crystalline substance at 0 K, entropy = 0

### ● For phase transformations

$$\Delta S_{\text{fusion}} = \int \frac{dp}{T} = \frac{1}{T} \int dp = \frac{Q}{T}$$

for constant pressure  $\Delta S_{\text{fus.}} = \frac{\Delta H_{\text{fus.}}}{T}$

for constant volume  $\Delta S_{\text{fus.}} = \frac{\Delta U_{\text{fusion}}}{T}$

$$\Delta S_{\text{vap}} = \int \frac{dQ}{T} = \frac{1}{T} \int dQ = \frac{Q}{T}$$

for constant Pressure,  $\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T}$

for constant Volume,  $\Delta S_{\text{vap}} = \frac{\Delta U_{\text{vap}}}{T}$





## Section (C) : Free energy

### ● **Gibb's free energy (G) :**

A system parameter to predict the spontaneity of chemical reaction was introduced by Gibb's so that entropy calculation for the surrounding need not be carried out.

It is a free energy at constant pressure.

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

&  $H = U + PV$

$$dH = dU + PdV + VdP \Rightarrow dG = dU + PdV + VdP - TdS - SdT$$

From 1<sup>st</sup> law of thermodynamics

$$dq = dU + PdV$$

& from 2<sup>nd</sup> law,  $dq = TdS$

$$dG = dq + VdP - TdS - SdT$$

$$dG = -SdT + VdP$$

At constant temperature,

$$dG = VdP$$

For ideal gas,  $V = \frac{nRT}{P}$

$$dG_m = V_m dP = \frac{RT}{P} dP$$

$$\int_1^2 dG_m = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$G_{m_2} - G_{m_1} = RT \ln \frac{P_2}{P_1}$$

Where  $G_m$  is free energy for 1 mole

If  $G_{m_1}$  is free energy for 1 mole in standard state and  $G_{m_2}$  is free energy for one mole in any other state.

$$G_m - G_m^\circ = RT \ln \frac{P}{1} \quad \& \quad G - G^\circ = nRT \ln \frac{P}{1}$$

For the reaction,  $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$$(\Delta G)_{\text{reaction}} = (\Sigma \Delta G)_{\text{product}} - (\Sigma \Delta G)_{\text{reactant}}$$

$$(\Delta G)_{\text{reaction}} = G_C + G_D - G_A - G_B$$

$$G_C - G_C^\circ = cRT \ln \frac{P_C}{1} \Rightarrow G_C = G_C^\circ + cRT \ln P_C$$

Similarly,  $G_D = G_D^\circ + dRT \ln P_D$  ;  $G_A = G_A^\circ + aRT \ln P_A$  ,  $G_B = G_B^\circ + bRT \ln P_B$

$$(\Delta G)_{\text{reaction}} = (G_C^\circ + cRT \ln P_C) + (G_D^\circ + dRT \ln P_D) - (G_A^\circ + aRT \ln P_A) - (G_B^\circ + bRT \ln P_B)$$

$$= (\Delta G)^\circ_{\text{reaction}} + RT \ln \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$$

$$\Delta G_{\text{reaction}} = \Delta G^\circ_{\text{reaction}} + RT \ln Q$$

### **Gibb's Helmholtz Equation :**

$$dG = VdP - SdT$$

At constant Pressure

$$dG = -SdT \Rightarrow \left( \frac{dG}{dT} \right)_P = -S \quad \& \quad \left( \frac{\partial \Delta G}{\partial T} \right)_P = -\Delta S$$

&  $G = H - TS \Rightarrow \frac{G - H}{T} = -S$

$$\frac{G - H}{T} = \left( \frac{\partial G}{\partial T} \right)_P$$

$$G = H + T \left( \frac{\partial G}{\partial T} \right)_P$$





$$\Delta G = \Delta H + T \left( \frac{\partial \Delta G}{\partial T} \right)_P$$

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

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{surr}} = \frac{-Q_{\text{system}}}{T} = \frac{-\Delta H_{\text{system}}}{T}$$

$$T \Delta S_{\text{univ}} = T \Delta S_{\text{system}} - \Delta H_{\text{system}}$$

Introducing a new thermodynamic function  $G =$  Gibb's free energy (State function and an extensive property)

$$G_{\text{system}} = H_{\text{system}} - TS_{\text{system}}$$

$$\therefore \Delta G = \Delta H - T \Delta S$$

$$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}} \dots \dots \dots \text{(ii)}$$

Comparing equation (i) and (ii)

$$\Delta G_{\text{system}} = -T \Delta S_{\text{universe}}$$

### New criteria of spontaneity :

- (i) If  $\Delta G_{\text{system}}$  is  $(-ve) < 0 \Rightarrow$  process is spontaneous
- (ii) If  $\Delta G_{\text{system}}$  is  $> 0 \Rightarrow$  process is non spontaneous
- (iii) If  $\Delta G_{\text{system}} = 0 \Rightarrow$  system is at equilibrium

So, at every temperature  $\Delta G \neq 0$

$\Delta H_{\text{system}}$	$\Delta S_{\text{system}}$	$\Delta G_{\text{system}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}}$
+ Ve	- Ve	+
- Ve	+ Ve	-
+ Ve	+ Ve	- Ve at high temperature
- Ve	- Ve	+ Ve at high temperature

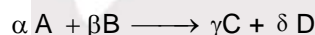
### $\Delta G^\circ =$ standrad free energy change :

When the reactants under standrad conditions gets converted into products which is also under standrad condition, then the free energy change is known as  $\Delta G^\circ$  (it is a constant) for 1 mole at 1 bar.

### At standrad conditions :

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

= constant for a GIVEN REACTION



$$\Delta G^\circ = (\text{Gibb's energy of product}) - (\text{Gibb's energy of reactant})$$

$$\Delta G^\circ = \gamma G_{m,C}^\circ + \delta G_{m,D}^\circ - \alpha G_{m,A}^\circ - \beta G_{m,B}^\circ, \text{ where } G_m^\circ \text{ can not be calculated as } H_m^\circ \text{ cannot be calculated.}$$

Hence, we can convert this relation in to Gibb's energy of formation of substance.

$$\Delta G^\circ = \gamma \Delta G_{f,C}^\circ + \delta \Delta G_{f,D}^\circ - \alpha \Delta G_{f,A}^\circ - \beta \Delta G_{f,B}^\circ$$

$\Delta G_f^\circ$  : standrad Gibb's energy of formation.

$$\Delta G_f^\circ \text{ (elements in their standard states)} = 0$$

$$\Delta G^\circ = \Delta G_{f,\text{product}}^\circ - \Delta G_{f,\text{reactants}}^\circ$$

### For a reaction in progress

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$Q$  is reaction quotient,  $\Delta G > 0$  backward is feasible,  $\Delta G < 0$  forward is feasible

At equilibrium  $\Delta G = 0 \therefore Q = K \therefore \Delta G^\circ = -RT \ln K$  at equilibrium.





## Solved Examples

**Ex-10.**  $K_a$  for  $\text{CH}_3\text{COOH}$  at  $25^\circ\text{C}$  is  $1.754 \times 10^{-5}$ . At  $50^\circ\text{C}$ ,  $K_a$  is  $1.633 \times 10^{-5}$ . What are  $\Delta H^\circ$  and  $\Delta S^\circ$  for the ionisation of  $\text{CH}_3\text{COOH}$ ?

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

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

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \Rightarrow \quad 27194 = \Delta H^\circ - 298 \Delta S^\circ$

$29605 = \Delta H^\circ - 323 \Delta S^\circ \quad \Rightarrow \quad \Delta H^\circ = -1.55 \text{ kJ/mol} \quad \Rightarrow \quad \Delta S^\circ = -96.44 \text{ J/mol.K}$

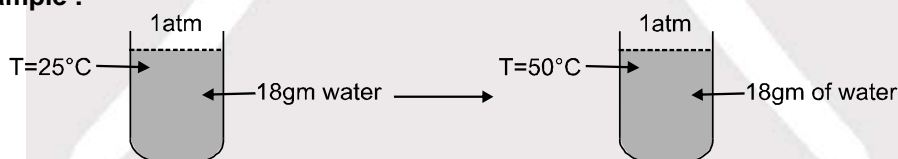
## 2. THERMOCHEMISTRY

### Section (A) : Calculation $\Delta U$ , $\Delta H$ & $W$ for chemical reaction

#### ○ Enthalpy of a substance :

- Every substance has a fixed value of enthalpy under any particular state. Though, its exact value cannot be calculated but it has some finite fixed value.
- The enthalpy of one mole of a substance called molar enthalpy in any particular state can be assigned symbol
- $H_m(\text{substance})$  : For example molar enthalpy of water vapours at  $398 \text{ K}$  and  $1 \text{ atm}$  pressure may be represented as  $H_m(\text{H}_2\text{O}, \text{g}, 398 \text{ K}, 1 \text{ atm})$ . In very simple words, enthalpy can be considered as heat constant (amount) of substance, and during reaction this heat is being released or absorbed.
- Molar enthalpy of substance under standard conditions is called standard molar enthalpy of a substance. Standard state of any substance means.
  - For a **GAS** standard state means ideal gas at  $1 \text{ bar}$  partial pressure at any give temperature.
  - For a **LIQUID** – pure liquid at one bar pressure at  $1 \text{ bar}$  pressure at any given temperature.
  - For a **PURE CRYSTALLINE SOLID** – pure crystalline solid at  $1 \text{ bar}$  pressure and at any given temperature
  - For any **SUBSTANCE or ION IN SOLUTION** – the species should be in unit molality (can also be taken as  $1 \text{ M}$  concentration), at one bar pressure and at any given temperature.
- Molar standard enthalpy of water vapours at  $398 \text{ K}$  will be represented as  $H^\circ(\text{H}_2\text{O}, \text{g}, 398 \text{ K})$  and molar standard enthalpy of liquid water at  $398 \text{ K}$  will be represented as  $H_m^\circ(\text{H}_2\text{O}, \text{l}, 398 \text{ K})$  (It is hypothetical but can be calculated).
- We cannot exactly calculate enthalpy content of a substance only the change in enthalpy can be calculated when substance is taken from one state to other.

