

**Important Terms and Definitions**

**System:** Refers to the portion of universe which is under observation.

**Surroundings:** Everything else in the universe except system is called surroundings. The Universe = The System + The Surroundings.

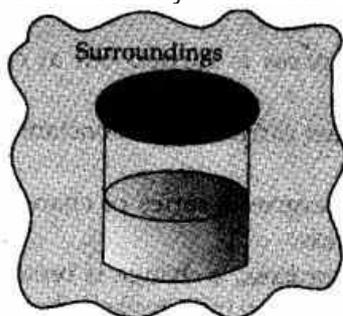


Fig. 6.1 System and the surroundings

**Open System:** In a system, when there is exchange of energy and matter taking place with the surroundings, then it is called an open system.

For Example: Presence of reactants in an open beaker is an example of an open system.

**Closed System:** A system is said to be a closed system when there is no exchange of matter ' but exchange of energy is possible.

For example: The presence of reactants in a closed vessel made of conducting material.

**Isolated System:** In a system, when no exchange of energy or matter takes place with the surroundings, is called isolated system.

For example: The presence of reactants in a thermoflask, or substance in an insulated closed vessel is an example of isolated system.

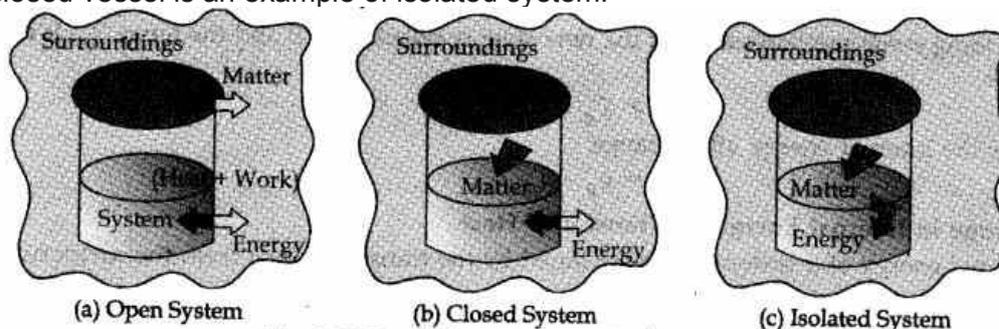


Fig. 6.2 Open, closed and isolated system.

**The state of the system:** The state of a thermodynamic system means its macroscopic or bulk properties which can be described by state variables:

Pressure (P), volume (V), temperature (T) and amount (n) etc.

They are also known as state functions.

**Isothermal process:** When the operation is carried out at constant temperature, the process is said to be isothermal. For isothermal process,  $dT = 0$  Where  $dT$  is the change in temperature.

**Adiabatic process:** It is a process in which no transfer of heat between system and surroundings, takes place.

**Isobaric process:** When the process is carried out at constant pressure, it is said to be isobaric. i.e.  $dP = 0$

**Isochoric process:** A process when carried out at constant volume, it is known as isochoric in nature.

**Cyclic process:** If a system undergoes a series of changes and finally returns to its initial state, it is said to be cyclic process.

**Reversible Process:** When in a process, a change is brought in such a way that the process could, at any moment, be reversed by an infinitesimal change. The change is called reversible.

• **Internal Energy**

It is the sum of all the forms of energies that a system can possess.

In thermodynamics, it is denoted by  $U$  which may change, when

- Heat passes into or out of the system
- Work is done on or by the system
- Matter enters or leaves the system.

**Change in Internal Energy by Doing Work**

Let us bring the change in the internal energy by doing work.

Let the initial state of the system is state A and Temp.  $T_A$  Internal energy =  $u_A$

On doing some mechanical work the new state is called state B and the temp.  $T_B$ . It is found to be

$$T_B > T_A$$

$u_B$  is the internal energy after change.

$$\therefore \Delta u = u_B - u_A$$

**Change in Internal Energy by Transfer of Heat**

Internal energy of a system can be changed by the transfer of heat from the surroundings to the system without doing work.

$$\Delta u = q$$

Where  $q$  is the heat absorbed by the system. It can be measured in terms of temperature difference.

$q$  is +ve when heat is transferred from the surroundings to the system.  $q$  is -ve when heat is transferred from system to surroundings.

