

# General Chemistry



## **Chapter 6: Chemical Thermodynamics**

# Chemical Thermodynamics

- **Self Study**
- **Fundamental Terms and Terminology**
  - *Thermodynamic system*
  - *Surroundings*
  - *System boundary*
  - *Universe*
  - *Types of Thermodynamic Systems (Open, closed and Isolated)*
  - *Property of thermodynamic systems (Extensive and Intensive Property)*
  - *State, State functions ( or Variables)*
  - *Thermodynamic Process (Isobaric, Isochoric, Isothermal and adiabatic)*

# Chemical Thermodynamics

- The study of the **flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation**, is called **Thermodynamics**
- It is the study of the interrelation of heat and work with chemical reactions or with physical changes of state
- **Fundamental Terms and Terminology**
  - **Thermodynamic system**: *a quantity of fixed mass under investigation*,
  - **Surroundings**: everything external to the system,
  - **System boundary**: interface separating system and surroundings, and
  - **Universe**: combination of system and surroundings.

contd..

- **System:**

- A system is either a quantity of matter or a region of space selected for study.

- **Surroundings:**

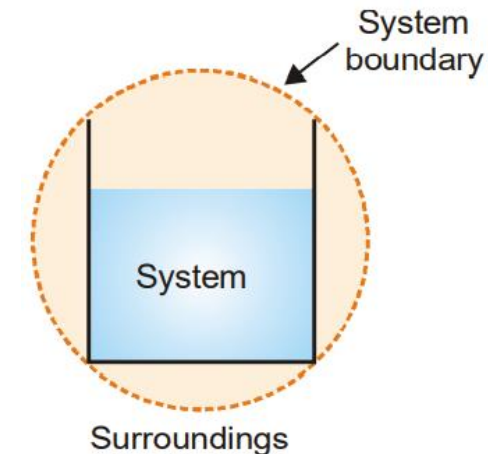
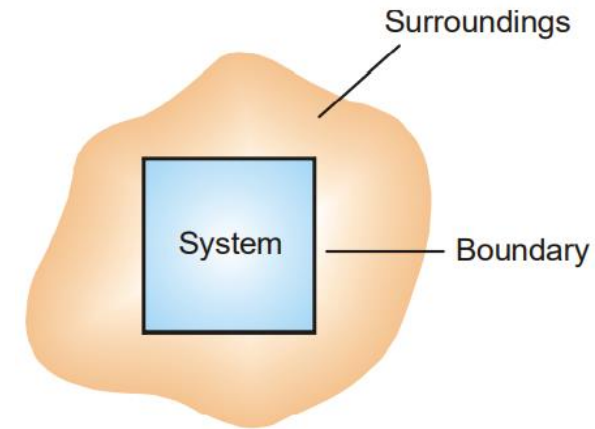
- Everything that is outside the system is known as the surroundings.

- **Boundary:**

- The closed surface that separates the system from its surroundings is known as the system boundary.

- **Universe:**

- It is the combination of system and surrounding.



Water containing in a beaker constitutes a system

# Types of Thermodynamic Systems

- Depending on the **nature of the boundary** ( what can pass through its boundaries), there are three types of thermodynamic systems:

## **i. Open System:**

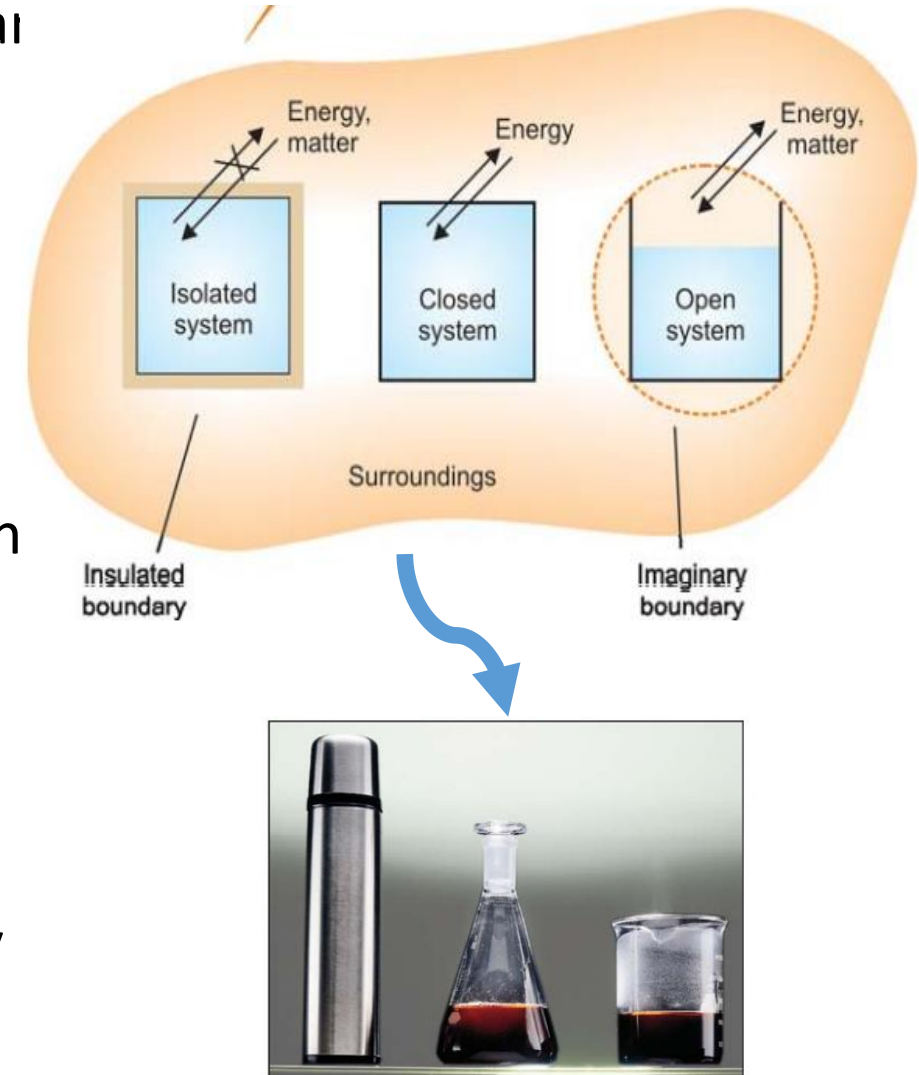
- An open system allows both matter and energy to enter or leave the system.

## **ii. Closed System:**

- A closed system contains the same matter within the system throughout the investigation. Therefore, no matter crosses the boundary of a closed system. However, energy can cross the boundary of a closed system.

## **iii. Isolated System:**

- In an isolated system, neither matter nor energy enters or leaves the system. i.e. a system which is not influenced by its surroundings.



# Property (of thermodynamic systems)

- A **property** is any characteristic of a system which can be **measured or calculated**. **Temperature** and **pressure** are examples of properties that can be measured. **Internal energy**, **enthalpy** and **entropy** are examples of properties that can be calculated.

There are two important classes of properties:

**i. Extensive Property:** (Depends on the quantity of matter )

- Any property that relates to the **quantity of all matter** present in the system is an extensive property. Extensive properties **can be added up**. Examples, **Volume( $V$ )**, **number of moles**, **total energy ( $E$ )**, **internal energy( $U$ )**, **enthalpy( $H$ )**, **total heat capacity( $C_p$ )**, **entropy( $S$ )**, and **Gibbs' free energy ( $G$ )** etc.

**ii. Intensive Property:** (Does not depends on the quantity of matter )

- Any property that is definable at a point in the system is an intensive property, and its value may change from one point of a system to another. Intensive properties **cannot be added up**. Examples, **pressure**, **temperature**, **density**, **viscosity**, **surface tension**, **Refractive index** and **concentration** etc.

## State, State Variables:

- **State:** The **condition at which a system exists** is called the state of a system. The state of a system is identified or described by its properties. i.e. when all its properties are fixed.
- **Variables** that define the **state of a system**.

## State Functions:

- System properties, such as ***pressure (P), volume (V), and temperature (T)*** are called ***state functions***.
  - A **change in the magnitude** of such properties **alters the state of the system**.
  - A change of system **from the initial state to the final state** (2nd state) will be accompanied by **change in the state variables**.
  - The **change in the state function is path independent** and defined by the properties in the initial and the final state only.
  - The value of a state function depends only on **the state of the system** and not on the **way in which the system came to be in that state**.
  - A **change in a state function** describes a difference between the two states. **It is independent of the process or pathway by which the change occurs.**

## Contd..

- For example, if we heat a sample of water from 0<sup>0</sup> C to 25<sup>0</sup> C, the change in temperature is equal to difference between the initial and final temperatures.

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 25^{\circ}\text{C}.$$

- The way in which the temperature change is brought about has no effect on the result.

### Independent and Dependent state variables

- Let one mole of a pure gas, the equation of state is : **PV= RT** where R is gas constant. If **P and T are specified**, the **value of third (V) is fixed automatically** and can be calculated from the equation of state.
- The variables (**P** and **T**) which must be necessarily specified to define the state of a system, are designated as **Independent state variables**. The remaining state variable (**V**) which depends on the value of P and T, is called **Dependent state variable**.



# Thermodynamic Process:

- When a system changes **from one state to another**, it is said to execute a **process**. We also define, a **Process**: a succession of changes of state.

## i. **Isobaric** (constant pressure):

- It is a process during which the pressure remains constant, while the other properties of the system may change. i.e. For an isobaric process,  $dp = 0$ .

## ii. **Isochoric**(constant volume):

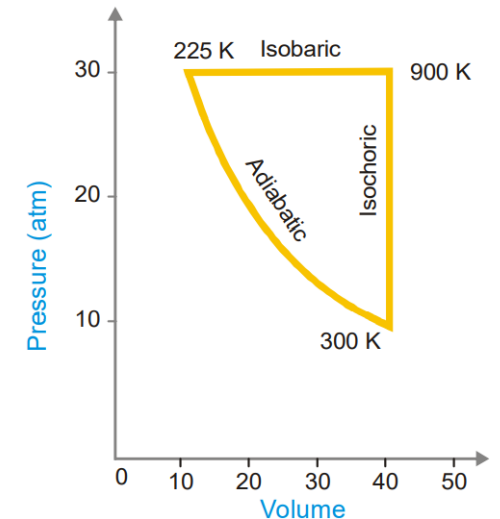
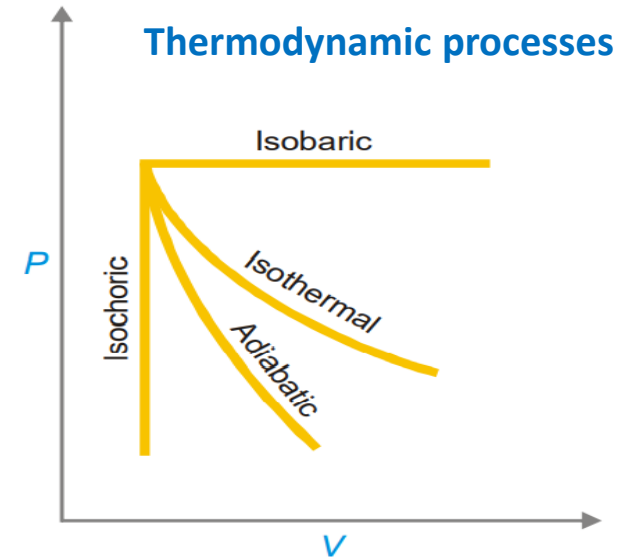
- During a constant volume process, volume remains constant while the other properties may change from one state to another. For isochoric processes  $dV = 0$ .

