<u>**Class 11, Chapter- 6: Thermodynamics**</u>

1. Thermodynamics: Science which deals with study of different forms of energy and quantitative relationship.

2. System & Surroundings: The part of universe for study is called system and remaining portion is surroundings.

3. Types of the System:

1) Open System: In an open system, there is exchange of energy and matter between system and surroundings.

2) Closed System In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.

3) Isolated system: In an isolated system, there is no exchange of energy or matter between the system and the surroundings

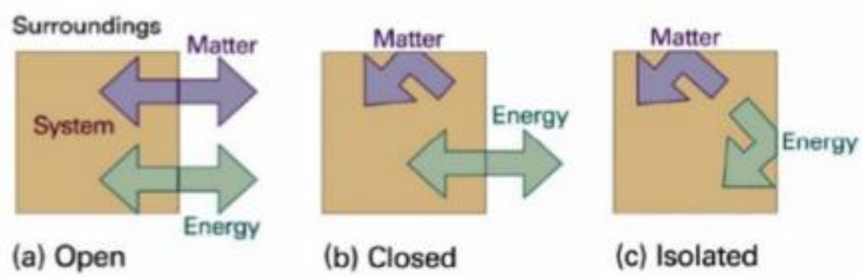


Figure 1- Open, closed and isolated system

4. State of a System: The state of a system means the condition of the system which is described in terms of certain observable properties such as temp (T), pressure (p), volume (v) etc. of the systems. These properties of a system are called state variables.

5. State Functions: A state function is defined as a property of a system that only depends on the initial and final state of the system, and is independent of the path followed in getting from one to the other.

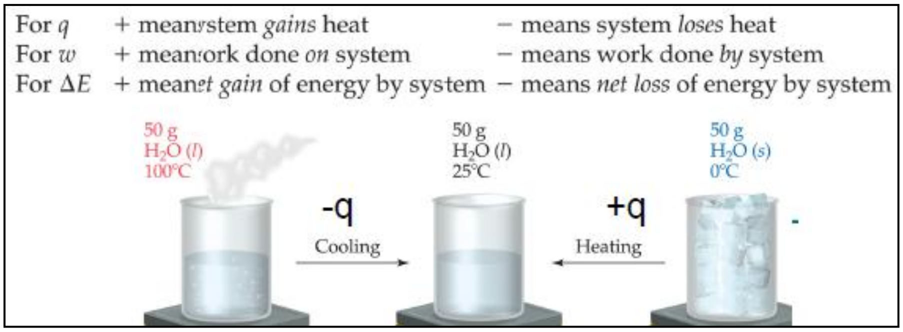
Internal energy (U), enthalpy (H) and entropy (S) are example of state function.

6. Internal Energy (U): A quantity which represents the total energy of the system. It may be chemical, electrical and mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy (U) of the system.

7. Heat (q): It is a form of energy which is exchanged between system and surrounding due to difference of temperature. Unit is Joule (J) or Calorie (1 Calorie = 4.18 J).

The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.

8. Work (w): The positive sign expresses that Work (w) is positive when work is done on the system. Similarly, if the work is done by the system, work will be negative.



9. First law of Thermodynamics: First law of Thermodynamics states that energy can be converted from one form to another with the interaction of heat, work and internal energy but it cannot be created nor destroyed; under any circumstances. Mathematical it can be represented as

$$\Delta U = q + w$$

Where

- ΔU is the total change in internal energy of a system.
- q is the heat exchanged b/w a system and its surroundings.
- w is the work done by the system.

10. Free expansion: Expansion of a gas in vacuum (where external pressure $p_{ex} = 0$) is called free expansion. This happens quickly, so there is no heat transferred (q = 0). No work is done (w = 0) during free expansion of an ideal gas due to external pressure is zero so does not displace anything.

$w = - p_{ex} \Delta V$

So equation $\Delta U = q + w$ can be expressed for free expansion

$\Delta U = q - p_{ex} \Delta V$

$\Delta U = 0$

Result there is no change in internal energy so temperature stays the same.

11. Isothermal Process and free expansion of an ideal gas: When a process is carried out in such a manner that the temp remains constant throughout this process, it is called an isothermal process.

In this process $\Delta T = 0$

Internal energy is due to motion of particles in a system. As internal energy is depends on temperature while temperature in isothermal process is constant so the internal energy will also be constant thus the change in internal energy $\Delta U = 0$.