When change of state is done both by doing work and transfer of heat.

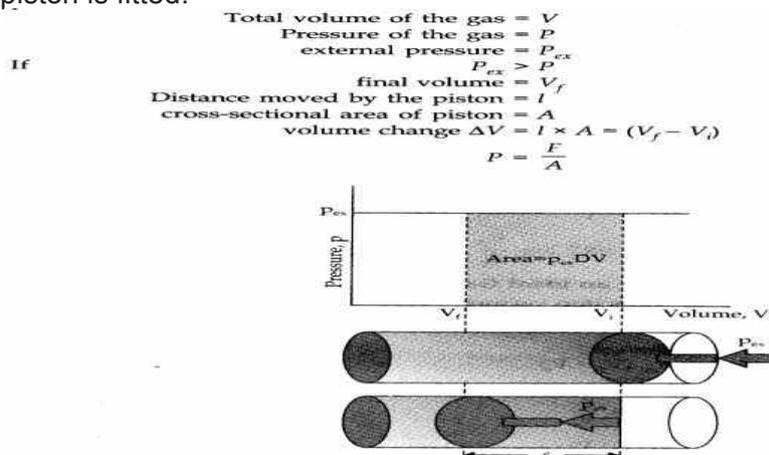
$$\Delta u = q + w$$

First law of thermodynamics (Law of Conservation of Energy). It states that, energy can neither be created nor be destroyed. The energy of an isolated system is constant.

$$\Delta u = q + w.$$

• **Work (Pressure-volume Work)**

Let us consider a cylinder which contains one mole of an ideal gas in which a frictionless piston is fitted.



**Fig. 6.3** Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure,  $P_{ex}$  (in single step) is equal to the shaded area.

$$\begin{aligned}
 F &= P \times A \\
 W &= F \times d. \text{ (force} \times \text{distance)} \\
 &= P_{ex} \times A \times l = P_{ex} (-\Delta V) \\
 W &= -P \Delta V
 \end{aligned}$$

-ve sign is used for work done by the system in case of expansion in volume by conversions.  
 If in a system volume expands from  $V_1$  to  $V_2$

$$W = -\int_{V_1}^{V_2} P_{ex} dV$$

• **Work Done in Isothermal and Reversible Expansion of Ideal Gas**

$$W_{rev.} = -\int_{V_i}^{V_f} P_{ex} dV = -\int_{V_i}^{V_f} (P_{in} \pm dP) dV$$

Since  $dP \times dV$  is very small we can write,

$$W_{rev.} = -\int_{V_i}^{V_f} P_{in} dV$$

For ideal gas

$$PV = nRT$$

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

Therefore, at constant temperature,

$$\begin{aligned}
 W_{rev.} &= -\int_{V_i}^{V_f} nRT \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \\
 &= -2.303 nRT \log \frac{V_f}{V_i}
 \end{aligned}$$

• **Isothermal and Free Expansion of an Ideal Gas**

For isothermal expansion of an ideal gas into vacuum  $W = 0$

Since,  $P_{ex} = 0$

$$\Delta U = 0, q = 0$$

(1) For isothermal irreversible change

$$q = -W = p_{ex} (V_f - V_i)$$

(2) For isothermal reversible change

$$\begin{aligned}
 q &= -W = nRT \ln \frac{V_f}{V_i} \\
 &= 2.303 nRT \log \frac{V_f}{V_i}
 \end{aligned}$$

For adiabatic change  $q = 0$

$$\Delta U = W_{ad}$$

• **Enthalpy (H)**

It is defined as total heat content of the system. It is equal to the sum of internal energy and pressure-volume work.

Mathematically,  $H = U + PV$

**Change in enthalpy:** Change in enthalpy is the heat absorbed or evolved by the system at constant pressure.

$$\Delta H = q_p$$

For exothermic reaction (System loses energy to Surroundings),

$\Delta H$  and  $q_p$  both are -Ve.

For endothermic reaction (System absorbs energy from the Surroundings).

$\Delta H$  and  $q_p$  both are +Ve.