## iii. **Isothermal** (constant temperature):

- It is a constant temperature process. For an isothermal process  $dT = 0$

## iv. **Adiabatic** (heat constant):

- It is a process taking place while the system remains thermally insulated from its surroundings. That is, no heat is transferred between the system and its surroundings For an adiabatic process  $dq = 0$
- When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or **cyclic process**. For a cyclic process  $dE = 0, dH = 0$



A cyclic process

# Work and Heat:

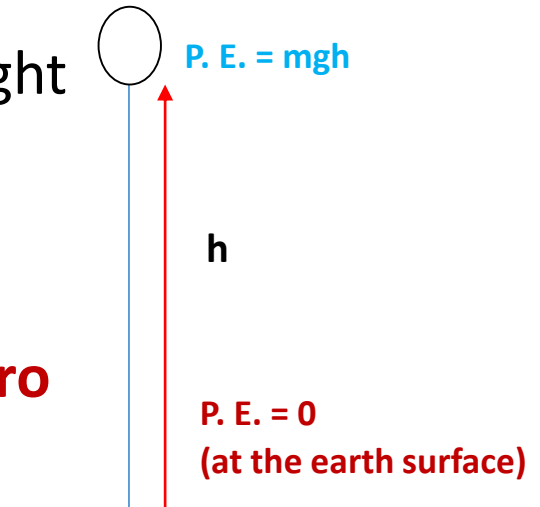
## Work ( $w$ ):

- In mechanics, work is defined as product of a force and displacement.  
i.e. Mechanical work ( $w$ ) = force  $\times$  displacement
- $w = f \times d$
- “Work is the means of transfer of energy from one mechanical system to another”

(I) Let a body of mass ( $m$ ) from earth surface has been lifted to a height ( $h$ ) against the gravitational acceleration ( $g$ ), then the force ( $mg$ ) is applied over a distance ( $h$ ) on the body and work is done which is:

$$w = f \times d = mg \times h$$

- Here, energy of body is changed from potential energy arbitrary **zero** at surface of the earth to a new value  **$mgh$**  at height ( $h$ ) in terms of work done.



Contd...

(II) Suppose, a constant acceleration (**a**) is applied on a body of mass, **m** over a distance  $r_2 - r_1$ , then **work done on the body** is given by,

$$w = ma \times (r_2 - r_1)$$

- We know that,

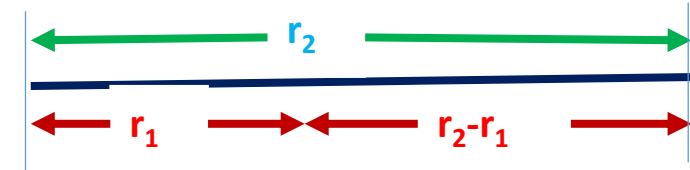
$$\text{Average velocity} = \frac{\text{Distance covered}}{\text{Time taken}}$$

$$\frac{V_1 + V_2}{2} = \frac{r_2 - r_1}{t}$$

$$r_2 - r_1 = \frac{V_1 + V_2}{2} \times t$$

$$w = f \times r = ma \times (r_2 - r_1) = m \times \frac{V_2 - V_1}{t} \times \left( \frac{V_1 + V_2}{2} \times t \right)$$

$$w = m \frac{V_2^2 - V_1^2}{2} = \frac{1}{2} m V_2^2 - \frac{1}{2} m V_1^2 = KE_2 - KE_1$$



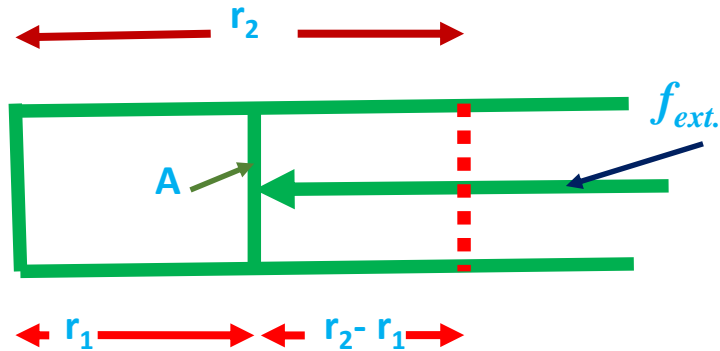
- This is just *final kinetic energy of the body minus the initial kinetic energy*.
- It shows that **work done on a simple mechanical system** is numerically to the **change in its energy**.

## Pressure –Volume work: work done in expansion (or compression) of a gas

- Let us consider, a gas is confined in a cylinder fitted with piston. If it is allowed to expand against external force ' $f_{\text{ext}}$ ', then **work done during the expansion of gas on the surrounding** can be given as:

$$w = -f_{\text{ext}} \cdot (r_2 - r_1) \quad [\text{here, -ve sign signifies that system does the work on the surrounding}]$$

- Then, work done in terms of pressure–volume is;
- $w = -\frac{f_{\text{ext}}}{A} \times (r_2 - r_1) \times A$  where,  $A$  is cross-sectional area of piston



Expansion of a gas against an external force,  $f_{\text{ext}}$ .

## Contd...

- But ,  $(r_2 - r_1)$ .  $A = \Delta V$ , volume change for the gas and  $f_{\text{ext}}/A$  is the force per unit area, or external pressure against which the gas expands.
- Then above eqn. becomes,  **$w = - P_{\text{ext}} \times \Delta V$  (if pressure is constant)**
- An infinitesimal volume change ( $dV$ ) produces an infinitesimal amount of work ( $dw$ ). Then  **$dw = - P_{\text{ext}} \times dV$**
- For infinitesimal volume change ( $dV$ ), the external pressure remains constant.

$$\int_0^w dw = - \int_{V_1}^{V_2} P_{\text{ex}} dV$$

$$w = -P_{\text{ex}} (V_2 - V_1) = -P_{\text{ex}} \Delta V$$

$$\therefore \mathbf{w = -P_{ex} \Delta V}$$

- At constant volume ( $\Delta V = 0$ ),  $w = 0$  and at zero external force ( $f_{\text{ex}} = 0$ ),  $w = 0$ .
- **+  $w$  = Contraction ( $V_2 < V_1$  ), (workdone on the system by surrounding)**
- **-  $w$  = Expansion ( $V_2 > V_1$  ), (workdone by the system on surrounding)**

# Work (W) is not a state function:

- Work done in going from initial to final state depends on the path followed.
- Let us consider, a gaseous system initially at  $P_1$  and  $V_1$  undergoes **expansion** ( $V_2 > V_1$ ) and goes to  $P_2$  and  $V_2$ . This process can be carried out by **two ways**:

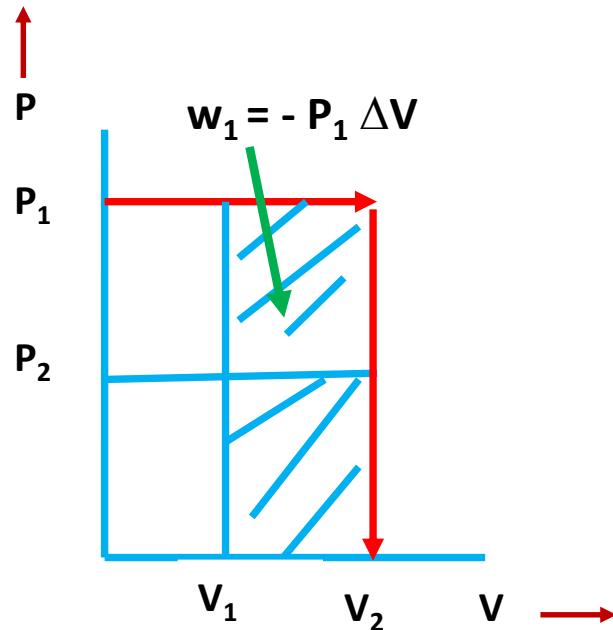


Fig (a) : At  $P_1$  &  $V_1$  to  $V_2$ ;

$$w_1 = -P_1 \Delta V$$

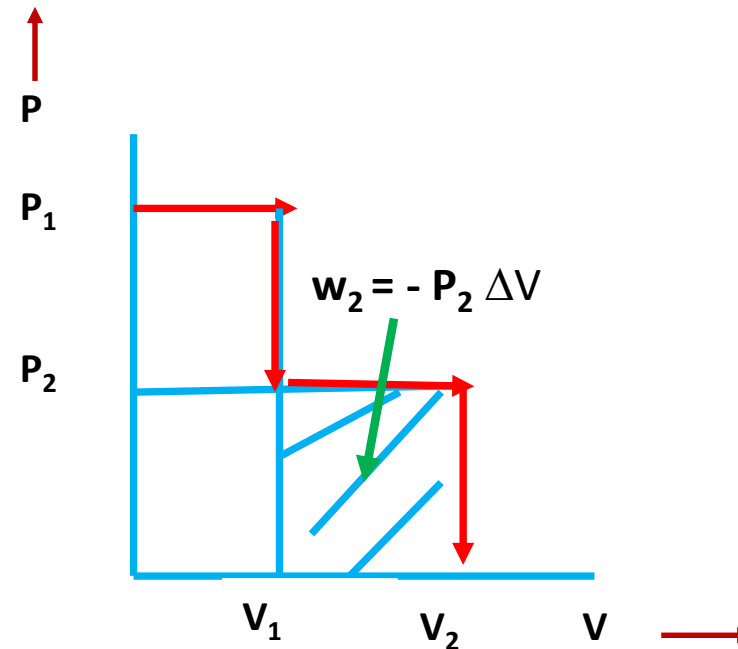


Fig (b) : At  $P_1$  to  $P_2$  &  $V_1$  to  $V_2$ ;

$$w_2 = -P_2 \Delta V$$

contd...

a. Keeping  $P_1$  constant, the volume changes from  $V_1$  to  $V_2$ . Then, keeping  $V_2$  volume constant,  $P_1$  is changed to  $P_2$ .

Expansion (Path I) :  $P_1 V_1 \xrightarrow{\text{work}} P_1 V_2 \longrightarrow P_2 V_2$

- Therefore, **Work ( $W_1$ ) = -  $P_1 \Delta V$**

b. Keeping  $V_1$  constant, the pressure changes from  $P_1$  to  $P_2$ . Then, keeping  $P_2$  pressure constant,  $V_1$  is changed to  $V_2$ .