So equation $\Delta U = q + w$ can be expressed for isothermal process as $q = -w$

a) For isothermal irreversible change $q = -w = p_{ex} * \Delta V$

$$q = -w = p_{ex} (h_f - h_i)$$

b) For isothermal reversible change $q = -w = nRT \ln h_f / h_i$

$$q = -w = 2.303\ nRT \log h_f / h_i$$

c) For adiabatic change, $q = 0$ thus $\Delta U = w_{ad}$

12. Adiabatic Process: Process is carried out in such a manner that no heat can flow from the system to the surrounding or vice versa or the total heat content (q) of the system remain constant, through other variables (pressure and temperature) may change.

In this process $q = 0$

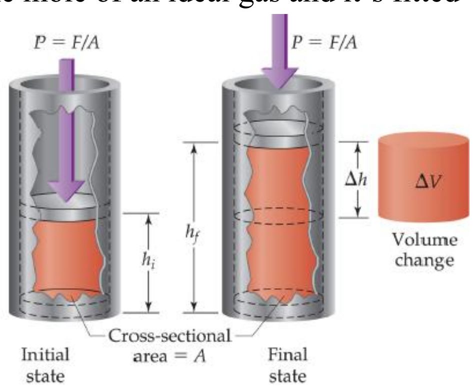
So equation $\Delta U = q + w$ can be expressed for adiabatic process as

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

13. Isochoric Process: Process during which the volume of the system is kept constant is called isochoric process. At constant volume, the system does not expand then there will be no work done ($w = 0$) due to no force over a distance, in that case equation $\Delta U = q + w$ can be expressed

$$\Delta U = q_v \text{ (at constant volume)}$$

14. Isobaric Process: Process during which the pressure of the system is kept constant is called Isobaric Process. At constant pressure, the system expands and work is done. It can be explained by a cylinder which contain one mole of an ideal gas and it's fitted with a piston



In that case, change in volume = h x A = ΔV

Where h = distance of piston moved and A = cross sectional area of piston

While pressure (p) = force / area =F/A

Force (F) on the piston = $p * A$

Work (w) = force x distance = $(p * A) * h$

$w = - p * \Delta V$

Negative sign indicate the **increase** in volume means that the system is doing work on the surroundings.

$$\Delta U = q + w = q - p * \Delta V$$

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

So new function is defined which is known as Enthalpy (H)

15. Enthalpy (H): When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. Enthalpy is a state function which depends entirely on the state function T, P and U. It expressed by following equation

$$H = U + pV$$

Enthalpy is usually expressed as the change in enthalpy (ΔH), for a process b/w initial and final state, we can write above equation as

$$\Delta H = \Delta U + \Delta pV$$

As p is constant, we can write

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

While $p\Delta V = \Delta ngRT$

Where Δng = No. of moles of gaseous products - No. of moles of gaseous reactants

So $\Delta H = \Delta U + \Delta ngRT$

16. Exothermic and Endothermic reactions: $\Delta H = -Ve$ for exothermic and $H = +Ve$ for endothermic reaction i.e. evolution and absorption of heat. For example

$C + O_2 \rightarrow CO_2 + 393.5$ KJ, $H = -393.5$ KJ (exothermic)

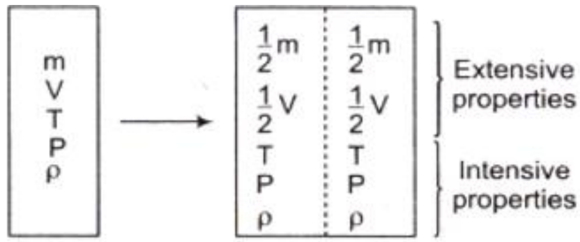
$N_2 + O_2 \rightarrow 2NO - 180.7$ KJ, $H = 180.7$ KJ (Endothermic)

17. Difference between Reversible Process & Irreversible Process:

Reversible Process	Irreversible Process
1. The process is carried out infinitesimally slowly 2. At any stage, the equilibrium is not disturbed 3. It takes infinite time for completion. 4. Work obtained in this process is maximum.	1. It is carried out rapidly 2. Equilibrium may exist only after the completion of the process. 3. It takes a finite time for completion. 4. Work obtained in this process is not maximum

18. 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, internal energy, enthalpy, heat capacity, etc. are extensive properties.