**Relation between  $\Delta H$  and  $\Delta U$ .**

Let us consider a general reaction  $A \longrightarrow B$

Let  $H_A$  be the enthalpy of reactant A and  $H_B$  be that of the products.

$$\begin{aligned}\therefore H_A &= U_A + PV_A \\ H_B &= U_B + PV_B \\ \Delta H &= H_B - H_A \\ &= (U_B + PV_B) - (U_A + PV_A) \\ \Delta H &= \Delta U + P\Delta V \quad (H_B - H_A) \\ \Delta H &= \Delta U + P\Delta V\end{aligned}$$

At constant pressure and temperature using ideal gas law,

$$\begin{aligned}PV_A &= n_A RT \quad (\text{For reactant A}) \\ PV_B &= n_B RT \quad (\text{For product B}) \\ \text{Thus, } PV_B - PV_A &= n_B RT - n_A RT \\ &= (n_B - n_A) RT \\ P\Delta V &= \Delta n_g RT \\ \therefore \Delta H &= \Delta U + \Delta n_g RT\end{aligned}$$

### Extensive property

An extensive property is a property whose value depends on the quantity or size of matter present in the system.

For example: Mass, volume, enthalpy etc. are known as extensive property.

### • Intensive property

Intensive properties do not depend upon the size of the matter or quantity of the matter present in the system.

For example: temperature, density, pressure etc. are called intensive properties.

### • Heat capacity

The increase in temperature is proportional to the heat transferred.

$$q = \text{coeff.} \times \Delta T$$

$$q = C\Delta T$$

Where, coefficient C is called the heat capacity.

C is directly proportional to the amount of substance.

$$C_m = C/n$$

It is the heat capacity for 1 mole of the substance.

### • Molar heat capacity

It is defined as the quantity of heat required to raise the temperature of a substance by  $1^\circ$  (kelvin or Celsius).

### • Specific Heat Capacity

It is defined as the heat required to raise the temperature of one unit mass of a substance by  $1^\circ$  (kelvin or Celsius).

$$q = C \times m \times \Delta T$$

where m = mass of the substance

$\Delta T$  = rise in temperature.

### Relation Between $C_p$ and $C_v$ for an Ideal Gas

At constant volume heat capacity =  $C_v$

At constant pressure heat capacity =  $C_p$

At constant volume  $q_v = C_v \Delta T = \Delta U$

At constant pressure  $q_p = C_p \Delta T = \Delta H$

For one mole of an ideal gas

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

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

On substituting the values of  $\Delta H$  and  $\Delta U$ , the equation is modified as

$$C_p \Delta T = C_v \Delta T + R\Delta T$$

$$\text{or } C_p - C_v = R$$

### • Measurement of $\Delta U$ and $\Delta H$ —Calorimetry

Determination of  $\Delta U$ :  $\Delta U$  is measured in a special type of calorimeter, called bomb calorimeter.

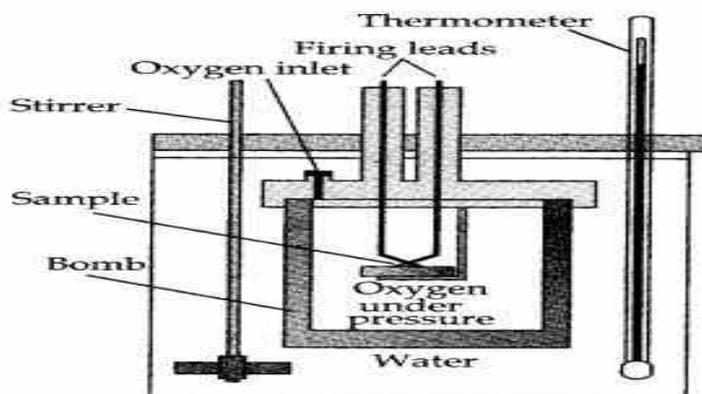


Fig. 6.4 Bomb calorimeter

Working with calorimeter. The calorimeter consists of a strong vessel called (bomb) which can withstand very high pressure. It is surrounded by a water bath to ensure that no heat is lost to the surroundings.

**Procedure:** A known mass of the combustible substance is burnt in the pressure of pure dioxygen in the steel bomb. Heat evolved during the reaction is transferred to the water and its temperature is monitored.