Expansion (Path II) :  $P_1 V_1 \longrightarrow P_2 V_1 \xrightarrow{\text{work}} P_2 V_2$

- Therefore, **Work ( $W_2$ ) = -  $P_2 \Delta V$**
- Both works are **negative** because for **expansion**,  $V_2 > V_1$  and  $\Delta V = +ve$
- Since  $P_2 < P_1$  for expansion, then  **$W_1 < W_2$** .
- Thus, work done depends on the path followed even though the initial and final states are same. So, work is not a state function

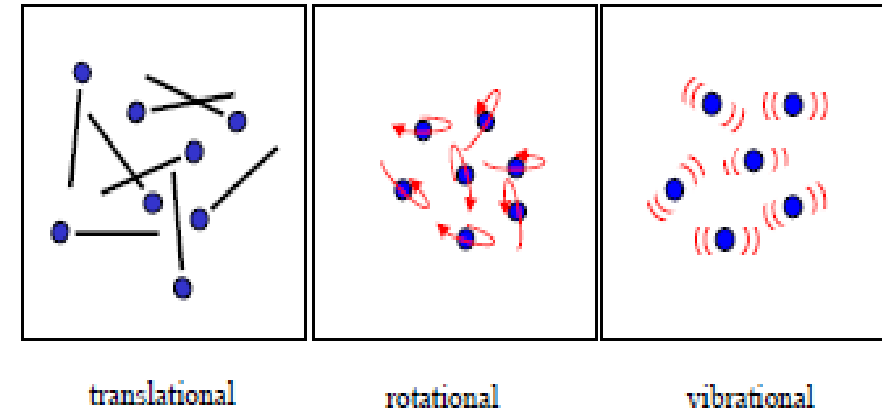
# First law of Thermodynamics

- **Internal Energy: E ( or U )**

- The term *internal energy* refers to **all of the energy contained within a chemical system**
- i.e. **all the kinetic and potential energy** possessed by all the components of a system; *total energy* stored within the molecule as **translational, rotational and vibrational** energies.

- An increase in the internal energy of a system can take three forms:

- (a) **an increase in temperature**
- (b) **a phase change**
- (c) **the initiation of a chemical reaction.**



- The **change in internal energy** will be the amount of energy exchanged between a system and its surroundings during a physical or chemical change. This can be given as:  $\Delta E = E_{\text{final}} - E_{\text{initial}}$

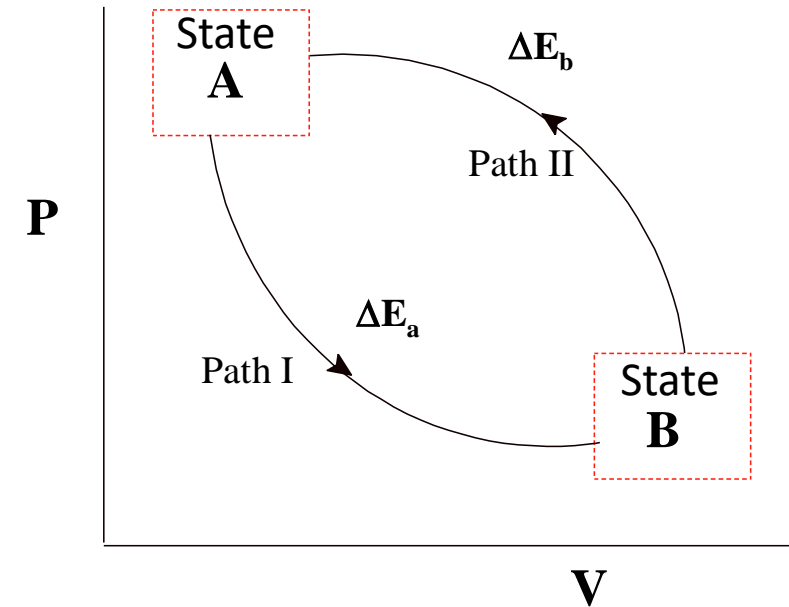
$$E_{\text{internal}} = E_{\text{Translational}} + E_{\text{Rotational}} + E_{\text{Vibrational}} + \text{others.}$$

(  $E_{\text{Translational}} > E_{\text{Rotational}} > E_{\text{Vibrational}}$  )



# Internal energy (E) is a state function

- **Internal energy** is a **state function** because, the **energy change** accompanying a process is **independent of the path followed** and depends only **upon initial and the final state of the system**.
- Let us consider that the system goes from A to B state by **path I** with  $\Delta E_a$  and from B to A by **path II** with  $\Delta E_b$  and assume  $\Delta E_a > \Delta E_b$  or  $\Delta E_a < \Delta E_b$
- When a **system completes one complete cycle**, an **extra energy equal to  $(\Delta E_a - \Delta E_b)$  or  $(\Delta E_b - \Delta E_a)$  is created**.
- By repeated this cycle continuously, **an unlimited amount of energy is created without losing anything**. **This is against first law of thermodynamics**.
- So, there must be  $\Delta E_a = \Delta E_b$ .



- **First Law of thermodynamics:**

- It is commonly known as the '**Law of conservation of energy**'.
- Energy can **neither be created nor be destroyed**, *but it can be changed from one to another form.*

## **Mathematical interpretation of First Law of Thermodynamics:**

- Let us **consider the effect of adding energy to a system as an amount of heat, q**. If **energy is conserved** and **system does no work** then '**q**' must appear as a **change in the internal energy of the system,  $\Delta E$** . Therefore,

$$\Delta E = q \dots\dots\dots (i) \quad \textbf{(no work done)}$$

- If **no heat is supplied or exchanged to or from the surrounding in a system** but a **work is done on the system** then the work done must appear as internal energy change of the system. In this case,

$$\Delta E = w \dots\dots\dots (ii) \quad \textbf{(no heat transferred)}$$

- If we consider that both processes are carrying out altogether within a system, then from equations ( i) and ( ii), we get  **$\Delta E = q + w$**  .....(iii)

- The equation (iii) is the **mathematical statement of 1<sup>st</sup> law of thermodynamics**. So, 1<sup>st</sup> law of thermodynamics may be stated that *net energy change of a closed system is equal to the sum of heat transferred to the system and work done on the system*.
- Thus, the internal energy of the system can be increased either by doing working or by supplying heat on the system or both.
- **Concept of heat and work:** Heat is the something that flows but work is the means by which energy can be transmitted. Work and heat both possess the same unit. In other word, work is the energy transmitted by the virtue of mechanical link between system and heat is energy transmitted due to the temperature difference.
- **To verify heat is not a state functions:**
  - Mathematically the first law of thermodynamics can be written as,  $\Delta E = q + w$ . Change in internal energy when a system at state one changed to another state is always constant whatever be the path followed. But work done (w) for different way can be different. To make the above equation valid heat changed (q) for different ways must be different. **So heat is not a state function.**

# Measurement of internal energy, $\Delta E$

- Let us consider the process where state of the system is changed at **constant temperature**, say 25°C. Following the I law of thermodynamics, the change in internal energy is given by;  **$\Delta E = q + w$**
- The pressure volume work is given by,  $w = - \int_{V_1}^{V_2} P dV$
- Thus,  $\Delta E = q - \int_{V_1}^{V_2} P dV$
- This expression is further simplified when the state of system is changed **at constant volume**. i.e. **chemical reaction is carried inside a container possessing fixed volume**.
- In this condition  **$dV = 0$**  and so the work done.  **$\Delta E = q_v$**  (heat changed at constant volume)
- i.e.  **$\Delta E$  measures the quantity of heat supplied in the system at constant volume**.  
To measure the change in internal energy for the state change, the quantity of heat change is measured carrying out the process at constant volume and temperature.
- **For exothermic process  $q_v = \text{negative}$  so,  $\Delta E = -ve$**
- **For endothermic process  $q_v = \text{positive}$  so,  $\Delta E = +ve$** .

# Calculation of enthalpy ( $\Delta H$ )

- We know that,  $H = E + PV$  .....(i)

- The change of enthalpy is given by,

$$\Delta H = \Delta E + \Delta(PV) = q + w + \Delta(PV)$$

$$\Delta H = q - P\Delta V + P\Delta V + V\Delta P$$

$$\therefore \Delta H = q + V\Delta P \text{ .....(ii)}$$

- At *constant pressure*,  $\Delta H = q_p$  .....(iii)
- For **exothermic process**,  $q_p = -ve$ ,  $\Delta H = -ve$ , **heat evolved**.
- For **endothermic process**,  $q_p = +ve$ ,  $\Delta H = +ve$ , **heat absorbed**.

## How close are $\Delta H$ and $\Delta E$ ?

- For only **solid and liquid** involving reactions, *very little volume change occurs* and at very low pressure (1 atm),  $\Delta(PV)$  is **very small** and can be **neglected**.

$$\Delta H \equiv \Delta E \text{ .....(iv)}$$

- For **gas involving reaction**,

$$\Delta H = \Delta E + \Delta(PV) \text{ or } \Delta H = \Delta E + \Delta nRT = \Delta E + RT\Delta n \text{ (at constant T).....(v)}$$

# Thermochemistry

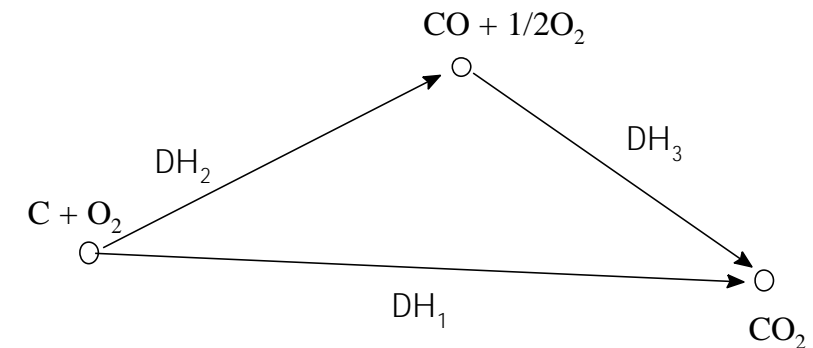
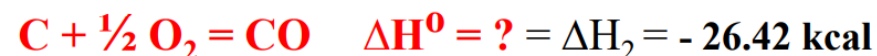
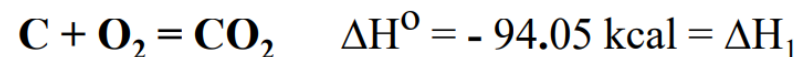
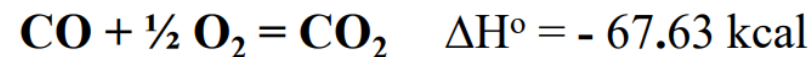
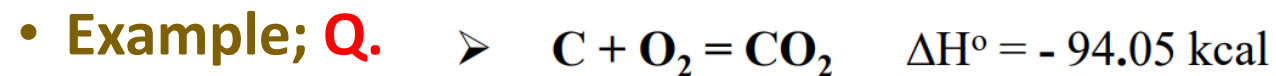
- **General terms/ definitions:**
- **Standard enthalpy change for reaction ( $\Delta H^0_{\text{rxn.}}$ ):**
  - The amount of heat change when chemical reaction occurs at standard condition (*Compounds in their most stable form, at 25 °C and at 1 atm. pressure*) is called standard heat change or enthalpy change of that reaction.
- **Standard enthalpy change of formation ( $\Delta H^0_f$ ):**
  - The amount of heat released or absorbed when one mole of the compound in its standard state is formed from the elements at standard state. (*The **standard heat of formation of pure element** is considered **zero***).
- **Standard enthalpy change of combustion ( $\Delta H^0_{\text{comb}}$ ):**
  - The amount of heat evolved/absorbed when one mole of that substance is completely combusted in presence of excess oxygen.
- **Standard Enthalpy (heat change) of reaction from enthalpy of formation:**
  - For a reaction, **Reactants  $\rightarrow$  products**
  - $$\Delta H^0_{\text{rxn}} = \sum \Delta H^0_{\text{f(products)}} - \sum \Delta H^0_{\text{f(reactants)}}$$