**For example :**



Let enthalpy content initially be  $H_{m,1}^\circ$  & finally enthalpy content be  $H_{m,2}^\circ$

Then,  $\Delta H^\circ = H_{m,2}^\circ - H_{m,1}^\circ$

= heat added at constant pressure to change temperature from  $25^\circ\text{C}$  to  $50^\circ\text{C}$ .

=  $C_p \Delta T = (18 \text{ cal/mole } ^\circ\text{C}) (25^\circ\text{C}) = 450 \text{ cal}$

## Solved Examples

**Ex-11.** Why does heat get released/absorbed during chemical reactions?

**Sol.** Because the reactants have a fixed enthalpy content before the reaction and when these are converted into the products which have a different enthalpy content. So, heat gets released or absorbed. Even if temperature of reactions remains constant yet due to change in bonding energies  $\Delta E \neq 0$ .

If  $H_{\text{products}} > H_{\text{reactants}}$

Reaction should be endothermic as we have to give extra heat to reactants to get these converted into products and

if  $H_{\text{products}} < H_{\text{reactants}}$



Reaction will be exothermic as extra heat content of reactants will be released during the reaction.

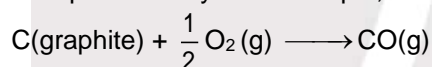
Enthalpy change of a reaction :  $\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$

$$\begin{aligned} \Delta H^{\circ}_{\text{reactions}} &= H^{\circ}_{\text{products}} - H^{\circ}_{\text{reactants}} \\ &= \text{positive} \quad - \quad \text{endothermic} \\ &= \text{negative} \quad - \quad \text{exothermic} \end{aligned}$$

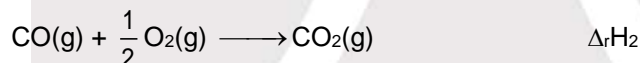
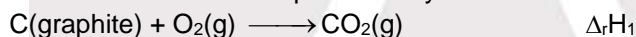
## Section (B) : Basics & Kirchoff's law

### ○ Hess's Law of constant heat summation :

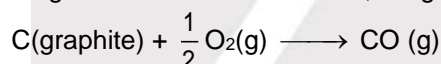
- The heat absorbed or evolved in a given chemical equation is the same whether the process occurs in one step or several steps.
- The chemical equation can be treated as ordinary algebraic expressions and can be added or subtracted to yield the required equation. The corresponding enthalpies of reactions are also manipulated in the same way so as to give the enthalpy of reaction for the desired chemical equation.
- Since  $\Delta_r H$  stands for the change of enthalpy when reactants (substances on the left hand side of the arrow) are converted into products (substances on the right hand side of the arrow) at the same temperature and pressure, if the reaction is reversed (i.e., products are written on the left hand side and reactants on the right hand side), then the numerical value of  $\Delta_r H$  remains the same, but **its sign changes**.
- The utility of Hess's law is considerable. In almost all the thermochemical numericals, Hess's law is used.
- One of the important applications of Hess's law is to determine enthalpy of reaction which is difficult to determine experimentally. For example, the value  $\Delta_r H$  for the reaction



which is difficult to determine experimentally, can be estimated from the following two reactions for which  $\Delta_r H$  can be determined experimentally.



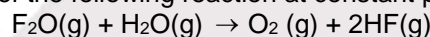
Subtracting the latter from the former, we get



Consequently,  $\Delta_r H = \Delta_r H_1 - \Delta_r H_2$

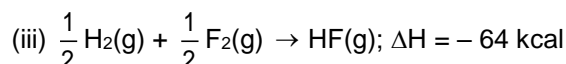
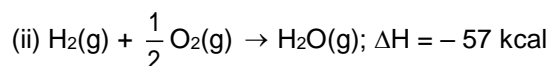
## Solved Examples

**Ex-12.** Calculate heat of the following reaction at constant pressure,



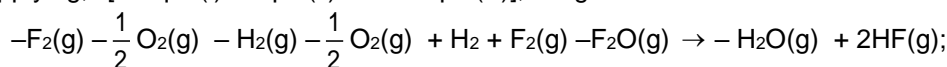
The heats of formation of  $\text{F}_2\text{O}(\text{g})$ ,  $\text{H}_2\text{O}(\text{g})$  and  $\text{HF}(\text{g})$  are 5.5 kcal, -57kcal and -64 kcal respectively.

**Sol.** Given that (i)  $\text{F}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{F}_2\text{O}(\text{g}); \Delta H = 5.5 \text{ kcal}$



$\text{F}_2\text{O}$  and  $\text{H}_2\text{O}$  in eqns. (i) and (ii) and in the eqn. given in the problem are on the opposite sides, while  $\text{HF}$  in eqn. (iii) and in the eqn. given in the problem is on the same sides.

Thus applying, [-Eqn. (i) -Eqn. (ii) + 2 × Eqn. (iii)], we get



$$\Delta H = -5.5 - (-57) + 2 \times (-64)$$

or  $\text{F}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{O}_2(\text{g}) + 2\text{HF}(\text{g}); \Delta H = -76.5 \text{ kcal.}$





### ○ Relation between energy and enthalpy of a reaction :

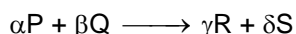
$$\Delta_r H = \Delta_r U + (\Delta v_g)RT$$

where  $\Delta v_g$  is the change in the stoichiometric number of gaseous species in going from reactants to products.

It should be noted that while computing  $\Delta v_g$  of a reaction, only the stoichiometric numbers of gaseous are counted and those of liquids and solids are completely ignored.

**Kirchoff's equation** (Variation of  $\Delta H^\circ$  with temperature)

Since the enthalpy (or standard enthalpy) of a substance is dependent on state of the substance, value of enthalpy of a substance changes with temperature and hence the enthalpy change of reaction is also dependent on temperature at which the reaction is being carried out. This change in enthalpy change (or  $\Delta E$  of reaction is carried out at constant volume) is represented by **Kirchoff's Equations**.



at temperature  $T_1$  let the standard enthalpy of reaction be  $\Delta H_1^\circ$ , then

$$\Delta H_1^\circ = \gamma H_m^\circ(R, T_1) + \delta H_m^\circ(S, T_1) - \alpha H_m^\circ(P, T_1) - \beta H_m^\circ(Q, T_1)$$

If the same reaction is carried out at temperature  $T_2$ , then

$$\Delta H_2^\circ = \gamma H_m^\circ(R, T_2) + \delta H_m^\circ(S, T_2) - \alpha H_m^\circ(P, T_2) - \beta H_m^\circ(Q, T_2)$$

Then, the change in enthalpy (or difference in enthalpy at these two temperatures)

$$\Delta H^\circ = \Delta H_2^\circ - \Delta H_1^\circ = \gamma \{H_m^\circ(R, T_2) - H_m^\circ(R, T_1)\} + \delta \{H_m^\circ(S, T_2) - H_m^\circ(S, T_1)\} \\ - \alpha \{H_m^\circ(P, T_2) - H_m^\circ(P, T_1)\} - \beta \{H_m^\circ(Q, T_2) - H_m^\circ(Q, T_1)\}$$

$H_m^\circ(R, T_2) - H_m^\circ(R, T_1) = C_{P,R}(T_2 - T_1)$  = Heat required at constant pressure to increase temperature of one mole of R from  $T_1$  to  $T_2$

**Similarly**

$$H_m^\circ(S, T_2) - H_m^\circ(S, T_1) = C_{P,S}(T_2 - T_1)$$

$$H_m^\circ(P, T_2) - H_m^\circ(P, T_1) = C_{P,P}(T_2 - T_1) \text{ and}$$

$$H_m^\circ(Q, T_2) - H_m^\circ(Q, T_1) = C_{P,Q}(T_2 - T_1)$$

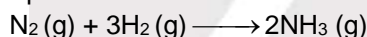
$$\text{so } \Delta H^\circ = \Delta H_2^\circ - \Delta H_1^\circ = \gamma C_{P,R}(T_2 - T_1) + \delta C_{P,S}(T_2 - T_1) - \alpha C_{P,P}(T_2 - T_1) - \beta C_{P,Q}(T_2 - T_1) \\ = [\gamma C_{P,R} + \delta C_{P,S} - \alpha C_{P,P} - \beta C_{P,Q}](T_2 - T_1) = \Delta C_P (T_2 - T_1)$$

$$\Delta C_P = \gamma C_{P,R} + \delta C_{P,S} - \alpha C_{P,P} - \beta C_{P,Q}$$

= Difference in molar heat capacities of products and reactants.

$$\text{so } \Delta H_2^\circ = \Delta H_1^\circ + \int \Delta C_P \cdot dT$$

For example for the reaction



$$\Delta H_2^\circ = \Delta H_1^\circ + \Delta C_P (T_2 - T_1)$$

$$\text{where } \Delta C_P = 2C_{P,NH_3} - C_{P,N_2} - 3C_{P,H_2}$$

\* for a constant volume reaction,  $\Delta E_2^\circ = \Delta E_1^\circ + \int \Delta C_V \cdot dT$

## Section (C) : Enthalpy of formation & combustion

### ○ Enthalpy of formation :

It is not possible to determine the absolute value of the molar enthalpy of a substance. However, based on the following convention, the relative values of standard molar enthalpies of formation of various substances can be built.

