THERMODYNAMICS

Introduction:

It is a branch of physical chemistry which deals with the study of thermal changes accompanying a physical or chemical transformation. According to law of conservation of energy.

"Total energy of the universe remains constant although it can be transformed from one form to the another".

SOME FUNDAMENTAL TERMS AND CONCEPTS :

(i) System and surroundings : The part of the universe chosen for thermodynamic study is called system. It is separated from rest of the universe by a real or imaginary boundary.

The remaining portion of the universe excluding the system is called surroundings.

(ii) Types of system :

(a) Isolated system : A system that cannot exchange mass and/or energy with the surroundings.

e.g., Milk kept in a thermos flask.

(b) Closed system : It exchanges only energy with the surroundings.

e.g., water in a closed bottle, heating of $CaCO_3$ in sealed tube.

(c) Open system : If exchanges both energy and mass from the surroundings.

e.g. tea in an open up.

(iii) State of a system and state variables : The state of system is determined by its observable properties. The system in which the values of observable properties are definite is said to be in definite state. The state of a system is specified by state functions because their values depend only on the state of the system and not on how it is reached.

(iv) The properties of a system which depend only on initial and final states and not on its path is called state function.

e.g., free energy, enthalpy, internal energy etc.

(v) Macro system and macroscopic properties : A very large number of molecules/atoms are present in this system. Properties of a macro system are called macro properties.

e.g., pressure, temperature, density, composition, viscosity, surface tension, colour, refractive index etc.

(a) Extensive properties : The properties which depends on the amount of substance present in the system.

e.g., mass, volume, heat capacity, entropy, enthalpy, free energy, internal energy etc.

(b) Intensive properties : These properties do not depends on the amount of substance present in the system.

e.g., temperature, density, viscosity, melting point, boiling point, surface tension, refractive index, pressure etc.

(vi) Thermodynamic processes : The process in which state of the system gets changed from one state to the another state. Macro properties get changed in this process. These are of the following types :

(a) Isothermal process : It is the process in which temperature of the system remains constant.

(b) **Adiabatic Process :** In a closed system, heat is not exchanged between system and surrounding. In this process, temperature can increase and can decrease also.

(c) **Isobaric process :** This process takes place at constant pressure.

(d) **Isochoric process :** The process which takes place at constant volume.

(e) **Cyclic process :** The process in which a system proceeds via many intermediate steps and returns to the initial state. The change in the value of state function is zero in cyclic proses.

Reversible process	Irreversible process
1. It is a slow process going through a series of smaller stages with each stage maintaining equilibrium between the system and surroundings.	1. In this process the system attains final state from the initial state with a measurable speed. During the transformation, there is no equilibrium maintained between the system and surroundings.
2. A reversible process can be made to proceed in forward or backward direction.	2. Irreversible process can take place in one direction only.
3. The driving force for the reversible process is small since the process proceeds in smaller steps.	3. There is a definite driving force required for the progress of the irreversible process.
4. Work done in a reversible process is greater than the corresponding work done in irreversible process.	4. Work done in an irreversible process is always lower than the same kind of work done in a reversible process.
5. A reversible process can be brought back to the initial state without making any change in the adjacent surroundings.	5. An irreversible process cannot be brought back to its initial state without making a change in the surroundings.

    (vii)   **Themodynamic equilibrium :** Which macro properties of a system do not change with time, the system is said to be in equilibrium.

(a) **Mechanical equilibrium :** When no work is done by one part of the system on its other part, it is aid to be in state of mechanical equilibrium. Pressure remain constant throughout the system.

(b) **Thermal equilibrium :** Temperature remains constant throughout the system. No transfer of heat takes place from one part of the system to the other.

(c) **Chemical equilibrium :** In this, composition of the system remains constant and definite.

Internal energy : The fixed amount of energy stored in a substance is called its internal energy. Internal energy is present in all the substances.

(i) Internal energy is a state function depends on the physical state of the system and is independent of method by which state has been attained.

(ii) Internal energy is the total of all types of energy e.g., potential energy, kinetic energy, vibrational energy, rotation energy.

(iii) For 1 mole of monoatomic gas $U = \dfrac{3RT}{2}$. The internal energy of ideal gases is a function of temperature only.

Heat and work :

(i) Heat absorbed by the system $(+q)$ = positive.

(ii) Heat released by the system $(-q)$ = negative.

(iii) Work done on the system by the surroundings $(+w)$ = positive (compression).

(iv) Work done by the system on the surrounding $(-w)$ = negative (expension).

Unit conversion :

$1\,L = 1\,dm^3 = 10^{-3}\,m^3 = 10^3\,cm^3$

$1\,atm = 1.01325\,bar = 101325\,Pa = 760\,torr = 760\,mmHg$

$1\,m = 100\,cm = 10^{-6}\,\mu m = 10^{-9}\,nm = 10^{-10}\,\text{Å}$

$1\,L\,atm = 101.33\,joule = 0.024\,kilocalories$

Standard temperature and pressure (STP)

Standard temperature $= 0°C = 273.15\,K$

Standard pressure $= 1\,atm = 760\,mmHg$

At these "standard" conditions, if you have 1.0 mole of a gas it will occupy a "standard molar volume".

Standard molar volume $= 22.414\,L$

EQUILIBRIUM CONSTANT & GIBBS FREE ENERGY :

The Equilibrium constant is related to the standard Gibbs free energy change for the reaction.

- **The relation is given by the equation :**

  $$\Delta G° = -RT \ln K_{eq}$$

- In the above equation,
- R is the universal gas constant
- T is the temperature.