# Hess' law of constant heat summation:

- It states that 'The total heat change (evolved or absorbed) at constant pressure for any chemical change is the same regardless of the path by which the change occurs'. i.e. **Total heat change for the direct reaction = sum of heat change in different steps of reactions.**

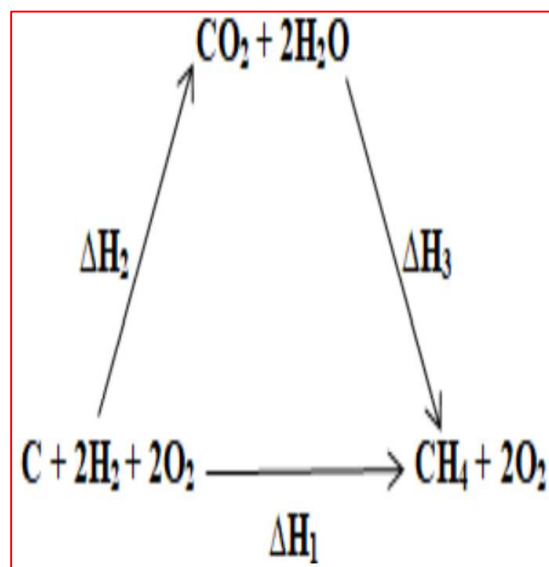
- For a reaction (*combustion of carbon*);

- $\Delta H_1 = \Delta H_2 + \Delta H_3$



- From Hess' law;**  
 $\Delta H_1 = \Delta H_2 + \Delta H_3$   
 $\therefore \Delta H_2 = \Delta H_1 - \Delta H_3 =$   
 $-94.05 \text{ kcal} - (-67.63 \text{ kcal})$   
 $= -26.42 \text{ kcal}$

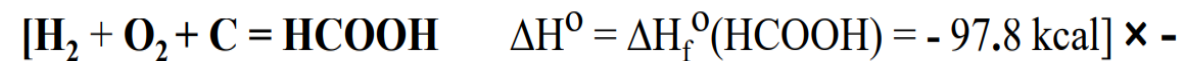
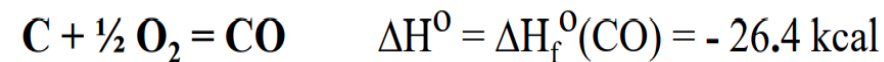
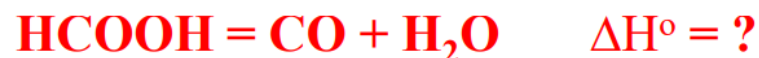
• Likewise, **Q.**



- From Hess' law;  $\Delta H_1 = \Delta H_2 + \Delta H_3 = -230.7 \text{ kcal} + 212.8 \text{ kcal} = -17.9 \text{ kcal}$
- $\Delta H_2 = \Delta H_f^\circ (\text{CO}_2) + 2 \times \Delta H_f^\circ (\text{H}_2\text{O}) = -94.1 \text{ kcal} + 2 \times (-68.3 \text{ kcal}) = -230.7 \text{ kcal}$
- $\Delta H_3 = -[\Delta H_{\text{comb}}^\circ (\text{CH}_4)] = -(-212.8 \text{ kcal}) = 212.8 \text{ kcal}$



• Next **Q.**

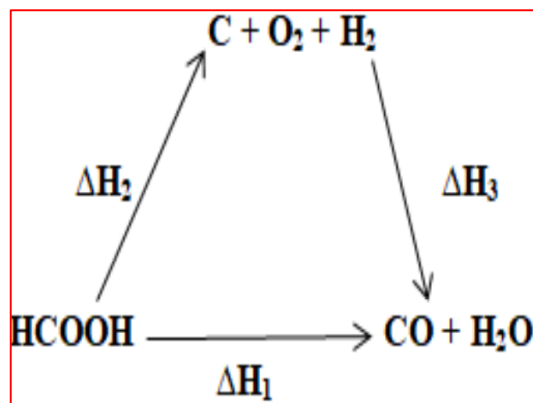


$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_{\text{f}}^\circ(\text{products}) - \sum \Delta H_{\text{f}}^\circ(\text{reactants})$$

$$\therefore \Delta H_{\text{rxn}}^\circ = \{\Delta H_{\text{f}}^\circ(\text{H}_2\text{O}) + \Delta H_{\text{f}}^\circ(\text{CO})\} - \Delta H_{\text{f}}^\circ(\text{HCOOH})$$

$$= \{-26.4 \text{ kcal} - 68.3 \text{ kcal}\} - (-97.8 \text{ kcal})$$

$$= +3.1 \text{ kcal}$$



- From Hess' law;  $\Delta H_1 = \Delta H_2 + \Delta H_3 = (+97.8 \text{ kcal}) + (-94.7 \text{ kcal}) = +3.1 \text{ kcal}$
- $\Delta H_2 = -\Delta H_{\text{f}}^\circ(\text{HCOOH}) = -(-97.8 \text{ kcal}) = +97.8 \text{ kcal}$
- $\Delta H_3 = \underline{\Delta H_{\text{f}}^\circ(\text{CO})} + \underline{\Delta H_{\text{f}}^\circ(\text{H}_2\text{O})} = -26.4 \text{ kcal} - 68.3 \text{ kcal} = -94.7 \text{ kcal}$

# Molar heat capacity

- The **amount of heat required to raise the temperature of one mole of substance through 1°C or 1K.**
  - **Heat is not a state function.** It depends on the path followed.
  - **Molar heat capacity at constant pressure ( $C_p$ ) and Molar heat capacity at constant volume ( $C_v$ )**
  - Thus,  $C_p = \frac{dq_p}{dT} = \frac{dH}{dT}$  .....(i) and  $C_v = \frac{dq_v}{dT} = \frac{dE}{dT}$  .....(ii)
  - Now, the **amount of heat required** for the change of temperature of **n mole** of substance from  **$T_1$  to  $T_2$**  from equation (i),
  - $dq_p = nC_p dT$  or  $\int_0^{q_p} dq_p = nC_p \int_{T_1}^{T_2} dT$  i.e.  $q_p = nC_p \Delta T$  (at constant  $C_p$ ).....(iii)
- Similarly, from equation (ii),
- $dq_v = nC_v dT$  or  $\int_0^{q_v} dq_v = nC_v \int_{T_1}^{T_2} dT$  i.e.  $q_v = nC_v \Delta T$  (at constant  $C_v$ ).....(iv)

# Relation between $C_p$ and $C_v$

- We have,  $H = E + PV$  .....(i)
- Differentiating it with respect to  $T$  on both sides, we get
- $\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(PV)}{dT}$  .....(ii)

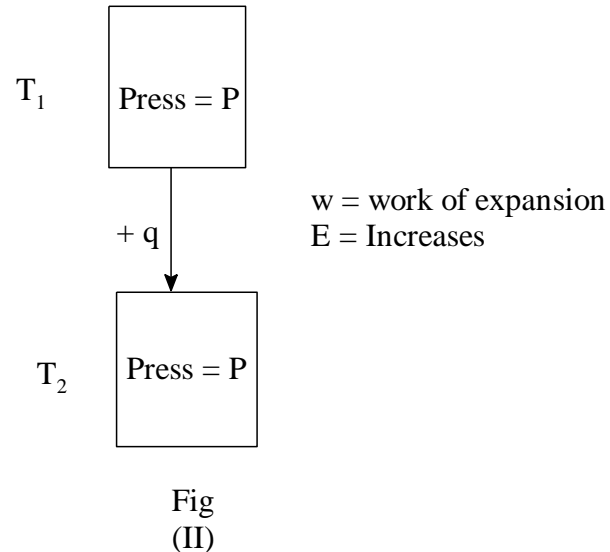
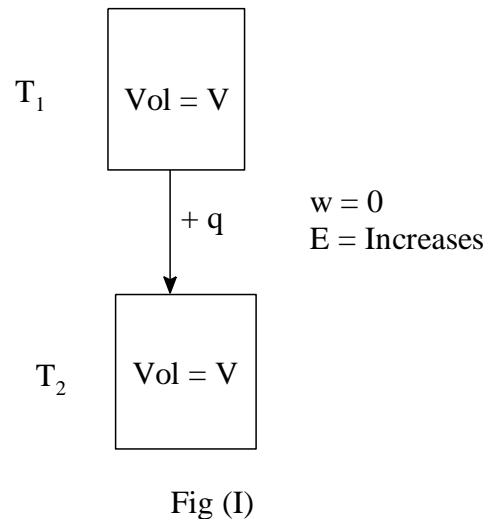
1). For one mole of gas,  $PV = RT$ ; then eqn. (ii) becomes

- $\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(RT)}{dT}$
- or  $C_p = C_v + R$  .....(iii)
- $C_p - C_v = R$  For gaseous reactions

2). For **solid** and **liquid** involving reactions,  $\frac{d(PV)}{dT}$  is generally small. So,  $C_p \cong C_v$