- "The standard enthalpy of formation of every element in its stable state of aggregation at one bar pressure and at specified temperature is assigned a zero value". The specified temperature is usually taken as 25°C.

A few examples are  $\Delta H_f^\circ(O_2, g) = 0$

$$\Delta H_f^\circ(C, \text{graphite}) = 0$$

$$\Delta H_f^\circ(C, \text{diamond}) \neq 0$$

$$\Delta H_f^\circ(Br_2, \text{liquid}) = 0$$

$$\Delta H_f^\circ(S, \text{rhombic}) = 0$$

$$\Delta H_f^\circ(S, \text{monoclinic}) \neq 0$$

$$\Delta H_f^\circ(P, \text{white}) = 0$$

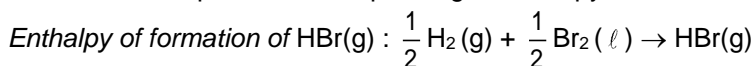
$$\Delta H_f^\circ(P, \text{black}) \neq 0$$

- "The standard enthalpy of formation of a compound is the change in the standard enthalpy when one mole of the compound is formed starting from the requisite amounts of elements in their stable state of aggregation".

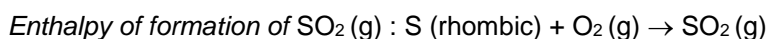




The chemical equations corresponding to enthalpy of formation of few substances are given below.



$$\Delta H_f^\circ(\text{HBr, g}) = H_m^\circ(\text{HBr, g}) - \frac{1}{2} H_m^\circ(\text{H}_2, \text{g}) - \frac{1}{2} H_m^\circ(\text{Br}_2, \ell) \quad \dots(1)$$



$$\Delta H_f^\circ(\text{SO}_2, \text{g}) = H_m^\circ(\text{SO}_2, \text{g}) - H_m^\circ(\text{S, rhombic}) - H_m^\circ(\text{O}_2, \text{g}) \quad \dots(2)$$

But above equations cannot be for calculation of enthalpy of reaction as the molar enthalpies of different species can not be exactly known.

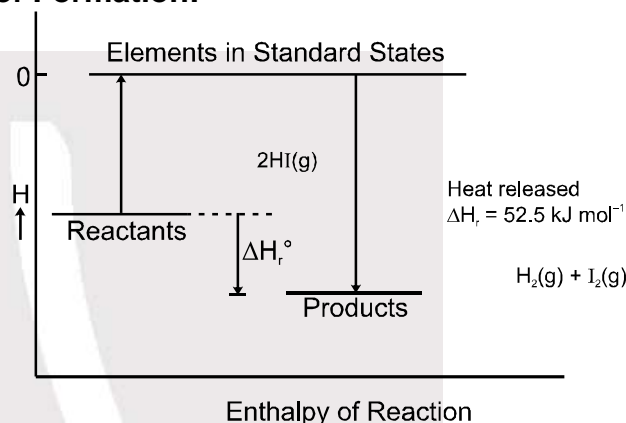
### ○ Enthalpy of Reaction from Enthalpies of Formation:

The enthalpy of reaction can be calculated by

$$\Delta H_r^\circ = \sum v_B \Delta H_f^\circ, \text{products} - \sum v_B \Delta H_f^\circ, \text{reactants}$$

$v_B$  is the stoichiometric coefficient

above equation holds good for any reaction as the same reference state is used for reactants and products (shown in figure).



## Solved Examples

**Ex-13.** Calculate the standard enthalpy of reaction  $\text{ZnO(s)} + \text{CO(g)} \longrightarrow \text{Zn(s)} + \text{CO}_2(\text{g})$ .

Given,  $\Delta H_f^\circ(\text{ZnO, s}) = -350 \text{ KJ/mole}$ ,  $\Delta H_f^\circ(\text{CO}_2, \text{g}) = -390 \text{ KJ/mole}$ ,  $\Delta H_f^\circ(\text{CO, g}) = -110 \text{ KJ/mole}$ .

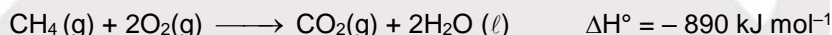
**Sol.**  $\Delta H^\circ = \{\Delta H_f^\circ(\text{CO}_2, \text{g}) - (\Delta H_f^\circ(\text{ZnO, s}) + \Delta H_f^\circ(\text{CO, g}))\}$

$$\Delta H^\circ_{\text{reaction}} = -390 - (-350 - 110) = 70 \text{ KJ}$$

### ○ Enthalpy of Combustion :

- It is the enthalpy change when one mole of a compound combines with the requisite amount of oxygen to give products in their stable forms.

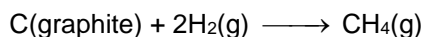
For example, the standard enthalpy of combustion of methane at 298 K is  $-890 \text{ kJ mol}^{-1}$ . This implies the following reaction :



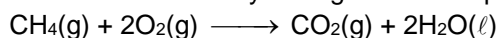
The standard enthalpy of combustion of methane at 298 K may be written as

$$\Delta H_c^\circ(\text{CH}_4, \text{g, 298 K}) = -890 \text{ kJ mol}^{-1}$$

- The data on the enthalpy of combustion can be determined experimentally.
- With the help of such data, we can determine the enthalpy of formation of a compound, which otherwise is difficult or impossible to determine experimentally. Consider for example, the enthalpy of formation of  $\text{CH}_4(\text{g})$ :



First of all, the combination of carbon and hydrogen does not occur readily. Secondly, if the reaction is even completed, the end product would not be pure methane. Therefore, the enthalpy of formation of methane can be determined indirectly through the enthalpy of combustion of methane :



$$\Delta H_c^\circ(\text{CH}_4, \text{g}) = \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2\Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_f^\circ(\text{CH}_4, \text{g})$$

therefore  $\Delta H_f^\circ(\text{CH}_4, \text{g}) = \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2\Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_c^\circ(\text{CH}_4, \text{g})$

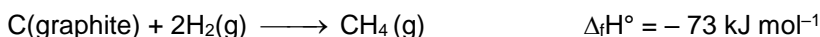
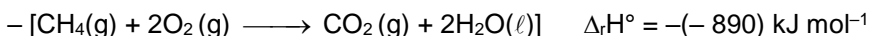
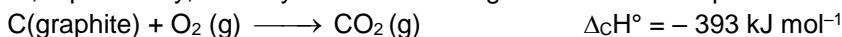




- The enthalpies of formation of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  can be determined experimentally by the combustion of carbon (graphite) and hydrogen. Thus, knowing the measured value of  $\Delta H_c^\circ(\text{CH}_4, \text{g})$ , the enthalpy of formation of  $\text{CH}_4$  can be calculated. The value is

$$\begin{aligned} \Delta H_f^\circ(\text{CH}_4, \text{g}) &= \Delta H_f^\circ(\text{CO}_2, \text{g}) + 2 \Delta H_f^\circ(\text{H}_2\text{O}, \ell) - \Delta H_c^\circ(\text{CH}_4, \text{g}) \\ &= [-393 + 2(-285) - (-890)] \text{ kJ mol}^{-1} = -73 \text{ kJ mol}^{-1} \end{aligned}$$

or, equivalently, we may add the following three chemical equations.



### ○ Measurement of Enthalpy of Combustion :

Enthalpy of combustion are usually measured by placing a known mass of the compound in a closed steel container (known as bomb calorimeter) which is filled with oxygen at about 30 bar pressure.

The calorimeter is surrounded by a known mass of water. The entire apparatus is kept in an insulated jacket to prevent heat entering into or leaving from the container, as shown in figure. The sample is ignited electrically to bring about the combustion reaction. The heat evolved is used in raising the temperature of water and the calorimeter.

If total heat capacity of calorimeter and all of its contents =  $C$ ,

rise in temperature =  $\Delta T$

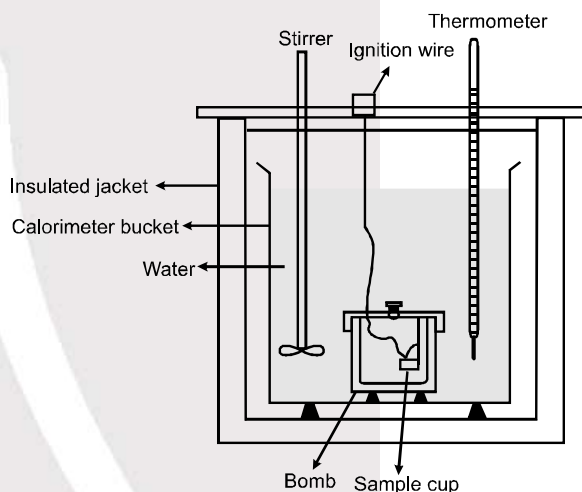
then heat released =  $q = C\Delta T$  of this heat is because of mass  $m$  of substance then :

$$\text{due to 1 mole, heat released} = \left(\frac{M}{m}\right) q = \Delta E_c^\circ$$

(Constant volume reaction).