19. Intensive property: Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc. are intensive properties.



Distribution of extensive and intensive properties

20. Heat capacity (C): The amount of energy requires raising the temperature of an object by one degree celsius (or one Kelvin) is its heat capacity.

21. Specific heat capacity(c): It is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one Kelvin). For finding out the heat (q), mathematically it can be expressed as

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

Where c = specific heat of the substance, m = mass of substance in kg, C = heat capacity and ΔT = change in temperature.

22. Relationship between Cp and CV for an ideal gas: Using the definition of enthalpy (H = U + pV), find out the relationship between the heat capacity at constant pressure (Cp) and heat capacity at constant volume (Cv) for ideal gases as accordingly-

Enthalpy for a one mole of ideal gas $\Delta H = \Delta U + R\Delta T$ ---------- (1)

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

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

Putting the ΔH and ΔU value in equation (1), we find out

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

$$Cp - CV = R$$

23. Measurement of ΔU and ΔH by Calorimetry instrument:

a) Measurement of ΔU by Bomb calorimeter:

- For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter. Here, a steel vessel (the bomb) is immersed in a water bath.
- The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings.
- A combustible substance is burnt so supplied pure oxygen in the steel bomb.
- Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored.
- Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume.
- Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$.

- Temperature change of the calorimeter produced by the completed reaction is then converted to q_v, by using the known heat capacity of the calorimeter with the help of equation **$q = c \times m \times \Delta T = C\Delta T$**

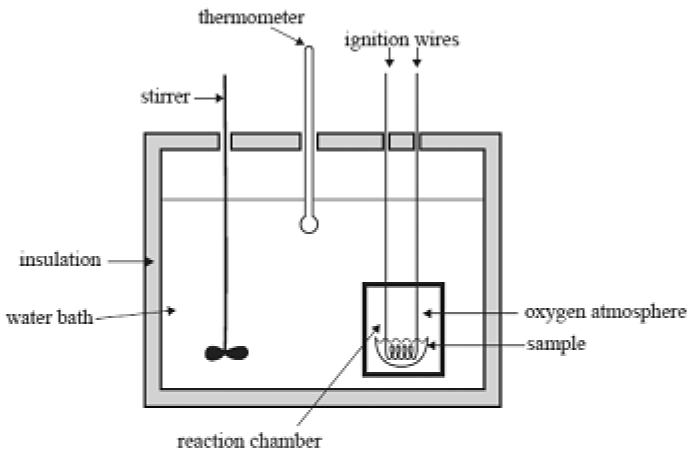
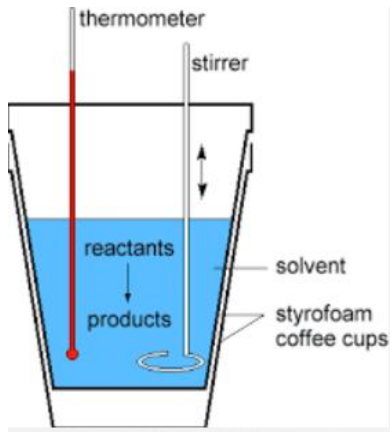


Figure: Bomb Calorimeter

b) Measurement of ΔH by Calorimeter:

- A constant-pressure calorimeter measures the change in enthalpy of a reaction at constant pressure.
- In that case, the gaseous pressure above the solution remains constant, and we say that the reaction is occurring under conditions of constant pressure.
- A Styrofoam cup with an inserted thermometer and a stirring rod can be used as a calorimeter, in order to measure the change in enthalpy/heat of reaction at constant pressure.
- It is constructed from two nested Styrofoam cups and a lid with two holes.
- In an exothermic reaction, heat is evolved and system loses heat surroundings so q_p will be negative and ΔH will also be negative.
- Similarly In an endothermic reaction, heat is absorbed so q_p is positive and ΔH will also be positive.