# Show that $C_p > C_v$

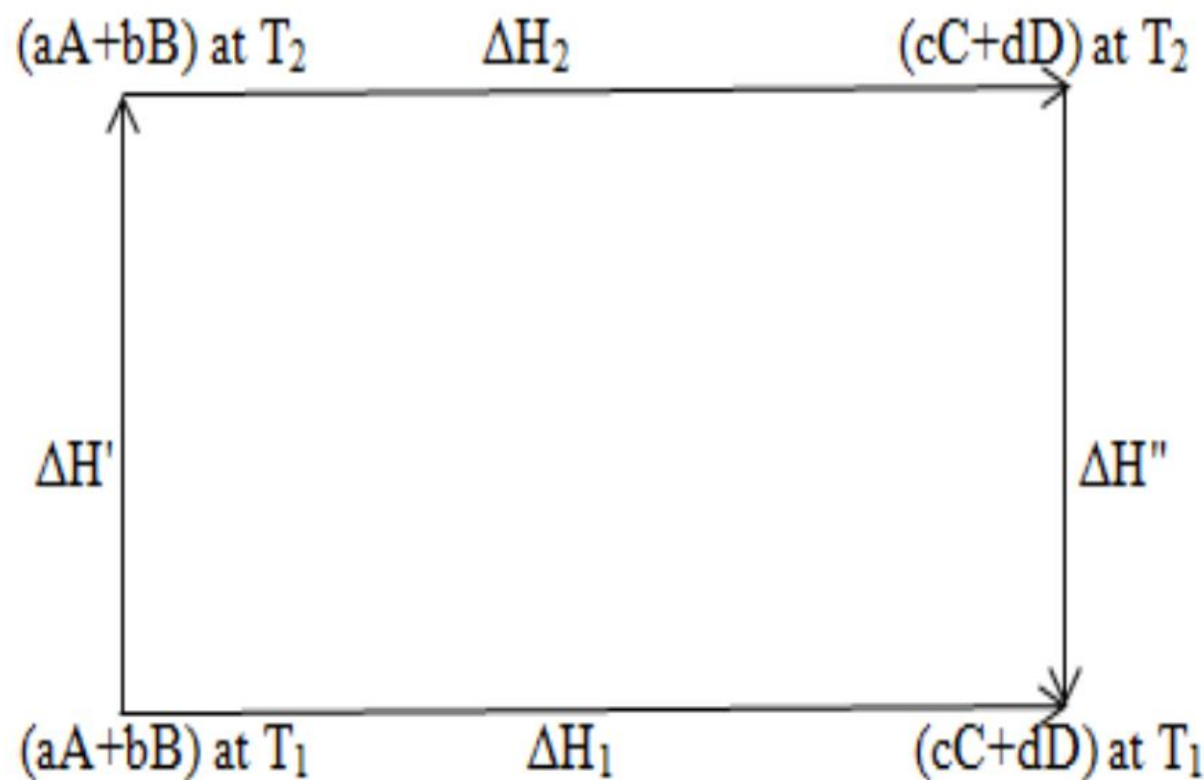
- If heat is supplied to the system at *constant volume*, it only increases the internal energy (Fig I).
- If  $q$  quantity of heat is applied at constant pressure, Internal energy increases as well as PV work will be happened (Fig II)



- At constant pressure  $P$ , temperature is raised from  $T_1$  to  $T_2$ . Which is the same for the process at constant volume, to raise temperature to  $T_2$  from  $T_1$ . In this case some **extra heat is required for doing work of expansion**. So  $C_p > C_v$ .

# Temperature dependence of $\Delta H$

- Consider a reaction,  **$a A + b B = c C + d D$**
- The **difference in enthalpy change ( $\Delta H_2 - \Delta H_1$ )** at two **different temperatures** can be calculated by applying Hess' law.



contd..

- **First path:**

Reactants at  $T_1$  are directly converted to products at  $T_1$ .

- **Second Path:**

Reactants at  $T_1$  are changed to  $T_2$  and they are reacted to give products at  $T_2$ .

Again, products at  $T_2$  are changed to  $T_1$ .

- From Hess' law:

$$\Delta H_1 = \Delta H' + \Delta H_2 + \Delta H''$$

$$\Delta H_2 - \Delta H_1 = -\Delta H'' - \Delta H' \quad \dots\dots\dots (i)$$

- We have,  $\Delta H = \int C_p dT$  , then

$$\Delta H' = \int_{T_1}^{T_2} C_{p(\text{reactants})} dT$$

$$\Delta H'' = \int_{T_2}^{T_1} C_{p(\text{products})} dT$$

Where,  $C_p (\text{reactants}) = \text{Total heat capacity of reactants} = a C_p(A) + b C_p(B)$

$C_p (\text{products}) = \text{Total heat capacity of products} = c C_p(C) + d C_p (D)$

contd..

From equation (i)

$$\Delta H_2 - \Delta H_1 = -\Delta H'' - \Delta H' = -\int_{T_2}^{T_1} C_{p(\text{products})} dT - \int_{T_1}^{T_2} C_{p(\text{reactants})} dT$$

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} C_{p(\text{products})} dT - \int_{T_1}^{T_2} C_{p(\text{reactants})} dT$$

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} (C_{p(\text{products})} - C_{p(\text{reactants})}) dT$$

$$\therefore \Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT = \Delta C_p (T_2 - T_1)$$

Where,  $\Delta C_p = C_p (\text{products}) - C_p (\text{reactants}) = c C_p (C) + d C_p (D) - a C_p (A) - b C_p (B)$

- The **difference of enthalpy change ( $\Delta H_2 - \Delta H_1$ )** at two different temperatures depends on the **difference of heat capacities of products and reactants**.

***Q. Find the  $\Delta H^\circ$  at 298K for the reaction,***



***$\Delta H^\circ_{298} = - 67,640 \text{kcal.}$***

***If  $C_p(CO) = 6.97$ ,***

***$C_p(O_2) = 7.05$ ,***

***$C_p(CO_2) = 8.96 \text{ cal/mol.deg}$***

# Spontaneous change and non-spontaneous change

## Non Spontaneous (Reversible) change

1. The process where state variables are changed by **an infinitesimal amount** and **can be reversed by reversing the external stress**
2. This process occurs in **infinite numbers of infinitesimally small steps**.
3. It is a **very slow process**.
4. It is **the imaginary process**., not possible in nature
5. System is always **virtually in equilibrium** with the surrounding (state functions of system and surrounding is same)
6. **All changes can be reversed by reversing the process.**
7. **Work done in reversible process is always less than in irreversible process** but **heat change will be always greater.**
8. Pressure and temperature changes are given by.

$$P_{\text{int}} = P_{\text{ext}} \pm dP_{\text{(very small)}}$$

$$T_{\text{int}} = T_{\text{ext}} \pm dT_{\text{(very small)}}$$

## Spontaneous (Irreversible) change

1. state variables get **changed by definite amount** and **differs from surrounding**.
2. This process occurs **in a single step**.
3. It is **very fast process**. Reactants and products are not at equilibrium in every steps.
4. **It is real.**
5. **Process cannot be reversed.**
6. Reverse as that of non spontaneous process. Occurs without the help of other support. **Gas at high pressure => gas at low pressure.**
7. **Work done in irreversible process is always greater than in reversible process** but **heat change will be always small.**
8. Pressure and temperature changes are.

$$P_{\text{int}} = P_{\text{ext}} \pm dP_{\text{(large)}}$$

$$T_{\text{int}} = T_{\text{ext}} \pm dT_{\text{(large)}}$$



# Work done in reversible process is always less than in spontaneous process:-

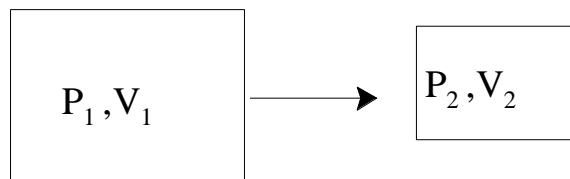
- Consider the reversible compression: For compression  $dV = \text{negative}$

$$W_{rev} = -\int_{V_1}^{V_2} P_{Ext} dV = -\int_{V_1}^{V_2} (P_{Int} + dP) dV = -\int_{V_1}^{V_2} P_{Int} dV$$

(Since  $P_{ex}$  and  $P_{int}$  differ by only an infinitesimal amount)

- For irreversible compression:  $W_{irrev} = -\int_{V_1}^{V_2} P_{Ext} dV$
- Comparison [ Here  $P_{ext} >> P_{int}$ , again note  $dV = \text{negative}$ , so both works are positive ]

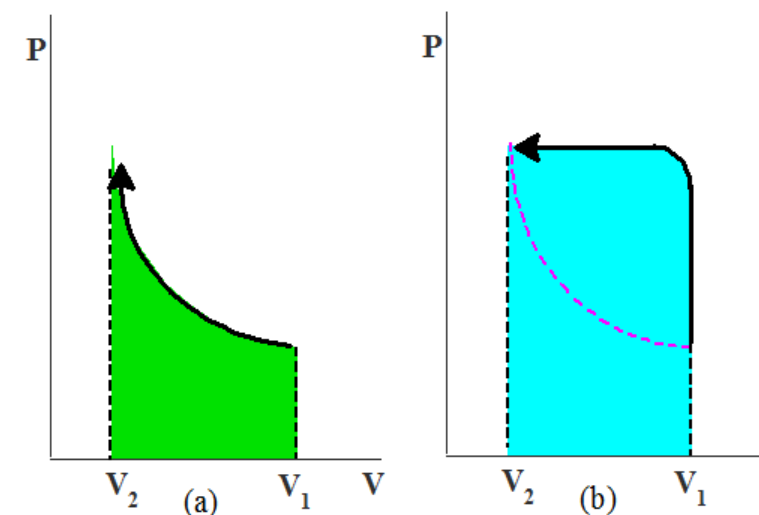
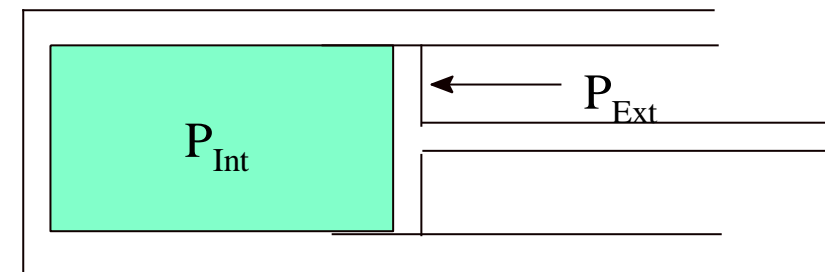
$$W_{irrev} = -\int_{V_1}^{V_2} P_{ex} dV > -\int_{V_1}^{V_2} P_{in} dV = W_{rev} \quad \text{i.e. } W_{rev} < W_{irrev}$$



Isothermal compression of gas

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

$$W_{irrev} = -\int_{V_1}^{V_2} P_{ex} dV = -P_2(V_2 - V_1)$$



The colored area is the work done in the isothermal compression of an ideal gas:  
**(a) Reversible path**  
**(b) Irreversible path**

- For Isothermal reversible compression of ideal gas,  $P_{ext} = P_{int}$  and  $P = nRT/V$
- For Isothermal irreversible compression of ideal gas, external pressure is suddenly increased from  $P_{ex} = P_1 = nRT/V_1$  to  $P_{ex} = P_2 = nRT/V_2$ . without an appreciable volume change i.e.  $V_1$  to  $V_2$  at constant external pressure,  $P_{ex} = P_2 = nRT/V_2$ .

contd....

- **Q. Work done in the Isothermal reversible and Irreversible expansion of a gas**

Consider isothermal expansion of the gas.