During the process volume remains constant

$$\Delta V = 0$$

Temperature change of the calorimeter is converted to  $q_v$ .  
The value of  $\Delta U$  can be calculated using the formula.

$$\Delta U = Q \times \Delta T \times \frac{M}{m}$$

$Q$  = heat capacity of the calorimeter.

$\Delta T$  = rise in temperature.

$m$  = mass of the substance taken

$M$  = Molecular mass of the substance.

**Determination of  $\Delta H$ :** At constant pressure heat evolved or absorbed is  $\Delta q_p$  is equal to the heat of reaction or enthalpy of reaction  $\Delta_r H$ .

In exothermic reaction,  $\Delta q_p$  and  $\Delta_r H$  both will be -ve (negative).

In endothermic reaction,  $\Delta q_p$  and  $\Delta_r H$  both will be +ve (positive).

Heat change at constant pressure can be done in a calorimeter shown in the fig. 6.5.

#### Enthalpy Change $\Delta_r H$ of a reaction

The enthalpy change in a chemical reaction is given by the symbol  $\Delta_r H$ .

$\Delta_r H = (\text{Sum of enthalpies of products}) - (\text{Sum of enthalpies of reactants})$

$$\Delta_r H = \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}}$$

$a_i$  and  $b_i$  are the stoichiometric coefficients.

**Standard enthalpy of reactions:** When reaction takes place at the standard state of substance the enthalpy of reaction is known as standard enthalpy.

It is denoted by  $\Delta H^\ominus$ .

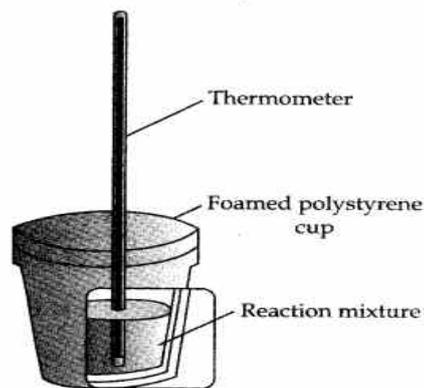


Fig. 6.5 Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).

### • Enthalpy Changes During Phase Transformation

**Enthalpy of fusion:** Enthalpy of fusion is the heat energy or change in enthalpy when one mole of a solid at its melting point is converted into liquid state.

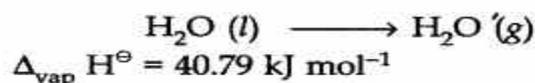
**For example:** Enthalpy of fusion of ice at 273 K is  $6.0 \text{ kJ mol}^{-1}$



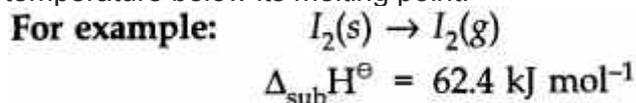
$$\Delta_{\text{fus}} H^\ominus = + 6.0 \text{ kJ mol}^{-1}$$

**Enthalpy of vaporisation:** It is defined as the heat energy or change in enthalpy when one mole of a liquid at its boiling point changes to gaseous state.

**For example:**

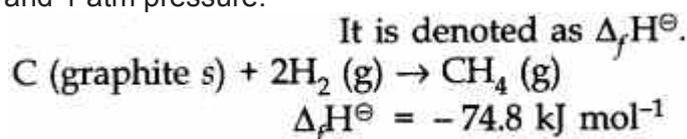


**Enthalpy of Sublimation:** Enthalpy of sublimation is defined as the change in heat energy or change in enthalpy when one mole of solid directly changes into gaseous state at a temperature below its melting point.

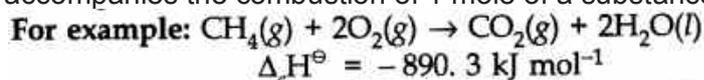


• **Standard Enthalpy of Formation**

Enthalpy of formation is defined as the change in enthalpy in the formation of 1 mole of a substance from its constituting elements under standard conditions of temperature at 298K and 1 atm pressure.



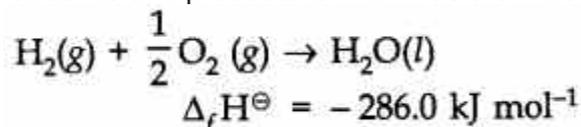
**Enthalpy of Combustion:** It is defined as the heat energy or change in enthalpy that accompanies the combustion of 1 mole of a substance in excess of air or oxygen.