Now,  $\Delta H_c^\circ$  can be calculated by using  $\Delta H_c^\circ = \Delta E_c^\circ + \Delta n_g RT$ .

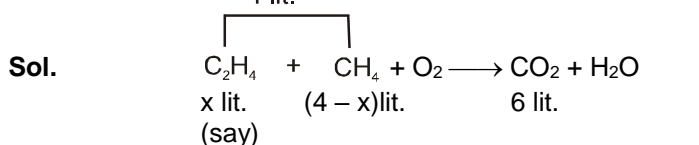
Where  $\Delta n_g$  is the change in stoichiometric number of gaseous species in the balanced chemical equation representing the combustion process.



Bomb calorimeter to determine enthalpy of combustion

## Solved Examples

- Ex-14.** A gas mixture of 4 litres of ethylene and methane on complete combustion at  $25^\circ\text{C}$  produces 6 litres of  $\text{CO}_2$ . Find out the amount of heat evolved on burning one litre of the gas mixture. The heats of combustion of ethylene and methane are  $-1464$  and  $-976 \text{ kJ mol}^{-1}$  at  $25^\circ\text{C}$ . [IIT-1991]



or  $x$  moles  $(4-x)$  moles 6 moles

Applying POAC for C atoms,

$$2 \times x + 1 \times (4-x) = 1 \times 6 ; x = 2 \text{ lit.}$$

Thus, the volume of  $\text{C}_2\text{H}_4 = 2 \text{ lit.}$ , and volume of  $\text{CH}_4 = 2 \text{ lit.}$

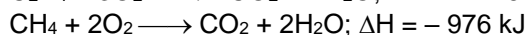
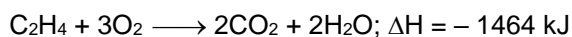
volume of  $\text{C}_2\text{H}_4$  in a 1 litre mixture =  $2/4 = 0.5 \text{ lit.}$

and volume of  $\text{CH}_4$  in a 1 litre mixture =  $1 - 0.5 = 0.5 \text{ lit.}$

Now, thermochemical reactions for  $\text{C}_2\text{H}_4$  and  $\text{CH}_4$  are







As  $\Delta H$  values given are at  $25^\circ\text{C}$ , let us first calculate the volume occupied by one mole of any gas at  $25^\circ\text{C}$  (supposing pressure as 1 atm)

$$\text{Volume per mole at } 25^\circ\text{C} = \frac{298}{273} \times 22.4 = 24.4 \text{ lit.}$$

$$\text{Thus, heat evolved in the combustion of 0.5 lit. of } \text{C}_2\text{H}_4 = -\frac{1464}{24.4} \times 0.5 = -30 \text{ kJ}$$

$$\text{and heat evolved in the combustion of 0.5 lit. of } \text{CH}_4 = \frac{976}{24.4} \times 0.5 = -20 \text{ kJ.}$$

$$\therefore \text{ total heat evolved in the combustion of 1 litre of the mixture} = -30 + (-20) = -50 \text{ kJ.}$$

## Section (D) : Bond enthalpy method & Resonance energy

### ○ Bond Enthalpies :

The **bond enthalpy** is the average of enthalpies required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. While **bond dissociation enthalpy** is the enthalpy required to dissociate a given bond of some specific compound. For example the enthalpy of dissociation of the O–H bond depends on the nature of molecular species from which the H atom is being separated. For example, in the water molecule.



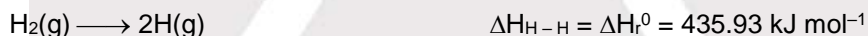
However, to break the O–H bond in the hydroxyl radical required a different quantity of heat :



The bond enthalpy,  $\Delta H_{\text{OH}}$ , is defined as the average of these two values, that is :

$$\Delta H_{\text{OH}} = \frac{501.87 \text{ kJ mol}^{-1} + 423.38 \text{ kJ mol}^{-1}}{2} = 462.625 \text{ kJ mol}^{-1}$$

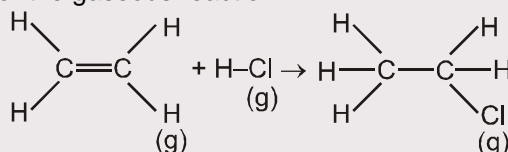
In the case of diatomic molecules, such as  $\text{H}_2$ , the bond enthalpy and bond dissociation enthalpy are identical because each refers to the reaction.



Thus, the bond enthalpy given for any particular pair of atoms is the average value of the dissociation enthalpies of the bond for a number of molecules in which the pair of atoms appears.

### ○ Estimation of Enthalpy of a reaction from bond Enthalpies :

Let the enthalpy change for the gaseous reaction

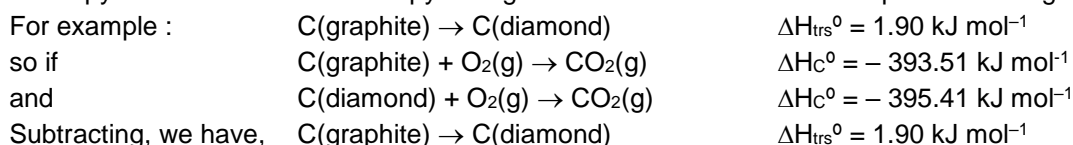


be required from the bond enthalpy data. This may be calculated as follows :

$$\begin{aligned} \Delta H &= \left( \begin{array}{l} \text{Enthalpy required to break reactants} \\ \text{into gaseous atoms} \end{array} \right) - \left( \begin{array}{l} \text{Enthalpy released to form products} \\ \text{from the gaseous atoms} \end{array} \right) \\ &= [4\Delta H_{\text{C-H}} + \Delta H_{\text{C=C}} + \Delta H_{\text{H-Cl}}]_{\text{R}} + [-5\Delta H_{\text{C-H}} - \Delta H_{\text{C-C}} - \Delta H_{\text{C-Cl}}]_{\text{P}} \\ &= (\Delta H_{\text{C=C}} + \Delta H_{\text{H-Cl}}) - (\Delta H_{\text{C-H}} + \Delta H_{\text{C-C}} + \Delta H_{\text{C-Cl}}) \end{aligned}$$

### Enthalpy of Transition :

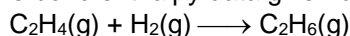
Enthalpy of transition is the enthalpy change when one mole of one allotropic form changes to another.





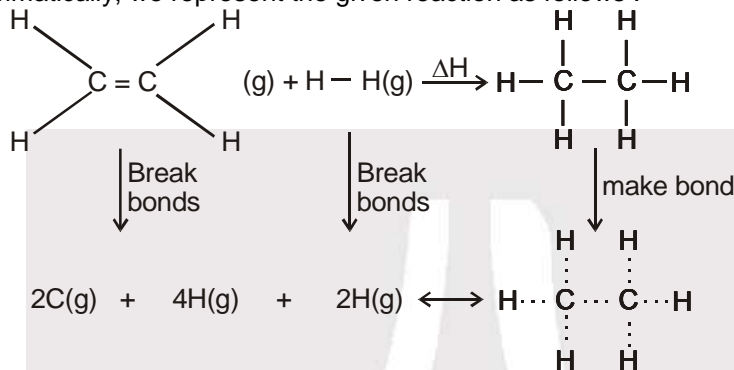
## Solved Examples

**Ex-15.** Using the bond enthalpy data given below, calculate the enthalpy change for the reaction



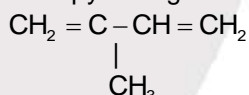
Data :	Bond	Bond enthalpy
	C – C	336 kJ mol <sup>-1</sup>
	C = C	606 kJ mol <sup>-1</sup>
	C – H	410 kJ mol <sup>-1</sup>
	H – H	431 kJ mol <sup>-1</sup>

**Sol.** Diagrammatically, we represent the given reaction as follows :



$$\begin{aligned}
 \Delta H_r &= (4\Delta H_{\text{C-H}} + \Delta H_{\text{C=C}} + \Delta H_{\text{H-H}}) - (6\Delta H_{\text{C-H}} + \Delta H_{\text{C-C}}) \\
 &= (4 \times 410 + 606 + 431) - (6 \times 410 + 336) \\
 &= 2677 - 2796 = -119 \text{ kJ/mol.}
 \end{aligned}$$

**Ex-16.** Using the bond enthalpy data given below, estimate the enthalpy of formation of gaseous isoprene



<b>Data:</b>	Bond enthalpy of C – H bond = 413.38 kJ mol <sup>-1</sup>
	Bond enthalpy of C – C bond = 347.69 kJ mol <sup>-1</sup>
	Bond enthalpy of C = C bond = 615.05 kJ mol <sup>-1</sup>
	Enthalpy of sublimation of carbon (graphite) = 718.39 kJ mol <sup>-1</sup>
	Enthalpy of dissociation of H <sub>2</sub> (g) = 435.97 kJ mol <sup>-1</sup>

**Sol.** For isoprene, we have to form

2C – C bonds ; 2C = C bonds and 8C – H bonds

**Method-1**

For which energy released is

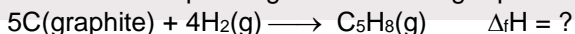
$$[2(+347.69) + 2(+615.05) + 8(+413.38)] \text{ kJ mol}^{-1} = 5232.52 \text{ kJ mol}^{-1}$$

that is,  $\Delta H$  (from gaseous atoms) = + 5232.52 kJ mol<sup>-1</sup>

The reaction corresponding to this is



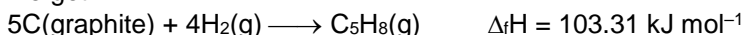
But we want  $\Delta_f H$  corresponding to the following equation



This can be obtained by the following manipulations :

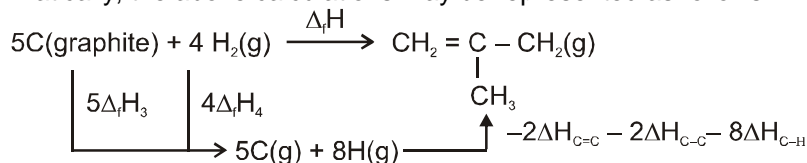


Adding, we get



**Method-2**

Diagrammatically, the above calculations may be represented as follows.