Here,  $dV = \text{positive}$  and  $P_{\text{int}} > P_{\text{ext}}$

Here work is **negative** so,  $w_{\text{rev}} < w_{\text{irrev}}$

- **Prove,  $q_{\text{irrev}} < q_{\text{rev}}$ :**

- From first law of thermodynamics

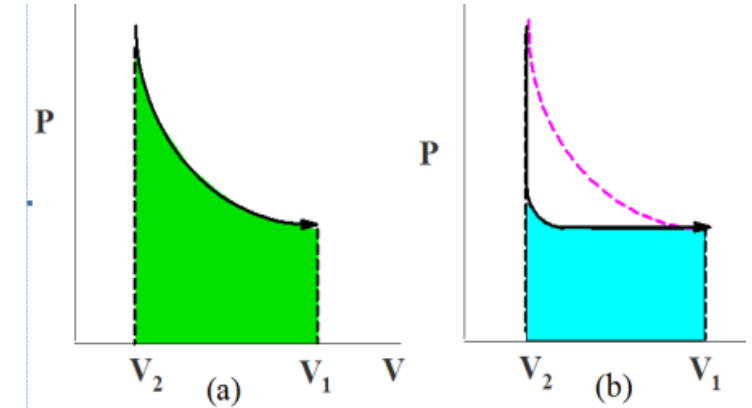
we have  $\Delta E = q + w$

- so,  $q_{\text{rev}} = \Delta E - w_{\text{rev}}$  and  $q_{\text{irrev}} = \Delta E - w_{\text{irrev}}$

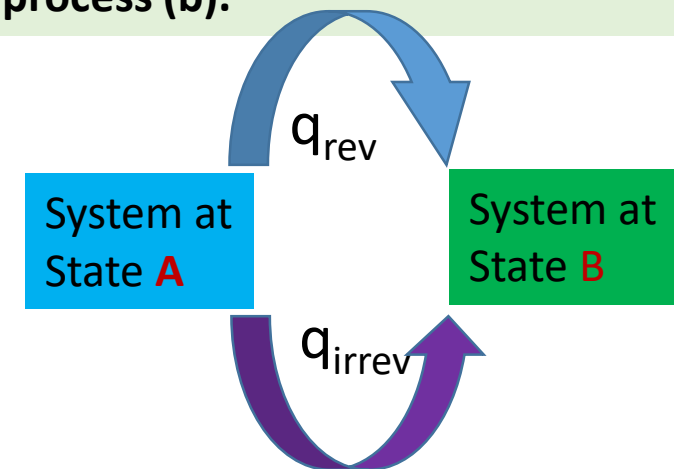
- Now, subtracting,  $q_{\text{rev}} - q_{\text{irrev}} = w_{\text{irrev}} - w_{\text{rev}} > 0,$

- Which proves that  $q_{\text{rev}} > q_{\text{irrev}}$ .

- *This also proves that **heat is not the state function***



Here work done is **more negative for reversible path (a)** than for irreversible process (b).



# Entropy and Second law of thermodynamics:

- **Entropy (S)** is also the **thermodynamic state function** which measures the **randomness or disorder ness of the system**, i.e. the extent to which atoms/ molecules/ions are distributed in a disordered state in a given volume.
- It is **the measure of degree of disorderness of the system**.  $S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$ .
- It is related to **the thermodynamic probability**.  $S = k \log W$  where,  $k$  is Boltzmann's constant, and  $W$  is the probability.
- **Increasing the entropy increases the no of probable arrangement** i.e. the **randomness**. (system with more probability has high randomness)
- **The change in entropy is defined as:** 
$$\Delta S = \int_1^2 \frac{dq_{\text{rev}}}{T} = \frac{q_{\text{rev}}}{T}$$

**Second Law of Thermodynamics:** States that: *The entropy of the universe in reversible process remains the same but increases in the irreversible process.*  
or, *The energy of the universe remains the constant but the available energy is decreasing.*

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} = 0; \text{ For reversible process}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}} > 0; \text{ For irreversible process}$$

# Entropy change in terms of change in volume

- Entropy change in terms of change in volume when a process carried at constant temperature:
- From kinetic theory of gas,  $E_{\text{trans}} = 3/2 RT$  (R is gas constant).
- If **temperature remains constant**, **translational energy and total internal energy of ideal gas are constant**.
- If internal energy E is due to the translational energy then  $E = E_{\text{trans}}$ .
- **For isothermal expansion of gas then**  
 $\Delta E = 0$ . also,  $\Delta E = q + w$ , thus,  **$q = -w$**
- That is,  **$q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \frac{V_2}{V_1}$**
- Now,  $\Delta S = \frac{q_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1}$  i.e.  **$\Delta S = nR \ln \frac{V_2}{V_1}$**
- Here, if  $V_2 > V_1$ , the *gas has expanded*, and **its entropy will be increased**.
- If  $V_2 < V_1$ , *there is compression of gas*, and a **decrease in entropy of gas will occur**.

**Isothermally a reversible expansion and irreversible expansion of gas could be feasible process but the irreversible compression could not be feasible.**

- In reversible expansion:

$$\Delta S_{gas} = \frac{q_{rev}}{T}, \quad \Delta S_{surr} = -\frac{q_{rev}}{T}$$
$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0 \quad \text{[justified for II Law of TD]}$$

- In irreversible isothermal expansion (a) let us consider expansion occurs from  $V_1$  to  $V_2$ ):

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

**(b) Again consider that expansion occurs at zero external force, at constant temperature.**

First law then used to calculate  $q = \Delta E - w = 0$  (both,  $w$  and  $\Delta E$  are zero for the given condition).

If no heat is lost/gain by surrounding, then entropy change of the surrounding is zero.

$$\Delta S_{univ} = \Delta S_{syst} + \Delta S_{surr} = nR \ln \frac{V_2}{V_1} - 0 = nR \ln \frac{V_2}{V_1} > 0 \quad \text{[justified for II Law of TD]}$$

- Q. In irreversible isothermal, compression let us consider compression from  $V_1$  to  $V_s$ :

- $\Delta S_{gas} = nR \ln \frac{V_s}{V_1}$
- If compression occurs with no outside influence, surely,  $\Delta S_{surr} = 0$
- $\Delta S_{univ} = nR \ln \frac{V_s}{V_1} - 0 = nR \ln \frac{V_s}{V_1} < 0$ . [is not justified for II Law of TD]

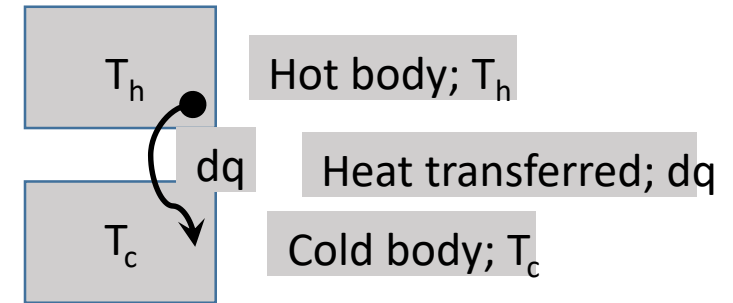
**This tells us that the isothermal irreversible compression of gas is not a feasible process.**

# Criterion of spontaneity in term of entropy change

- When two blocks of different temperature ( $T_c$  and  $T_h$ ) come together then, **does this spontaneous heat flow produce an increase in entropy?**

## I. If the cold body absorbs heat reversibly from hot body:

- Total entropy change,  $dS = dS_c + dS_h = \frac{dq}{T_c} - \frac{dq}{T_h} = > 0$
- Since,  $T_h > T_c$ , total entropy change is greater than zero as the second law requires. i.e. **obeys second law**



## II. If heat is passed from cold block to hot one, then entropy change will be

$$dS = dS_c + dS_h = -\frac{dq}{T_c} + \frac{dq}{T_h} = < 0$$

- The flow of heat from a cold to a hot body violates II law of TD, So the process is not feasible.

# Temperature dependence of entropy

- Calculation of entropy change which accompanies a finite temperature change.
- Then, the entropy change may be expressed by;  $\Delta S = \int \frac{dq_{rev}}{T}$  .....(i)
- Then, the process takes place depending at constant pressure or at constant volume. We can replace  $dq_{rev}$  by
- $dq_{rev} = nC_p dT$  (at constant pressure) and  $dq_{rev} = nC_v dT$  (at constant volume)
- Now,  $\therefore \Delta S = \int_{T_1}^{T_2} \frac{nC_p dT}{T}$  .....(ii)       $\Delta S = \int_{T_1}^{T_2} \frac{nC_v dT}{T}$  .....(iii)
- For very small change in temperature (small temperature interval),  $C_p$  and  $C_v$  will be constant.
- Finally, we obtain the following relations;  
 $\therefore \Delta S = nC_p \ln \frac{T_2}{T_1}$  .....(iv) and       $\Delta S = nC_v \ln \frac{T_2}{T_1}$  .....(v)

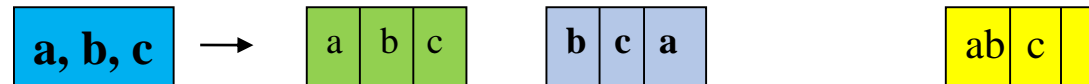
# Molecular interpretation of entropy:

- A system can be explained either in terms of **(a) Macroscopic properties and (b) Microscopic properties:**

**(a) Macroscopic properties :** Bulk properties like **V, T, P** etc. If the system has **different macroscopic properties it will be in different state**. These states are termed as **macro states**.

**(b) Microscopic properties:** Properties of the system including properties of individual **molecules or unit (i.e. position and velocity of atom or molecule)**. A **system in the same macro states can have different microscopic properties**. The **different states** depending on these microscopic properties are called **microstates**.

- For example, if we take system containing elements a, b, c and arrange them in different order as in figure,



**Single macro state** **Different microstates**

*Fig: if macroscopic properties only depends on the elements then it can have different microstates*

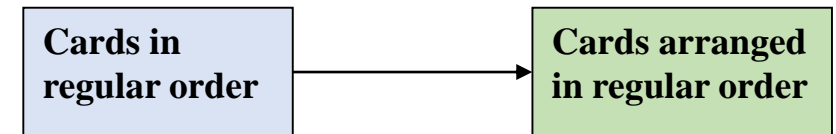


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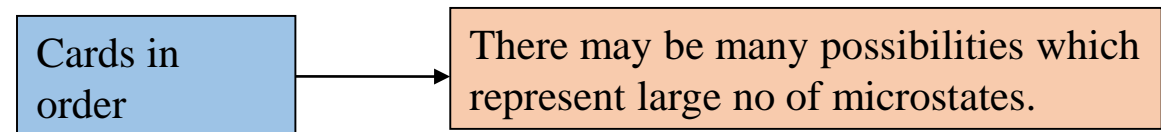
- We say, for the system in the **same macro state** (i.e. in **equilibrium w.r.t macroscopic properties**) can have **large number of microstates** (i.e. *system is not in equilibrium w.r.t. microscopic properties, microscopic properties are varying with time*)
- In this version, **Entropy is the measure of number of microstates associated with particular macro state.**

For example, if we consider macrostates as **a deck of cards, then**

**(a) A deck of cards can be arranged in a regular pattern**

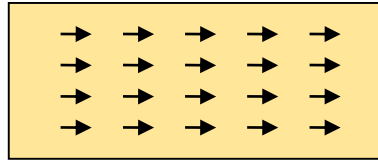


**(b) if cards are arranged in different pattern,**

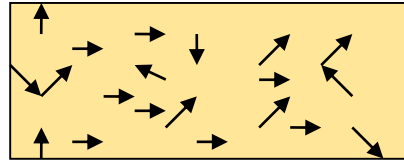


- If we **shuffled the cards in a deck**, their **disorder ness increases**. This shows that system has more probability to exist in disorder state (i.e. in the macrostate with large number of microstates) than in the ordered state. That is **entropy increases the molecular chaos of the system.**

- **Disordered System:-** The system with relatively small amount of information's about its microscopic properties is called **disordered system**.