The negative sign of enthalpy change indicates that this is an exothermic reaction.

• **Thermochemical Equation**

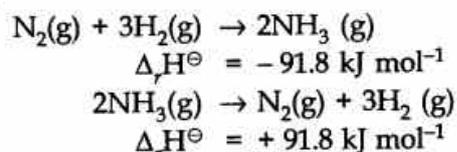
A balanced chemical equation together with the value of  $\Delta H$  and the physical state of reactants and products is known as thermochemical equation.



**Conventions regarding thermochemical equations**

1. The coefficients in a balanced thermochemical equation refer to the number of moles of reactants and products involved in the reaction.
2. The numerical value of  $\Delta_r H^\ominus$  refers to the number of moles of substance specified by an equation.
3. If a chemical reaction is reversed, the value of  $\Delta_r H^\ominus$  is reversed in sign.

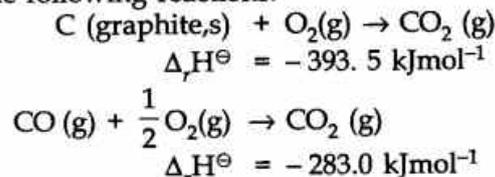
For example:



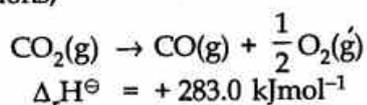
• **Hess's Law of Constant Heat Summation**

The total amount of heat evolved or absorbed in a reaction is same whether the reaction takes place in one step or in number of steps.

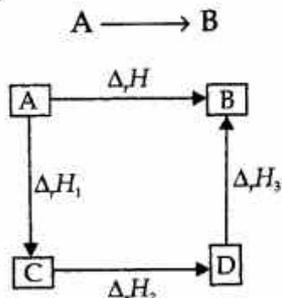
Let us consider the following reactions:



On combining the two reactions,



In general it can be represented as,



### • Born-Haber Cycle

It is not possible to determine the Lattice enthalpy of ionic compound by direct experiment. Thus, it can be calculated by following steps. The diagrams which show these steps is known as Born-Haber Cycle.

1.  $\text{Na (s)} \longrightarrow \text{Na (g)}$   
 $\Delta_{\text{sub}} H^\ominus = 108.4 \text{ kJ mol}^{-1}$
2.  $\text{Na (g)} \longrightarrow \text{Na}^+ \text{ (g)} + e^- \text{ (g)}$   
ionization enthalpy  $\Delta_i H^\ominus = 496 \text{ kJ mol}^{-1}$
3.  $\frac{1}{2} \text{Cl}_2 \text{ (g)} \longrightarrow \text{Cl (g)}$   
bond dissociation enthalpy  $\frac{1}{2} \Delta_{\text{bond}} H^\ominus = 121 \text{ kJ mol}^{-1}$
4.  $\text{Cl (g)} + e^- \text{ (g)} \longrightarrow \text{Cl}^- \text{ (g)}$   
The electron gain enthalpy  $\Delta_{\text{eg}} H^\ominus = -348.6 \text{ kJ mol}^{-1}$
5.  $\text{Na}^+ \text{ (g)} + \text{Cl}^- \text{ (g)} \longrightarrow \text{Na}^+ \text{Cl}^- \text{ (s)}$

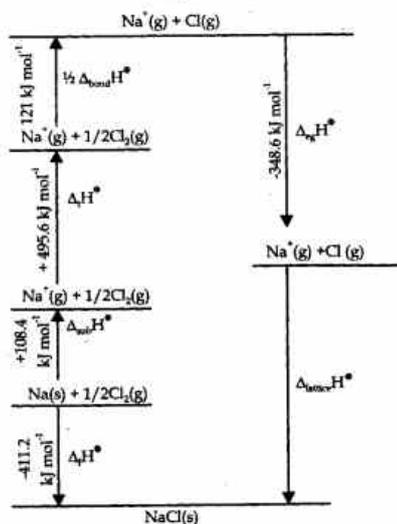


Fig. 6.6 Enthalpy diagram for lattice enthalpy of NaCl

Applying Hess's law

$$\Delta_{\text{Lattice}} H^\ominus = 411.2 + 108.4 + 121 + 496 - 348.6$$

$$\Delta_{\text{Lattice}} H^\ominus = +788 \text{ kJ}$$

### • Spontaneity

**Spontaneous Process:** A process which can take place by itself or has a tendency to take place is called spontaneous process.