Applying Hess's law, we get

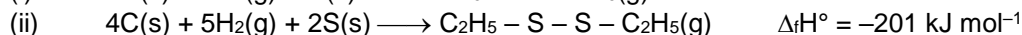
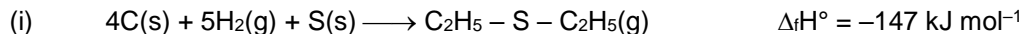
$$\begin{aligned}\Delta_f H &= 5\Delta_f H_3 + 4\Delta_f H_4 - 2\Delta_f H_{C=C} - 2\Delta_f H_{C-C} - 8\Delta_f H_{C-H} \\ &= (5 \times 718.39 + 4 \times 435.97 - 2 \times 615.05 - 2 \times 347.69 - 8 \times 413.38) \text{ kJ mol}^{-1} \\ \Delta_f H &= 103.31 \text{ kJ mol}^{-1}\end{aligned}$$

**Ex-17.** Find the bond enthalpy of S – S bond from the following data :

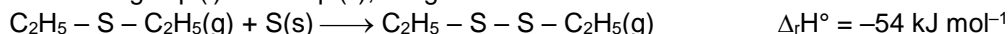


**Sol.** Given that

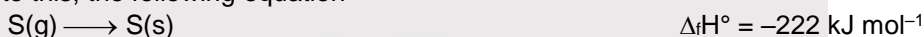
**Method-1**



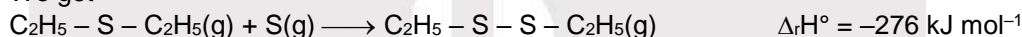
Subtracting Eq. (i) from Eq. (ii), we get



Adding to this, the following equation



We get

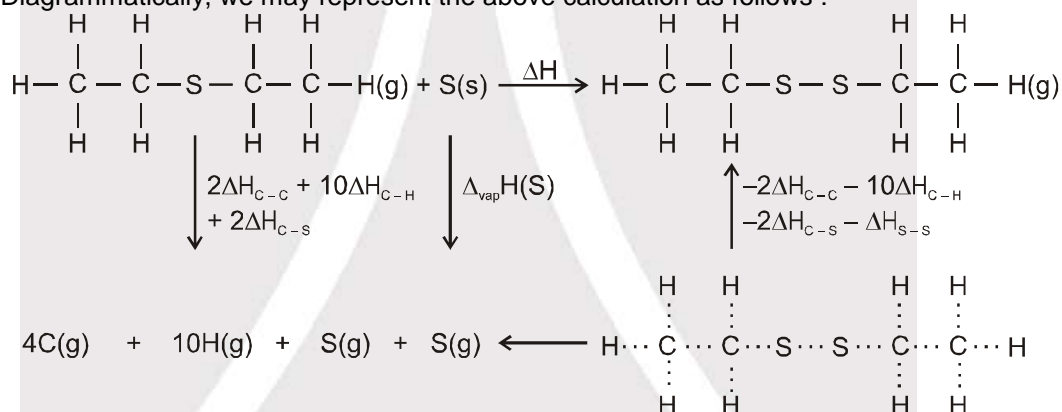


In the last equation 276 kJ of heat evolved because of the S–S bond formation.

Hence, the bond enthalpy of S – S is 276 kJ mol<sup>-1</sup>.

**Method-2**

Diagrammatically, we may represent the above calculation as follows :



**According to Hess's law :**

$$\begin{aligned}\Delta_f H^\circ &= \text{Enthalpy involved in bond breaking } \Delta_{\text{vap}}H^\circ(\text{s}) - \text{Enthalpy involved in bond making} \\ \Delta_f H^\circ &= [2\Delta_{\text{H}_{\text{C}-\text{C}}} + 10\Delta_{\text{H}_{\text{C}-\text{H}}} + 2\Delta_{\text{H}_{\text{C}-\text{S}}} + \Delta_{\text{vap}}H^\circ(\text{S})] + [-2\Delta_{\text{H}_{\text{C}-\text{C}}} - 10\Delta_{\text{H}_{\text{C}-\text{H}}} - 2\Delta_{\text{H}_{\text{C}-\text{S}}} - \Delta_{\text{H}_{\text{S}-\text{S}}}] \\ &= \Delta_{\text{vap}}H^\circ(\text{S}) - \Delta_{\text{H}_{\text{S}-\text{S}}} \\ \text{or } \Delta_{\text{H}_{\text{S}-\text{S}}} &= \Delta_{\text{vap}}H^\circ(\text{S}) - \Delta H^\circ \\ &= \Delta_{\text{vap}}H^\circ(\text{S}) - [\Delta_f H^\circ(\text{C}_2\text{H}_5 - \text{S} - \text{S} - \text{C}_2\text{H}_5) - \Delta_f H^\circ(\text{C}_2\text{H}_5 - \text{S} - \text{C}_2\text{H}_5)] \\ &= [222 - \{-201 - (-174)\}] \text{ kJ mol}^{-1} = 276 \text{ kJ mol}^{-1}\end{aligned}$$

### ○ Resonance energy :

Difference between energy of resonance hybrid and resonating structure in which resonance hybrid have lower energy because stabilised by resonance.

$$\begin{aligned}\Delta H^\circ_{\text{resonance}} &= \Delta H^\circ_{\text{f, experimental}} - \Delta H^\circ_{\text{f, calculated}} \\ &= \Delta H^\circ_{\text{combustion, calculated}} - \Delta H^\circ_{\text{combustion, experimental}}\end{aligned}$$

## Solved Examples

**Ex-18.** Calculate the heat of formation of benzene from the following data, assuming no resonance. Bond energies :

$$\text{C} - \text{C} = 83 \text{ kcal}, \quad \text{C} = \text{C} = 140 \text{ kcal}, \quad \text{C} - \text{H} = 99 \text{ kcal}$$

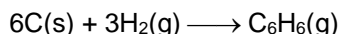
Heat of atomisation of C = 170.9 kcal

Heat of atomisation of H = 52.1 kcal





**Sol.** We have to calculate  $\Delta H$  for the reaction



**For reactants :**

Heat of atomisation of 6 moles of C =  $6 \times 170.9$  kcal

Heat of atomisation of 6 moles of H =  $6 \times 52.1$  kcal

**For products :**

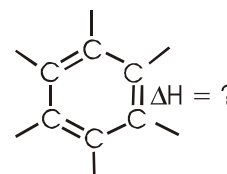
Heat of formation of 6 moles of C – H bonds =  $-6 \times 99$

Heat of formation of 3 moles of C–C =  $-3 \times 83$

Heat of formation of 3 moles of C = C bonds =  $-3 \times 140$

on adding, we get heat of formation of  $\text{C}_6\text{H}_6$ , i.e.,

$$\Delta_f H = 6 \times 170.9 + 6 \times 52.1 - 6 \times 99 - 3 \times 83 - 3 \times 140 = -75 \text{ kcal}$$

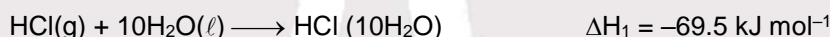


## Section (E) : Enthalpy of solution & Born Haber's cycle

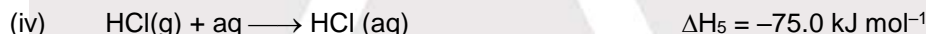
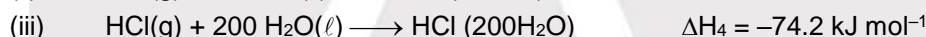
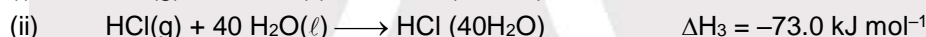
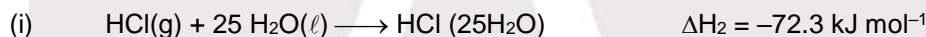
### ○ Integral enthalpy of solution

The integral enthalpy of solution at the given concentration is the enthalpy change when one mole of the solute is dissolved in a definite quantity of solvent to produce a solution of a desired concentration.