Highly ordered  
(less existence)



More disordered  
(high probability of existence)

- Entropy Change ( $\Delta S$ ) associated with Phase Change

(connection between entropy and molecular chaos)

*(1) If solid is melted reversibly at constant pressure, it absorbs the heat equal to enthalpy of fusion( $\Delta H_f$ ), then entropy change up on fusion at constant temperature is given by:*

$$\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_f}{T_f} > 0 \dots\dots\dots (i)$$

Where,  $\Delta H_f$  = enthalpy change in fusion = heat absorbed (at constant pressure),  $T_f$  = fusion temperature.

*(2) if liquid is vaporized at constant temperature, it absorbs heat so the randomness of molecules further increases i.e. entropy of the system also increases. The entropy change up on vaporization is:*

$$\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{vap}}{T_{vap}} > 0 \dots\dots\dots (ii)$$

Where,  $\Delta H_{vap}$  = enthalpy change in boiling = heat absorbed (at constant pressure),  $T_f$  = boiling temperature.

# Third law of thermodynamics:

- *It states that the entropy of the perfect crystal of all pure element or compounds is zero at the absolute zero of temperature .*
- In perfect crystal (no crystal defect) the molecules are highly ordered and which has **only one microstate** so has **zero entropy**. But if there are certain defects then that crystal can have many possible molecular arrangements.
- if temperature is increased molecules start to vibrate and number of microstates increases increasing the entropy. So in these conditions solid crystal has positive entropy.

## Application of Third law of thermodynamics (to calculate absolute entropy)

- **To calculate absolute entropy of solid at temperature T:**
- Consider a system of solid at higher temperature T. If  $S_0$  and  $S_T$  represents the entropy of that pure solid at temperature 0K and T K respectively then, we have,

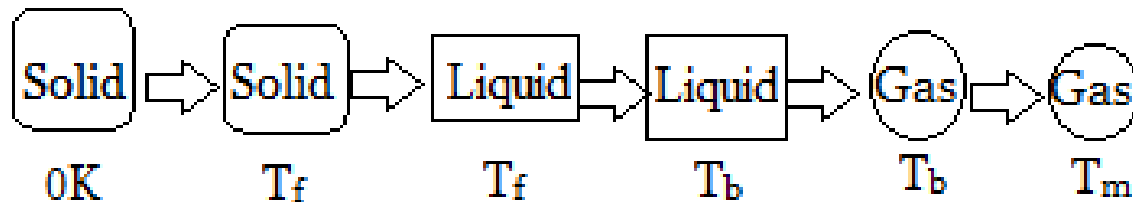
$$S_T - S_0 = \int_0^T \frac{C_P dT}{T} \quad \therefore S_T^0 = \int_0^T \frac{C_P dT}{T} \quad \text{Since, } S_0 = 0, \text{ according to the third Law of thermodynamics}$$

contd...

- **To calculate absolute entropy of liquid at temperature T:**

$$S_T^0 = \int_0^{T_f} \frac{C_P dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^T \frac{C'_P dT}{T}$$

- **To calculate absolute entropy of gas at temperature T:**
- If we consider the system of one mole of pure gas then, we can calculate its absolute entropy from entropy at zero °K( $S_0$ ). The steps are,



- Where  $C_p$ ,  $C_p'$ ,  $C_p''$  represents the molar specific heat capacities of solid, liquid and gas respectively.

$$S_T^0 = \int_0^{T_f} \frac{C_P dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_{vap}} \frac{C'_P dT}{T} + \frac{\Delta H_{vap}}{T_{vap}} + \int_{T_{vap}}^T \frac{C''_P dT}{T}$$

contd...

- **Standard Entropy change of reaction ( $\Delta S^\circ_{\text{rxn}}$ ):** Similar to the enthalpy, standard entropy change of reaction  $aA + bB = cC + dD$  is,
- $\Delta S^\circ_{\text{rxn}} = \{cS^\circ(C) + dS^\circ(D)\} - \{aS^\circ(A) + bS^\circ(B)\}$
- $\Delta S^\circ_{\text{rxn}} = \sum nS^\circ_{\text{products}} - \sum mS^\circ_{\text{reactants}}$ . Where  $S^\circ$  = standard absolute entropy substances
- *Q, calculate entropy change in  $H_{2(g)} + Cl_{2(g)} = 2HCl_{(g)}$ .  $S^\circ$  for  $H_{2(g)} = 131.0$ ,  $Cl_{2(g)} = 223.0$  and  $HCl_{(g)} = 187.0 \text{ J/Kcal}$ .  
Ans **20J/K***
- *Q, Calculate the standard entropy change (in J/K) for the reaction,  
 $2NaHCO_{3(s)} = Na_2CO_{3(s)} + CO_{2(g)} + H_2O_{(g)}$  [ $S^\circ NaHCO_3 = 155$ ,  $S^\circ Na_2CO_3 = 136$ ,  $S^\circ H_2O_{(g)} = 188.7$  and  $S^\circ CO_{2(g)} = 213.6 \text{ J/Kmol}$ ]*

#### Unit of entropy:-

SI unit is represented by EU:  $\text{J K}^{-1}\text{mol}^{-1}$

CGS unit by eu:  $\text{cal K}^{-1}\text{mol}^{-1}$

1eu=4.8EU. Entropy unit is the amount of heat absorbed per Kelvin temperature for one mole of substance.

# Free Energy (Gibbs Free Energy)

- It is a new thermodynamic state function:  $G = H - TS$  .....(i)

## Criterion of spontaneity in terms of Gibbs Free Energy (G)

- Taking the differential of equation (i), we get

$$dG = dH - d(TS) \text{ or, } dG = dH - TdS - SdT \text{ .....(ii)}$$

- At constant **P and T**;  $dT = 0$ ,  $dH = dq$ . Then the eqn. (ii) becomes,

$$dG = dq - TdS \text{ .....(iii)}$$

$$dG = dq - dq_{rev} \text{ .....(iv) (Because, } TdS = dq_{rev} \text{ )}$$

- In reversible process,  $dq = dq_{rev}$  So,  $dG = 0$  .....(v)
- In irreversible process:-  $q < q_{rev}$  i.e.  $dq < dq_{rev}$  So,  $dG < 0$  .....(vi)
- For **finite changes**;

$$\Delta G = 0 \text{ (for reversible process) .....(vii)}$$

$$\Delta G < 0 \text{ (for irreversible process) .....(viii)}$$

**Note:**  $\Delta S$  can also predict the condition of spontaneity and reversibility, for that we have to calculate the  $\Delta S_{\text{univ}}$ . But only the measuring of  $\Delta G_{\text{syst}}$  can predict the spontaneity of reaction. where  $\Delta G = 0$  reversible,  $\Delta G < 0$  spontaneity to wards the forward direction, and  $\Delta G > 0$  spontaneity to wards the back ward direction.

Q. If heat of vaporization of water is 9710 cal, and the entropy change is 26 eu (consider 1 mole  $\text{H}_2\text{O}$ ), Calculate the temperature at which (a) Liquid and vapour will be at equilibrium (b) Evaporation is spontaneous (c) Evaporation is not possible at 1 atm pressure???

□ The free energy change is given by;  $\Delta G = \Delta H - T\Delta S$

- For the process at constant temperature,  $\text{H}_2\text{O(l)} = \text{H}_2\text{O(g)}$  (P = 1 atm)
- Then we have,  $\Delta G = 9710 - T26$  ( $\Delta H = 9710\text{cal}$  &  $\Delta S = 26 \text{ eu}$ )
- For, liquid and vapor equilibrium,  $\Delta G = 0$ . Then,  $0 = 9710 - T26$  or, **T = 373K**
- For the spontaneity of evaporation of water to the vapor at 1 atm,  $\Delta G < 0$ .
- Then,  $T > \frac{9710}{26}$  (or 373.46) > 373K i.e. formation of water vapor at 1 atm is spontaneous at the temperature greater than 100°C (373K).
- Now,  $T < 373 \text{ K}$ ,  $\Delta G = +\text{ve}$ , evaporation of water is not spontaneous but reverse is feasible. i.e. condensation of a supersaturated vapor is feasible.

# Free Energy and Equilibrium constant

- **Standard free energy change( $\Delta G^\circ$ ):**

- It is defined as the free energy change that accompanies the conversion of reactants in their standard states to the products in their standard states.

- **Standard free energy change of formation ( $\Delta G^\circ_f$ ):**

- The free energy change that occurs when one mole of a compound in its standard state is formed from its elements in their standard states.

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

- The standard free energy of formation of all pure elements is taken to be zero.

- **Standard free energy change for the reaction ( $\Delta G^\circ_{\text{rxn}}$ .)**

- If we take the general reaction,  $aA + bB = cC + dD$  then,

$$\begin{aligned}\Delta G^\circ_{\text{rxn}} &= \sum \Delta G^\circ_f (\text{products}) - \sum \Delta G^\circ_f (\text{reactants}) \\ &= c \Delta G^\circ_f (C) + d \Delta G^\circ_f (D) - a \Delta G^\circ_f (A) - b \Delta G^\circ_f (B).\end{aligned}$$

At equilibrium  $\Delta G^\circ_{\text{rxn}} = 0$



# Expression of Free Energy in terms of Pressure and its relation with Equilibrium constant

- Starting from the definition:  $G = H - TS$ .....(i)

$$G = E + PV - TS$$

- Now, the change:  $dG = dE + PdV + VdP - TdS - SdT$
- $dG = dq - PdV + PdV + VdP - TdS - SdT$  [w (pressure-volume) =  $-PdV$ ]
- $dG = \cancel{dq} - \cancel{PdV} + \cancel{PdV} + VdP - \cancel{TdS} - \cancel{SdT}$  (if  $dq = TdS$ , and  $T = \text{constant}$ )
- For the pressure change at constant 'T', we obtain

$$dG = VdP \text{ .....(ii)}$$

- For one mole gas,**  $dG = \frac{RT}{P} dP$  .....(iii)
- Integrating between  $\bar{G}^0$  to  $G$  and  $P^0(1 \text{ atm})$  to  $P$

$$\int_{G^0}^G dG = \int_{P^0}^P RT \frac{1}{P} dP$$

$$\text{Or, } \bar{G} - \bar{G}^0 = RT \ln \frac{P}{P_0} = RT \ln P$$

contd..