Coffee Cup Calorimeter

24. Enthalpy Change of a reaction (Reaction Enthalpy): The difference b/w the sum of the enthalpies of the products and the sum of the enthalpies of the reactants is called the reaction enthalpy. The enthalpy change of a chemical reaction is given by the symbol ΔrH.

$$\Delta rH = \text{(sum of enthalpies of products)} - \text{(sum of enthalpies of reactants)}$$

$$\Delta rH = \Sigma\ nH_{Products} - \Sigma\ mH_{Reactants}$$

Where n and m are the coefficients of the products and the reactants in the balanced chemical equation

25. Standard enthalpy of reaction (ΔH^o): It is the enthalpy change that occurs in a system when one mole of matter is transformed by a chemical reaction under standard conditions of temperature (298 k) and pressure (1 bar).
Standard conditions are denoted by adding the superscript ^{o} to the symbol ΔH like ΔH^o

26. Different types of Enthalpies of reactions:

1) Standard enthalpy of fusion ($\Delta_{fus}H^o$): It's also known as latent heat or heat of fusion. The enthalpy change during melting of one mole of a solid substance in to a liquid at constant pressure (atmospheric pressure) is called standard enthalpy of fusion or molar enthalpy of fusion. During phase change, temperature remains constant (at 273k). e.g.

$$H_2O(s) \rightarrow H_2O\ (l); \quad \Delta_{fus}H^o = 6.00\ kJ\ mol^{-1}$$

2) Standard enthalpy of vaporization ($\Delta_{vap}H^o$): Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, ΔvapH0. e.g.

$$H_2O\ (l) \rightarrow H_2O\ (g); \quad \Delta_{vap}H^o = 40.79\ kJ\ mol^{-1}$$

3) Standard enthalpy of sublimation ($\Delta_{sub}H^o$): It is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar). Sublimation is direct conversion of a solid into its vapour.
For example, Solid CO_2 (dry ice) sublimes at 195K with $\Delta_{sub}H^o$ = 25.2 kJ mol–1;
Naphthalene sublimes slowly and for this $\Delta_{sub}H^o = 73.0\ kJ\ mol^{-1}$

4) The standard enthalpy of formation: It is the standard enthalpy of formation of one mole of a compound from its elements in their most stable states of aggregation is called Standard Molar Enthalpy of Formation. Its symbol is Δ_fH^o.
Example- formation of HBr $\quad H_2 + Br_2 \rightarrow 2HBr; = -72.8\ kjmole^{-1}$
Because here two moles, instead of one mole of the products is formed from elements so

$$\tfrac{1}{2} H_2 + \tfrac{1}{2} Br_2 \rightarrow HBr; = -36.4\ kjmole^{-1}$$

5) Standard enthalpy of combustion: It is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.

6) Enthalpy of atomization (symbol: ΔaH^o): It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In case of diatomic molecules, like dihydrogen the enthalpy of atomization is also the bond dissociation enthalpy. In some cases, the enthalpy of atomization is same as the enthalpy of sublimation.

7) Bond Enthalpy ($\Delta_{bond}H^o$): $\Delta rH = \Sigma$ bond enthapies$_{reactants}$ - Σ bond enthapies$_{products}$

8) Enthalpy of Solution ($\Delta_{sol}H^o$): Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

9) Lattice Enthalpy The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

27. Hess's Law of constant heat summation: The change in enthalpy is same whether the reaction takes place in one step or in several steps. Because ΔH is a state function and it is pathway independent. It depends only on initial state of the reactants and the final state of the product.

If a series of reactions are added together, the net change in the heat of the reaction is the sum of the enthalpy changes for each step. i.e.

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 + \text{--------}$$

Rules for using Hess's Law:

1) If the reaction is multiplied (or divided) by some factor, ΔH must also be multiplied (or divided) by that same factor.

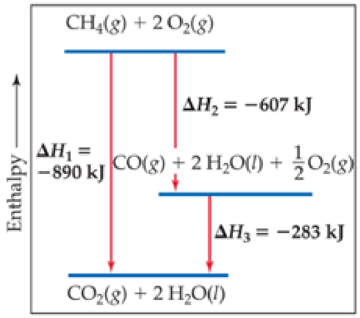
2) If the reaction is reversed (flipped), the sign of ΔH must also be reversed.