While recording integral enthalpies of solution it is a general practice to state the amount of the solvent in which 1 mole of solute is dissolved ; Thus



indicates that when 1 mole of hydrogen chloride gas is dissolved in 10 mol of water, there is an evolution of 69.5 kJ of heat. Other values are



**Whenever amount of solvent is not specified then take its amount to be very large just like in equation no. (iv).**

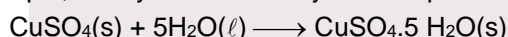
### ○ Enthalpy of Hydration :

Enthalpy of hydration is used in following two ways.

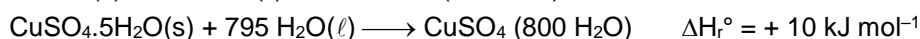
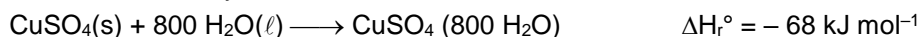
- Enthalpy of hydration of anhydrous or partially hydrated salts :

Enthalpy of hydration of a given anhydrous or partially hydrated salt is the enthalpy change when it combines with the requisite amount of water to form a new hydrated stable salt.

For example, the hydration of anhydrous cupric sulphate is represented by



There is a almost invariably a liberation of heat in such reactions, i.e. the value of  $\Delta H$  is negative.



by subtraction, we get



- Enthalpy of hydration of gaseous ions.

Enthalpy of hydration of any gaseous ion is the enthalpy change when 1 mole of the gaseous ion is hydrated in large amount of water to form aqueous ion.

By convention, the standard enthalpy of formation of  $\text{H}^+(\text{aq})$  is taken to be zero.

Enthalpy of hydration of  $\text{Cl}^-$  gaseous ions will be represented by :





### Section (F) : Enthalpy of neutralization

- The amount of heat released when one gram equivalent of an acid is neutralised by one gram equivalent of a base.

or

- The amount of heat released in formation of one mole of water when an acid is neutralised by a base.

or

- Enthalpy of neutralization is defined as the enthalpy change when one mole of  $H^+$  in dilute solution combines with one mole of  $OH^-$  to give rise to undissociated water, i.e.

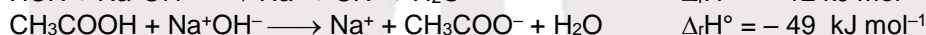


**Remember :**

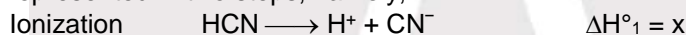
- For **Strong Acid + Strong Base**, heat of neutralisation is always equal to  $-13.7$  kcal/mole or  $-57.1$  kJ/mole.
- For any other combination of **acid and base** this heat is less than  $-13.7$  kcal/mole or  $-57.1$  kJ/mole.

#### ○ Enthalpy of Ionization of Weak Electrolyte :

- Whenever a weak acid (or base) reacts with a strong base (or acid), the release of heat is less than  $57.1 \text{ kJ mol}^{-1}$ .
- It is because of the fact that these acids or bases are not completely ionized in solution. Some of the heat is consumed in ionizing these acids and bases this heat is known as enthalpy of ionization. Examples are :



The enthalpy of ionization can be calculated as follows. The neutralization of a weak acid, say HCN, may be represented in two steps, namely,



The complete reaction is obtained by adding the above two steps. Thus



**Obviously,**  $\Delta H^\circ = \Delta H^\circ_1 + \Delta H^\circ_2$

$$\Delta H^\circ_1 = \Delta H^\circ - \Delta H^\circ_2 = [-12 - (-57.1)] = 45.1 \text{ kJ/mole}$$

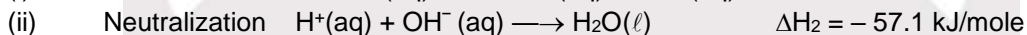
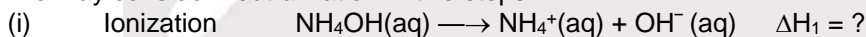
- **Greater the enthalpy of ionization of any weak acid or weak base, weaker will be the acid or base.**

### Solved Examples

**Ex-19.** Enthalpy of neutralization of HCl by NaOH is  $-57.1 \text{ kJ/mol}$  and by  $NH_4OH$  is  $-51.1 \text{ kJ/mol}$ . Calculate the enthalpy of dissociation of  $NH_4OH$ .

**Sol.** Given that,  $H^+(aq) + NH_4OH(aq) \longrightarrow NH_4^+(aq) + H_2O(\ell) \quad \Delta H = -51.1 \text{ kJ/mole}$

We may consider neutralization in two steps.



Thus,  $\Delta H = \Delta H_1 + \Delta H_2$

Therefore,  $\Delta H_1 = \Delta H - \Delta H_2 = -51.1 \text{ kJ/mol} + 57.1 \text{ kJ mol}^{-1} = 6.0 \text{ kJ/mol}$

### Enthalpy of Precipitation :

Enthalpy of precipitation is the enthalpy change when one mole of a precipitate is formed.



### Solved Examples

**Ex-20.** Calculate  $\Delta H^\circ$  for the reaction,  $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$  at  $25^\circ C$ .

Given  $\Delta_f H^\circ(Ag^+, aq) = 105 \text{ kJ mol}^{-1}$ ,  $\Delta_f H^\circ(Cl^-, aq) = -167 \text{ kJ mol}^{-1}$  and  $\Delta_f H^\circ(AgCl, s) = -127 \text{ kJ mol}^{-1}$

**Sol.** For the reaction  $Ag^+(aq) + Cl^-(aq) \longrightarrow AgCl(s)$

We have 
$$\Delta H^\circ = \Delta_f H^\circ(AgCl, s) - \Delta_f H^\circ(Ag^+, aq) - \Delta_f H^\circ(Cl^-, aq)$$

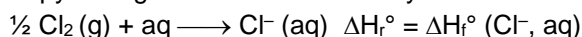
$$= [-127 - 105 - (-167)] \text{ kJ mol}^{-1} = -65 \text{ kJ mol}^{-1}$$



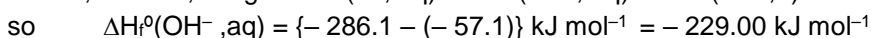
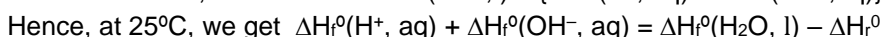
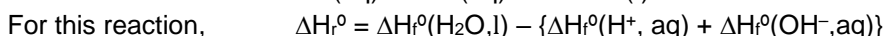
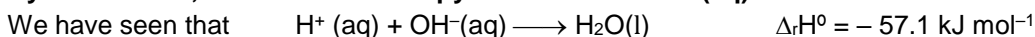


### ○ Enthalpy of Formation of ions :

The enthalpy change when one mole of hydrated ions is obtained from element in its standard state as.

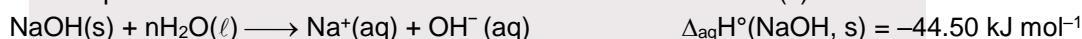


**By convention, the standard enthalpy of formation of  $\text{H}^+(\text{aq})$  is taken to be zero.**

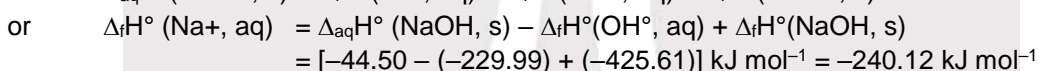
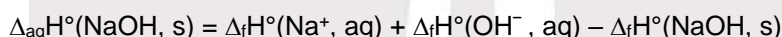


- With the enthalpies of formation of these two ions, the enthalpy of formation of any other ion can be found from the enthalpies of formation and solution of its pure compound with  $\text{H}^+$  or  $\text{OH}^-$ . For example, the enthalpy of formation of  $\text{Na}^+$  can be calculated from the enthalpy of formation and enthalpy of infinite dilute solution of  $\text{NaOH}$ . The two values are :

- The chemical equation for the formation of infinite dilute solution of  $\text{NaOH}(\text{s})$  is



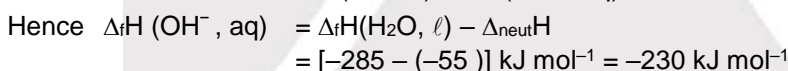
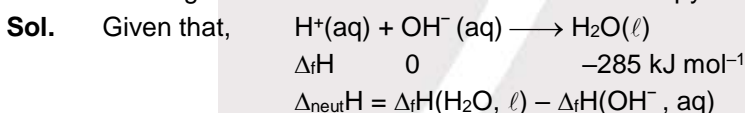
Since there are equal amounts of water on both sides of the above equation, the two enthalpies give no net effect and thus



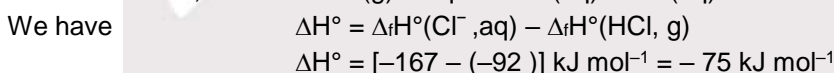
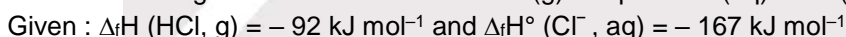
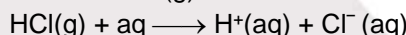
- Similarly, from  $\text{NaCl}(\text{aq})$  or  $\text{HCl}(\text{aq})$ , the enthalpy of formation of  $\text{Cl}^-(\text{aq})$  can be determined, and so on. The changes in enthalpy of any ionic reaction can then be found from these ionic enthalpies of formation and the usual enthalpies of formation of compounds.