Spontaneous process need not be instantaneous. Its actual speed can vary from very slow to quite fast.

**A few examples of spontaneous process are:**

- (i) Common salt dissolves in water of its own.
- (ii) Carbon monoxide is oxidised to carbon dioxide of its own.

### • Entropy (S)

The entropy is a measure of degree of randomness or disorder of a system. Entropy of a

substance is minimum in solid state while it is maximum in gaseous state.  
The change in entropy in a spontaneous process is expressed as  $\Delta S$

Mathematically,

$$\text{Change in entropy } (\Delta S) = S_{\text{final state (product)}} - S_{\text{initial state (reactions)}}$$

For reversible and isothermal process,

$$\text{Change in entropy } \Delta S = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$$

When a system is in equilibrium,  $\Delta S = 0$

**Second law of thermodynamics:** The entropy of universe is continuously increasing due to spontaneous processes taking place in it.

$$\Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \text{ i.e., } \Delta S_{\text{total}} > 0$$

### • Gibbs Energy and Spontaneity

A new thermodynamic function, the Gibbs energy or Gibbs function  $G$ , can be defined as  $G = H - TS$

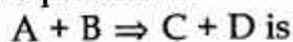
$$\Delta G = \Delta H - T\Delta S$$

Gibbs energy change = enthalpy change – temperature x entropy change  $\Delta G$  gives a criteria for spontaneity at constant pressure and temperature, (i) If  $\Delta G$  is negative ( $< 0$ ) the process is spontaneous.

(ii) If  $\Delta G$  is positive ( $> 0$ ) the process is non-spontaneous.

• Free Energy Change in Reversible Reaction

**The criterion for equilibrium**



$$\Delta_r G = 0$$

When all the reactants and products are in standard state,

$\Delta_r G^\ominus$  is related to the equilibrium constant of the reaction as

$$0 = \Delta_r G^\ominus - RT \ln K$$

$$\Delta_r G^\ominus = -RT \ln K$$

$$\Delta_r G^\ominus = -2.303 RT \log K$$

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

$$= -RT \ln K$$

Since  $\Delta_r G^\ominus$  depends upon the value of  $\Delta_r H^\ominus$  for strongly endothermic reactions, the value of  $\Delta_r H^\ominus$  may be large and +ve. In such case K will be much smaller than 1, and the reaction is unlikely to form product in large amount.

In case of exothermic reactions  $\Delta_r H^\ominus$  is large and negative and  $\Delta_r G^\ominus$  is likely to be large and negative too.

In such cases, K will be much larger than 1.

**Third law of thermodynamics:** The entropy of a perfectly crystalline substance is zero at zero kelvin.

- **Thermodynamics:** Deals with the energy changes in chemical or physical process.

- **First law of thermodynamics**

$$\Delta U = q + w \quad (\text{Where } w \text{ is the work done on the system})$$

- **Change in internal energy and enthalpy is related as**

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

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

$\Delta H$  is negative for exothermic reactions and positive for endothermic reactions.

Heat changes at constant pressure

$$\Delta H = q_p$$

- **Hess's law**

Enthalpy change for chemical reaction can be determined by

$$\Delta_r H = \sum_f (a_i \Delta_f H_{\text{products}}) - \sum_i (b_i \Delta_f H_{\text{reactants}})$$

- **Entropy:** Is a measure of disorder or randomness.

For a spontaneous change, total entropy change is positive.

For Bilated system

$$\Delta U = 0, \quad \Delta S > 0$$

Entropy change can be measured by the equation

$$\Delta S = \frac{q_{rev}}{T} \quad \text{for a reversible process.}$$

- **Gibbs energy**

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

For a spontaneous change

$$\Delta G_{sys} < 0 \quad \text{and at equilibrium}$$

$$\Delta G_{sys} = 0$$

Standard Gibbs energy is related to equilibrium constant by

$$\Delta_r G^\ominus = -RT \ln K$$

**Note-**The above content has been absolutely prepared from home