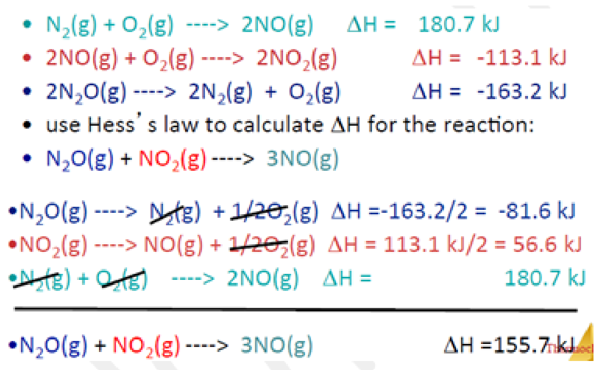
For example:

C (s) + 1/2O2 (g) = CO (g) ΔrH0 =-110.5 kJmol-1

CO (g) + 1/2O2 (g) = CO2 (g) ΔrH0 =-283.0 kJmol-1

C (s) + O2 (g) = CO2 (g) ΔrH0 = -393.5 kJmol-1





28. Spontaneous & Non Spontaneous Processes: A process which can take place by itself is called spontaneous process. A process which can neither take place by itself or by initiation is called non Spontaneous.

29. Driving Force: The force which is responsible for spontaneity of a process is called the driving force.

30. Entropy(S): Entropy is a measure of randomness or disorder of the system. i.e. Gas>Liquid>Solid.

31. Entropy change (ΔS): It is defined as the amount of heat (q) observed isothermally and reversibly divided by the absolute temperature (T) at which the heat is absorbed.

$$\text{Entropy change } (\Delta S) = \frac{q_{(rev.)}}{T}\ J.K^{-1}.mol^{-1}$$

32. Spontaneity in term of Entropy change: The total entropy change for the system and surroundings of a spontaneous process is given by

$$\Delta S_{(total)} = \Delta S_{(universe)} = \Delta S_{(system)} + \Delta S_{(surrounding)}$$

If $\Delta S_{(total)}$ is +ve, the process is spontaneous.

If $\Delta S_{(total)}$ is –ve, the process is non spontaneous.

33. Second law of Thermodynamics: The entropy of universe is continuously increasing due to spontaneous process taking place in it or in any spontaneous process, the entropy of the universe always increases. A spontaneous process cannot be reversed.

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding} > 0$$

34. Gibbs free energy: It is defined as maximum amount of energy available to a system during the process that can be converted into useful work. It is a state function which denoted by symbol G and it is expressed by

$$G = H - TS$$

Where H is the enthalpy of the system, S is its entropy and T is the absolute temperature.

Gibbs free energy change: The change in free energy may be expressed as

$$\Delta G = \Delta H - T\Delta S \text{ ----------------(1)}$$

This equation is called **Gibbs-Helmholtz equation**

35. Gibbs free energy and spontaneity: Gibbs-Helmholtz equation is very useful in predicting the spontaneity of a process means changes in Gibbs free energy help to predict whether a reaction will be spontaneous in the forward or reverse direction (or whether it is at equilibrium!). ΔG gives criteria for spontaneity at constant pressure and temperature and it can be explained as

We know the total entropy change during a process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} \text{ …. (2)}$$

If the system is thermal equilibrium with surrounding, then the temperature of surrounding is equal to the system. If enthalpy of surrounding is increases then it will be equal to decrease in the enthalpy of the system, in that case entropy change of the surrounding,

$$\Delta S_{surr} = \frac{\Delta H_{surr}}{T} = -\frac{\Delta H_{sys}}{T}$$

$$\Delta S_{total} = \Delta S_{sys} + (-\Delta H_{sys}/T)$$

$$T\Delta S_{total} = T\Delta S_{sys} - \Delta H_{sys}$$

For spontaneous process, we know $\Delta S_{total} > 0$, so

$$T\Delta S_{sys} - \Delta H_{sys} > 0$$

$$-(\Delta H_{sys} - T\Delta S_{sys}) > 0$$

By using equation (1), it can be written as

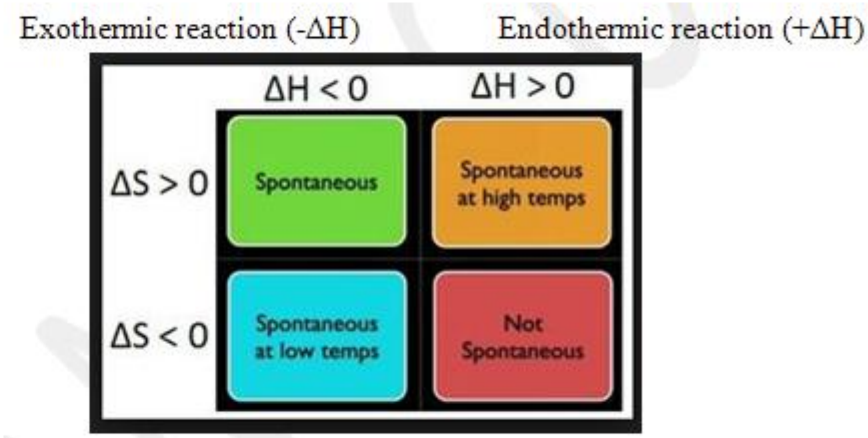
$$-\Delta G > 0$$

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

From that equation $T\Delta S_{sys}$ is the energy which is not available to do useful work. So ΔG is the net energy is available to do useful work and is thus a measure of the free energy. For this reason, it is also known as the free energy of the reaction.