## Solved Examples

**Ex-21.** The enthalpy of formation of  $\text{H}_2\text{O}(\text{l})$  is  $-285 \text{ kJ mol}^{-1}$  and enthalpy of neutralization of a strong acid and a strong base is  $-55 \text{ kJ mol}^{-1}$ . What is the enthalpy of formation of  $\text{OH}^-$  ions ?

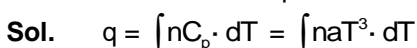


**Ex-22.** Calculate the enthalpy change when one mole of  $\text{HCl}(\text{g})$  is dissolved in a very large amount of water at  $25^\circ\text{C}$ . The change in state is :



## MISCELLANEOUS SOLVED EXAMPLES

1. Find (in terms of "a") the amount of energy required to raise the temperature of a substance from 3 K to 5 K. At low temperatures.  $C_P = aT^3$ .



$$= na \left[ \frac{T^4}{4} \right]_3^5 = \frac{na}{4} [(5)^4 - (3)^4]$$

$$= \frac{na[625 - 81]}{4} = 136 na.$$

**Ans.**  $q = 136 na.$





2. A thermally isolated vessel contains 100 g of water at 0°C. When air above the water is pumped out, some of the water freezes and some evaporates at 0°C itself. Calculate the mass of the ice formed such that no water is left in the vessel. Latent heat of vaporization of water at 0°C =  $2.10 \times 10^6$  J/kg and latent heat of fusion of ice =  $3.36 \times 10^5$  J/kg.

**Sol.** Total mass of the water =  $M = 100$  g  
 Latent heat of vaporization of water at 0°C  
 $= L_1 = 21.0 \times 10^5$  J/Kg  
 & Latent heat of fusion of ice =  $L_2 = 3.36 \times 10^5$  J/Kg  
 Suppose, the mass of the ice formed =  $m$   
 Then, the mass of water evaporated =  $M - m$ .  
 Heat lost by the water in freezing = Heat taken by water in evaporation.  
 Thus,  $mL_2 = (M - m) L_1$  or  $m = 86$  g.

**Ans.** 86.2 g

3. Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.1 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is  $4.2 \text{ J g}^{-1} \text{ K}^{-1}$ , what is the final temperature of water ?

**Sol.**  $W = -2.1 [6 - 4] = -2.1 \times 2$   
 $= -4.2 \text{ atm} \times \text{lit.}$   
 $= -4.2 \times 101.325 \text{ J}$   
 This work is used to heat up the water

$$\text{Specific heat of H}_2\text{O} = 4.2 \frac{\text{J}}{\text{gram} \cdot \text{K}}$$

Heat required for increasing temperature by 1°C of 1 mole =  $4.2 \times 18 = 75.6 \text{ J}$   
 $4.2 \times 101.325 = 75.6 [T - 293]$   
 $5.63 = T - 293$   
 $T = 298.63 \text{ K}$

**Ans.** 298.63 K

4. 1 mole of ice at 0°C and 4.6 mm Hg pressure is converted to water vapour at a constant temperature and pressure. Find  $\Delta H$  and  $\Delta E$  if the latent heat of fusion of ice is 80 cal/g and latent heat of vaporisation of liquid water at 0°C is 596 cal/g and the volume of ice in comparison to that of water (vapour) is neglected.

**Sol.** No. of mole = 1 mole  
 $T = 273 \text{ K}$ .  
 $Pv = nRT$ .  
 $\frac{4.6}{760} v = 1 \times 0.0821 \times 273$   
 $v = 3699 \text{ lit} \approx [3700 \text{ lit}]$   
 latent heat of fusion = 80 cal/gram Latent heat of vaporisation = 596 cal/gram  
 $\Delta H = 80 \times 18 + 596 \times 18 = [80 + 596] \times 18$   
 $\Delta H = 12168 \text{ cal}$   
 $\Delta H = \Delta E + P [V_2 - V_1]$   
 $12168 = \Delta E + \frac{4.6}{760} [3699] \times 24.24$

$$\Rightarrow \Delta E = 12168 - \frac{4.6}{760} \times 3699 \times 24.24$$

$$= 12168 - 542.72 = 11625.28 \text{ cal.}$$

**Ans.** 12168 cal, 11625.28 cal

5. For Ag,  $\bar{C}_p$  ( $\text{JK}^{-1} \text{ mol}^{-1}$ ) is given by  $24 + 0.006 T$ . Calculate  $\Delta H$  if 3 mol of silver are raised from 27°C to its melting point 927°C under 1 atm pressure.

**Sol.**  $\Delta H = \int_{T_1}^{T_2} nC_p dT = \int_{T_1}^{T_2} 3(24 + .006T) dT = 3 [24 (T_2 - T_1) + \frac{1}{2} \times 0.006 (T_2^2 - T_1^2)]$   
 $= 3 \times 25650 = 76950 \text{ J}$

**Ans.** 76950 J



6. Calculate the amount of heat evolved during the complete combustion of 100 ml of liquid benzene from the following data.

- (i) 18 g of graphite on complete combustion evolve 590 KJ heat  
 (ii) 15889 KJ heat is required to dissociate all the molecules of 1 litre water into  $H_2$  and  $O_2$ .  
 (iii) The heat of formation of liquid benzene is 50 kJ/mol  
 (iv) Density of  $C_6H_6$  ( $\ell$ ) = 0.87 g/ml

Sol. (i)  $C(s) + O_2(g) \longrightarrow CO_2(g)$ ;  $\Delta H_f^\circ = -393.33$  KJ/mol

(ii)  $H_2(g) + \frac{1}{2} O_2(g) \longrightarrow H_2O(\ell)$ ;  $\Delta H_f^\circ = -286$  KJ/mol

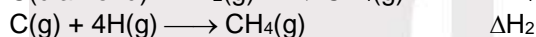
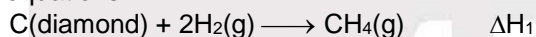
(iii)  $C_6H_6(\ell) + \frac{15}{2} O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(\ell)$

$$\therefore \Delta H^\circ = [6(-393.33) + 3(-286)] - 50 = -3268 \text{ KJ/mole}$$

$\therefore$  Heat evolved from 87 g benzene = 3645 KJ

Ans. 3645 KJ

7. For the equations



Predict whether

(A)  $\Delta H_1 = \Delta H_2$

(B)  $\Delta H_1 > \Delta H_2$

(C)  $\Delta H_1 < \Delta H_2$

(D)  $\Delta H_1 = \Delta H_2 + \Delta_{\text{vap}}H(C) + \Delta_{\text{diss}}H(H_2)$

Ans. (B)

8. The standard molar enthalpies of formation of cyclohexane (l) and benzene (l) at  $25^\circ\text{C}$  are  $-156$  and  $+49$  KJ  $\text{mol}^{-1}$  respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at  $25^\circ$  is  $-119$  KJ  $\text{mol}^{-1}$ . Use these data to estimate the magnitude of the resonance energy of benzene.

Sol. Enthalpy of formation of 3 carbon-carbon double bonds

$$= \Delta H_f(\text{Cyclohexene}) - \Delta H_f(\text{Benzene})$$

$$= -156 - (+49) \text{ kJ} = -205 \text{ kJ.}$$

Given that,  $\text{Cyclohexene} + H_2 \longrightarrow \text{Cyclohexane}$   $\Delta H = 119$  kJ

Theoretical enthalpy of formation of 3 double bonds in benzene ring

$$= 3 \times (-119) \text{ kJ} = -357 \text{ kJ.}$$

$\therefore$  resonance energy of benzene =  $-357 - (-205) \text{ kJ} = -152 \text{ kJ mole}^{-1}$

Ans.  $-152 \text{ kJ mole}^{-1}$

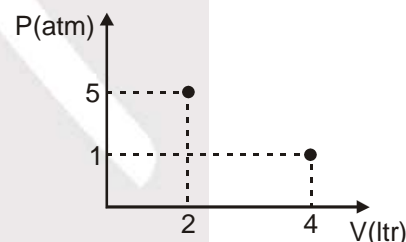
9. Following graph shows a single stage expansion process, then workdone by the system is

(A)  $-9104$  J

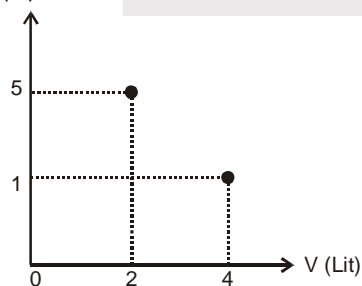
(B)  $-202.6$  J

(C)  $-506$  J

(D)  $-101.3$  J



Sol.



$$W = -P_{\text{ext}}(V_2 - V_1) = -1 \times 2 \times 101.325 \text{ J} = -202.6 \text{ J}$$

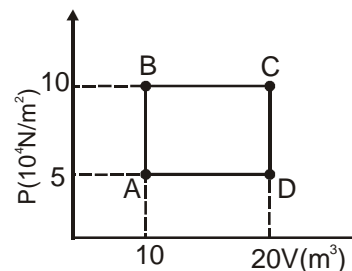
Ans. (B)







10. A sample of 2 kg of helium (assumed ideal) is taken through the process ABC and another sample of 2 kg of the same gas is taken through the process ADC. Then the temperature of the states A and B are (Given  $R = 8.3$  joules/mol K) :
- (A)  $T_A = 120.5$  K,  $T_B = 120.5$  K  
 (B)  $T_A = 241$  K,  $T_B = 241$  K  
 (C)  $T_A = 120.5$  K,  $T_B = 241$  K  
 (D)  $T_A = 241$  K,  $T_B = 482$  K