- or,  $G - \bar{G}^0 = RT \ln P$  .....(iv)
- Similar expression for **n mole** of gas,  $nG = n\bar{G}^0 + nRT \ln P$  .....(v)
- Now we use the reaction,  $aA + bB = cC + dD$ , and calculate  $\Delta G$  as:

$$\begin{aligned}\Delta G &= \sum G_{(\text{products})} - \sum G_{(\text{reactants})} = cG(C) + dG(D) - aG(A) - bG(B) \\ &= cG^0(C) + dG^0(D) - aG^0(A) - bG^0(B) + cRT \ln P_C + dRT \ln P_D - aRT \ln P_A - bRT \ln P_B\end{aligned}$$

- $\Delta G = \Delta G^0 + RT \ln \left[ \frac{(P_C)^c \times (P_D)^d}{(P_A)^a \times (P_B)^b} \right]$  or  $\Delta G = \Delta G^0 + RT \ln Q$
- At equilibrium condition,  $Q = K$  and  $\Delta G = 0$ ; So,  $\Delta G^0 = -RT \ln K$  .....(vi)
- The equation (vi) can be written as;

$$K = e^{-\Delta G^0/RT} = 10^{-\Delta G^0/2.3RT} \text{ .....(vii)}$$

- **The meaning of sign of  $\Delta G^0$**  : (i) If  $\Delta G^0 < 0$ , *the exponent* will be +ve,  $K > 1$  (*unity*) and will increase as  $\Delta G^0$  becomes more –ve. i.e. reaction proceeds to completion greatly with the largest –ve value of  $\Delta G^0$ .

contd..

- (ii) If  $\Delta G^0 > 0$ , the exponent will be -ve,  $K < 1$  (unity) and some product will be present at equilibrium, most materials will be in the form of reactants. (iii) A rare case in which  $\Delta G^0 = 0$  corresponds to an equilibrium constant of unity.
- The equation(vii) can be written as

$$K = e^{\Delta S^0/R} \times e^{-\Delta H^0/RT} = 10^{\Delta S^0/2.3R} \times 10^{-\Delta H^0/2.3RT} \dots\dots\dots(viii)$$

if we use the relation as  $\Delta G^0 = \Delta H^0 - T\Delta S^0$

- The equation shows that the larger  $\Delta S^0$  is, larger the K is. Thus the tendency toward maximum molecular chaos influences the magnitude of eqm. constant.
- Also, more negative  $\Delta H^0$  is, the larger K is. So, tendency of atoms to seek the state of lowest energy helps determine the eqm. Constant.

### Temperature dependence of equilibrium:

- $\Delta G^0 = -RT \ln K$
- $\Delta G^0 = \Delta H^0 - T\Delta S^0$

## Temperature dependence of equilibrium:

$$\Delta G^0 = -RT \ln K$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

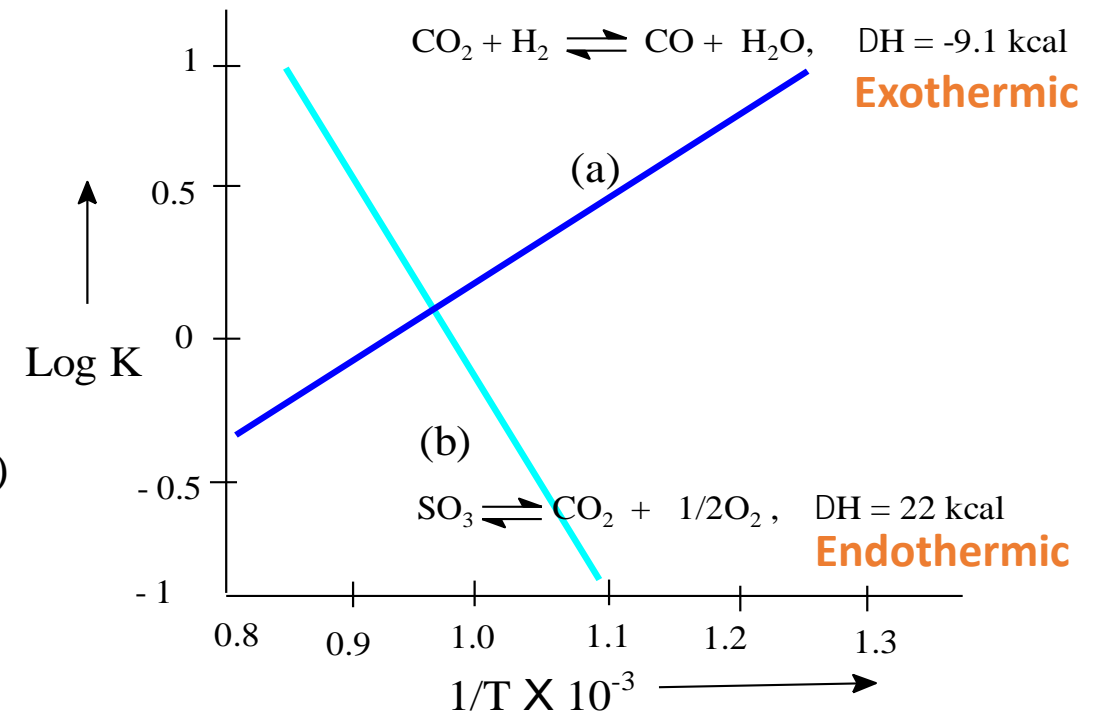
- $\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$
- If  $\Delta H^0$  and  $\Delta S^0$  are independent of temperature, then **lnK** is the linear function of **1/T**.
- In this curve, *slope* = -  $\Delta H^0/R$  and *intercept* =  $\Delta S^0/R$
- If the **reactions** are carried at two different temperatures **T<sub>1</sub>** and **T<sub>2</sub>** then,

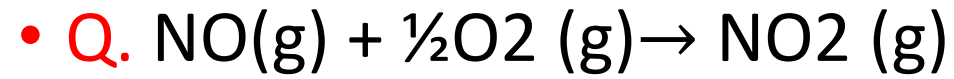
$$\ln K_1 = -\frac{\Delta H^0}{RT_1} + \frac{\Delta S^0}{R} \quad \text{and} \quad \ln K_2 = -\frac{\Delta H^0}{RT_2} + \frac{\Delta S^0}{R}$$

Combining these gives (subtracting the 1<sup>st</sup> eqn. from 2<sup>nd</sup> one)

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H^0}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Thus knowing the value of  $\Delta H^0$  and equilibrium constant at one temperature we can calculate the equilibrium constant at other temperature.





$$\Delta G^0 = -8.33 \text{ kcal and } \Delta H^0 = -13.5 \text{ kcal}$$

- Calculate eqm. Constant at  $298^0 \text{ K}$  and  $598^0 \text{ K}$

# Potential of electrochemical Cell, The Nernst equation:-

- Here we have to establish a relation between  $\Delta G^0$  and  $\Delta \epsilon^0$ . For this we need a connection between electrical work and Gibbs free energy.

We have  $G = H - TS$ . If we expand this equation for small change in free energy, as.

$$dG = dE + PdV + VdP - TdS - SdT \quad (H = E + PV)$$

$$= dq + dw + PdV + VdP - TdS - SdT \quad (dE = dq + dw)$$

$$dG = \cancel{TdS} + dw + PdV + V\cancel{dP} - \cancel{TdS} - \cancel{SdT} \quad (dq = TdS)$$

At constant temperature and pressure,  $dG = dw + PdV$

Where,  $dw$  = all the work done like electrical, PV work etc. =  $dw_{elec} + dw_{pv}$  thus,

$$dG = dw_{elec} - \cancel{PdV} + \cancel{PdV} \dots\dots(i) \text{ for finite change we can write, } \Delta G = w_{elec}$$

- This is the physical meaning of Gibbs free energy change: That is change in Gibbs free energy at constant temperature and pressure represents the other work done by the system except the pressure volume work.
- Now, Electrical work = charge  $\times$  potential =  $q \times \Delta \epsilon$  ( $\Delta \epsilon$  = potential change)

contd..

- Electrical work due to flow of n moles of electrons,

$$W_{\text{elec}} = -nF\Delta\varepsilon \dots\dots\dots \text{(ii)}, F = 96500\text{C and for galvanic cell, } \textbf{work is negative}.$$

- Thus  $\Delta G = -nF\Delta\varepsilon \dots\dots\dots \text{(iii)},$

- And at standard condition,  $\Delta G^\circ = -nF\Delta\varepsilon^\circ \dots\dots\dots \text{(iv)}$

- Also we have,  $\Delta G = \Delta G^\circ + RT\ln Q \dots\dots\dots \text{(v)}$

- So comparing (iii), (iv) and (v) we get,

- $\Delta\varepsilon = \Delta\varepsilon^\circ - RT/nF \ln Q = \Delta\varepsilon^\circ - RT/nF 2.303\log Q \dots\dots\dots \text{(5)}$

- = 8.312J/mol.K, [R = 8.312J/mol.K, T = 298K, F = 96500Coul (J/V)]

$$\Delta E = \Delta E^\circ - \frac{0.059}{n} \log Q$$

# Problems

- **Q.** Calculate the enthalpy of formation of  $\text{Ca(OH)}_2(\text{s})$  from the following data.  
 $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}), \Delta H = -68.3 \text{ kcal}$ ;  $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca(OH)}_2(\text{s}), \Delta H = -15.3 \text{ kcal}$ ;  $\text{Ca}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s}), \Delta H = -151.8 \text{ kcal}$ .

Solution:

$$\begin{array}{l} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}), \Delta H_1 = -68.3 \text{ kcal} \\ \text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca(OH)}_2(\text{s}), \Delta H_2 = -15.3 \text{ kcal} \\ \text{Ca}(\text{s}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{CaO}(\text{s}), \Delta H_3 = -151.8 \text{ kcal.} \\ \hline \text{Ca}(\text{s}) + \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{Ca(OH)}_2(\text{s}) \end{array}$$

- From Hess law, total enthalpy of reaction can be written as:  
$$\Delta H_{\text{Reaction}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$
$$= -68.3 - 15.3 - 151.8 \text{ kcal} = -235.4 \text{ kcal. (enthalpy of formation of Ca(OH)}_2\text{)}$$



- **Q.** Calculate  $\Delta G^0$  and  $K$  at  $25^\circ \text{C}$  for the reaction  $\text{NO(g)} + \frac{1}{2}\text{O}_2 \text{(g)} \rightarrow \text{NO}_2 \text{(g)}$  from data tabulated in this chapter. Which factor, enthalpy or entropy, makes  $K$  greater than unity and thereby provides the principle driving forces for the reaction?
- Solution
- $\Delta H^0 = \sum \Delta H_f^\circ (\text{P}) - \sum \Delta H_f^\circ (\text{R}) = 8.09 - 21.6 = -13.51 \text{ kcal}$
- $\Delta G^0 = \sum \Delta G_f^\circ (\text{P}) - \sum \Delta G_f^\circ (\text{R}) = 12.39 - 20.72 - 0 = -8.33 \text{ kcal}$
- $\Delta S^0 = \sum S^\circ (\text{P}) - \sum S^\circ (\text{R}) = 57.5 - (50.3 + \frac{1}{2} \times 49.0) = -17.3 \text{ eu}$  [eu = energy unit]
- $\Delta G^0 = \Delta H_{\text{reaction}} - T \Delta S_{\text{reaction}} = -13510 + 298 \times 17.3 = -13510 + 5155.4 = -8354.6 = -8.355 \text{ kCa}$
- **Now,**  $\Delta G^0 = -RT \ln K$  or  $K = e^{-\Delta G^0/RT}$