ΔG gives criteria for spontaneity at constant temperature and pressure, which are as

- If ΔG is negative, process is spontaneous when $\Delta G = 0$, the process is in equilibrium if ΔG is positive, the process does not take place.
- For endothermic process may be non spontaneous at low temp.
- For exothermic process may be non spontaneous at high temp and Spontaneous at low temp.



36. Standard Free Energy Change (ΔG^0): It is defined as free energy change measured at 298 K and 1 atm Pressure.

37. Gibbs Energy Change and Equilibrium Constant:

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

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

$$\Delta_r G^0 = \Delta_r H^0 - T\,\Delta_r S^0 = -2.303RT \log K$$

For strongly endothermic reaction, the value of $\Delta_r H^0$ may be large and positive so value of K is much smaller than one and the reaction is unlikely to form much product.

For strongly exothermic reaction, the value of $\Delta_r H^0$ may be large and negative so value of K is larger than one and the reaction is likely to form much product.

6. Thermodynamics: Some Important Formulas

1. **$\Delta U = q + w$**
2. **Unit of q (heat) = Joule (1 Calorie = 4.18 joule)**
3. **Free expansion (in vaccum): $\Delta U = 0$ ($q = 0$ and $p_{ext} = 0$ so, $w = - p_{ext} . \Delta V = 0$)**
4. **For Isothermal process $\Delta T = 0$ So, $\Delta U = 0$, $q = - w$)**
5. **For adiabatic process: $q = 0$ so $\Delta U = w$**
6. **Isochoric process: $V = 0$ so $\Delta U = q_v$ (at constant volume)**
7. **Isobaric Process: $\Delta H = \Delta U + \Delta pV$ (at constant pressure)**
8. **$\Delta H = \Delta U + \Delta n RT$ (Δn = no. of mole of product – no. of mole of reactant)**
9. **Extensive property = mass, volume, U, H; Intensive property = T, P, density**
10. **ΔH= –Ve for exothermic and H= +Ve for endothermic reaction**
11. **$q=c \times m \times \Delta T = C\Delta T$ (c = specific heat capacity, C = heat capacity)**
12. **$Cp - CV = R$**
13. **ΔrH (Reaction Enthalpy) = (sum of enthalpies of products) – (sum of enthalpies of reactants)**
14. **Reaction Enthalpy $\Delta rH = \Sigma\, nH_{Products} - \Sigma\, mH_{Reactants}$**
15. **standard conditions of temperature (298 k) and pressure (1 bar) & its denoted by adding the superscript ^{o} to the symbol ΔH like ΔH^{o}**
16. **Bond Enthalpy ($\Delta_{bond}H^{o}$) $\Delta rH = \Sigma$ bond enthapies$_{reactants}$ - Σ bond enthapies$_{products}$**
17. $$\text{Entropy change } (\Delta S) = \frac{q_{(rev.)}}{T}\ J.K^{-1}.mol^{-1}$$
18. $$\Delta S\ \text{fusion} = \frac{\Delta H\ \text{fusion}}{Tm}$$
19. $\Delta S_{(total)} = \Delta S_{(universe)} = \Delta S_{(system)} + \Delta S_{(surrounding)}$

    If $\Delta S_{(total)}$ is +ve, the process is spontaneous.

    If $\Delta S_{(total)}$ is –ve, the process is non spontaneous.
20. **Gibbs free energy change $\Delta G = \Delta H - T\Delta S$ (If ΔG is -ve, process is spontaneous when $\Delta G = 0$, the process is in equilibrium if ΔG is +ve, the process doesn't take place.**
21. **$\Delta_r G^0$ - 2.303RT log K (k = equilibrium constant)**
22. **$\Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0 = - 2.303RT \log K$**