Sol.  $\frac{0.5 \times 10^5}{1.01 \times 10^5} \times 10 \times 10^3 = \frac{2 \times 1000}{2} \times 0.082 T_A$

$$\frac{1}{1.01} = 0.082 T_A$$

$T_A = 120.5$  K  
 at constant volume

$$\frac{P_A}{T_A} = \frac{P_B}{T_B}$$

$$T_B = \frac{P_B \cdot T_A}{P_A} = \frac{10}{5} \times 120.5 = 241 \text{ K.}$$

Ans. (C)

11. In an isothermal expansion of a gaseous sample the correct relation is (consider  $w$  (work) with sign according to new IUPAC convention)  
 [The reversible and irreversible processes are carried out between same initial and final states.]  
 (A)  $w_{\text{rev}} > w_{\text{irrev}}$  (B)  $w_{\text{irrev}} > w_{\text{rev}}$  (C)  $q_{\text{rev}} < q_{\text{irrev}}$  (D) can not be predicted

Ans. (B)

12. One mole of an ideal monoatomic gas is caused to go through the cycle shown in figure. Then, the change in the internal energy in expanding the gas from a to c along the path abc is :
- (A)  $3 P_0 V_0$  (B)  $6 RT_0$   
 (C)  $4.5 RT_0$  (D)  $10.5 RT_0$

Sol.  $Pv = nRT$  at point C  
 $2P_0 \times 4V_0 = 1 \times RT_C$

$$T_C = \left[ \frac{8P_0 V_0}{R} \right]$$

at point a  
 $P_0 V_0 = 1 \times RT_0$

$$T_0 = \frac{P_0 V_0}{R}; \quad T_C = 8 T_0$$

Change in internal energy =  $[nC_v dT]$

For path a to b =  $1 \times \frac{3}{2} R \times [3T_0] = \frac{9}{2} RT_0$

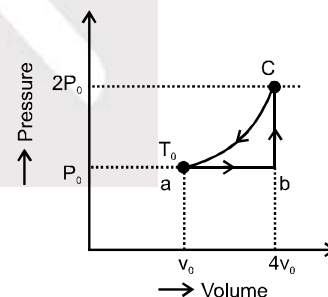
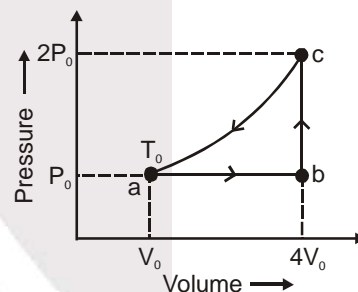
For path b to c =  $1 \times \frac{3}{2} R \times [4T_0] = 6T_0 R$

Total change =  $\frac{9}{2} RT_0 + 6RT_0 = \frac{21RT_0}{2} = 10.5 RT_0$ .

So total change in internal energy  
 $\Delta U = 10.5 RT_0$

Ans. (D)

13. A certain mass of gas is expanded from (1L, 10 atm) to (4L, 5 atm) against a constant external pressure of 1 atm. If initial temperature of gas is 300 K and the heat capacity of process is  $50 \text{ J/}^\circ\text{C}$ . Then the enthalpy change during the process is (1L atm  $\approx 100$  J)
- (A)  $\Delta H = 15$  kJ (B)  $\Delta H = 15.7$  kJ (C)  $\Delta H = 14.4$  kJ (D)  $\Delta H = 14.7$  kJ







**Sol.**  $\Delta H = \Delta E + \Delta(PV)$  &  $\Delta E = q + W = (50 \times 300 - 3 \times 100) \text{ J}$  [as  $T_f = 2 \times 300 \text{ K} = 600 \text{ K}$ ] = 14.7 kJ  
 $\Delta H = 14700 + 10 \times 100 = 15700 \text{ J} = 15.7 \text{ kJ}$ .

**Ans (B)**

**14.** One mole of an ideal monoatomic gas expands isothermally against constant external pressure of 1 atm from initial volume of 1L to a state where its final pressure becomes equal to external pressure. If initial temperature of gas is 300 K then total entropy change of system in the above process is :  
 [R = 0.082 L atm mol<sup>-1</sup> K<sup>-1</sup> = 8.3 J mol<sup>-1</sup>K<sup>-1</sup>].

- (A) 0 (B)  $R \ln(24.6)$  (C)  $R \ln(2490)$  (D)  $3/2 R \ln(24.6)$

**Sol.**  $\Delta S = nR \ln\left(\frac{V_f}{V_i}\right) = R \ln\left(\frac{P_i}{P_f}\right) = R \ln\left(\frac{300R}{1L \times 1 \text{ atm}}\right) = R \ln(24.6)$

**Ans. (B)**

**15.** For a perfectly crystalline solid  $C_{p,m} = aT^3$ , where a is constant. If  $C_{p,m}$  is 0.42 J/K-mol at 10 K, molar entropy at 10 K is :

- (A) 0.42 J/K-mol (B) 0.14 J/K-mol (C) 4.2 J/K-mol (D) zero

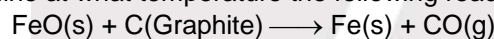
**Sol.**  $0.42 = a(10)^3 \Rightarrow a = 0.42 \times 10^{-3}$   
 $S_m = \int_0^{10} \frac{C_{p,m}}{T} dT = \int_0^{10} aT^2 = \frac{a}{3}[10^3 - 0] = \frac{0.42}{3} = 0.14 \text{ J/K-mol}$

**Ans. (B)**

**16.** Given the following data :

Substance	$\Delta H^\circ$ (kJ/mol)	$S^\circ$ (J/mol K)	$\Delta G^\circ$ (kJ/mol)
FeO(s)	-266.3	57.49	-245.12
C (Graphite)	0	5.74	0
Fe(s)	0	27.28	0
CO(g)	-110.5	197.6	-137.15

Determine at what temperature the following reaction is spontaneous ?



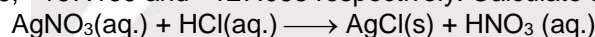
- (A) 298 K (B) 668 K (C) 966 K  
 (D)  $\Delta G^\circ$  is +ve, hence the reaction will never be spontaneous

**Sol.**  $\text{FeO(s)} + \text{C(graphite)} \longrightarrow \text{Fe(s)} + \text{CO(g)}$

- (1)  $\Delta H = 0 + [-110.5] - (-266.3)$   
 $= -110.5 + 266.3$   
 $= +155.8 \text{ kJ/mole}$   
 (2)  $\Delta S = 27.28 + 197.6 - 57.49 - 5.74 = 161.65 \text{ J/mole}$   
 (3)  $\Delta G = \Delta H - T\Delta S = 0 = 155.8 - T \times 161.65 \times 10^{-3}$   
 $T \times 161.65 \times 10^{-3} = 155.8 \Rightarrow T = 963.8 \text{ K}$

**Ans. (C)**

**17.** If  $\Delta H_f^\circ$  for  $\text{Ag}^+$  (infinitely diluted),  $\text{NO}_3^-$  (infinitely diluted),  $\text{Cl}^-$  (infinitely diluted) and  $\text{AgCl(s)}$  are 105.579, -207.36, -167.159 and -127.068 respectively. Calculate the enthalpy change for the reaction



- (A) 21.471 KJ/mol (B) 145.688 KJ/mol (C) -65.488 KJ/mol (D) None

**Sol.**  $\Delta H_{\text{reaction}}^\circ = [\Delta H_f^\circ(\text{AgCl}) + \Delta H_f^\circ(\text{H}^+) + \Delta H_f^\circ(\text{NO}_3^-)] - [\Delta H_f^\circ(\text{Ag}^+) + \Delta H_f^\circ(\text{NO}_3^-) + \Delta H_f^\circ(\text{Cl}^-) + \Delta H_f^\circ(\text{H}^+)]$   
 $= -127.068 - [105.579 - 167.159] = -65.488 \text{ KJ/mol}$

**Ans. (C)**

**18.** What is the work done against the atmosphere when 25 grams of water vaporizes at 373 K against a constant external pressure of 1 atm ? Assume that steam obeys perfect gas laws. Given that the molar enthalpy of vaporization is 9.72 kcal/mole, what is the change of internal energy in the above process ?

- (A) 1294.0 cal, 11247 cal (B) 921.4 cal, 11074 cal  
 (C) 1025.6 cal ; 12474.3 cal (D) 1129.3 cal, 10207 cal

**Sol.** Mole of  $\text{H}_2\text{O} = 1.39$

$$Pv = nRT$$

$$1 \times v = 1.39 \times 0.082 \times 373 \Rightarrow v = 42.51 \text{ lit}$$

$$w = P_{\text{ext.}} dv = 1 \times [42.80] \text{ atm} \times \text{lit.} = 42.80 \times 101.325 \text{ J} = \frac{42.80 \times 101.325}{4.2} = 1025.6 \text{ cal}$$

$$\Delta H = \Delta U + [P\Delta v]. = 12470.6 \text{ cal.}$$

$$\Delta U = \Delta H - P\Delta v = 13500 - 1025.6 = 12474.3 \text{ cal}$$

**Ans. (C)**