- K_{eq} is the equilibrium constant

- **Temperature Dependency :** Equilibrium constant K_c depends on the temperature of the reaction and the relation is given by Van't Hoff equation.

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

- In the above equation,
- K_1 is the equilibrium constant at absolute temperature T_1.

- K_2 is the equilibrium constant at absolute temperature T_2.

- R is the ideal gas constant.
- ΔH reaction enthalpy assumed to be constant over the temperature range.
- This equation can be used to estimate a new equilibrium constant at a new absolute temperature assuming a constant standard enthalpy change over the temperature range.

- Now, Let's understand the change in the equilibrium constant for two different kinds of reactions. Endothermic & Exothermic. Using the definition of Gibbs free energy & Gibbs free energy Isotherm equation, we have :

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

$$\Delta G° = -RT \ln K_{eq}$$

$$\ln K_{eq} = -\frac{\Delta H°}{RT} + \frac{\Delta S°}{R}$$

- In the above equation,
- K_{eq} is the equilibrium constant at temperature T.
- $\Delta H°$ and $\Delta S°$ are constants and are enthalpy and entropy of the system respectively.
- The graph of this equations is called the Van't Hoff plot. The plot is used to estimate the enthaply and entropy and entropy of chemical reaction.
- From the plot between "$\ln K_{eq}$" & "1/T", we have $-\Delta H / R$ as the slope, and $\Delta S / R$ as the intercept of the linear fit.

Exothermic reactions :

- For an exothermic reaction, heat is released, making the net enthalpy change negative.
- $\Delta H < 0$, so slope ($-\Delta H / R$) is positive.
- Van't Hoff plot has a positive slope.

Exothermic Reaction

Slope = $-\Delta H/R$
Interception = $\Delta S/R$

$\ln K_{eq}$

1/T (1/K)
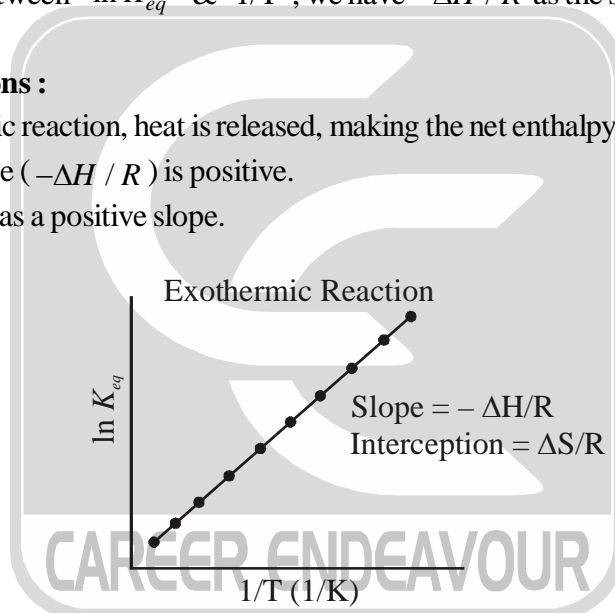
Endothermic reactions :

- For an endothermic reaction, heat is absorbed, making the net enthalpy change positive.
- $\Delta H > 0$, so slope ($-\Delta H / R$) is negative.
- Van't Hoff plot has a negative slope

SOLVED PROBLEMS

1. For the reaction $A \rightleftharpoons B + C$, at equilibrium, the concentration of A is 1×10^{-3} M, B is 0.15 M and C is 0.05 M. The $\Delta G°'$ for the hydrolysis of A at 27 ºC will be   **[TIFR-2011]**

(a) –5.0 kJ/mol   (b) –17.3 kJ/ml   (c) –11.2 kJ/mol   (d) None of these

Soln. : $A \rightleftharpoons B + C$

$$K_{eq} = \frac{[B][C]}{[A]} = \frac{0.515 \times 0.05}{10^{-3}} = 7.5$$

Gibb's free energy equation -

$\Delta G = \Delta G° + RT \ln \theta_c$ ...(i)

$\theta_c \rightarrow$ reaction quotient

At equilibrium $\Delta G = 0, \theta_c = K_{eq}$

Equation (i) reduce to

$\Rightarrow \Delta G° = -RT \ln K_{eq}$

$= -8.314 \times 300 \ln 7.5 = -5,025.57$ J/ mol $= -0.5$ kJ/mol

Correct option (a)

2. Which of these is the closest to the value of 1 kcal/mole? **[TIFR-2011]**

   (a) $2/3 \times 10^{-20}$ Joules   (b) $2/3$ Joules   (c) 2×10^{-20} Joules   (d) 3×10^{-10} Joules

Soln. : 1 cal $= 4.184$ joules

1 K cal $= 4184$ joules

$1 \text{ K cal/mol} = \dfrac{4184}{6.023 \times 10^{23}} = 694.67 \times 10^{-23} = 0.695 \times 10^{-20} \simeq \dfrac{2}{3} \times 10^{-20}$ joules

Correct option (a)

3. Given the following values of ΔH and ΔS, which one of the following processes can take place at 300°K without violating the second law of thermodynamics? **[TIFR-2013]**

	$\Delta H \left(\text{Kcal.Mol}^{-1} \right)$	$\Delta S \left(\text{cal.Mol}^{-1}.°K^{-1} \right)$
(a)	−20	+80
(b)	−20	−80
(c)	+20	+30
(d)	+20	−30

Soln. : For a reaction to be spontaneous, ΔG must be negative.

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

$\Delta G = -20 \times 10^3 - 300 \times 80$

$\quad = -20,000 - 24,000 = -44,000$ calmol^{-1} (spontaneous)

$\Delta G = 20 \times 10^3 - 300 \times (-80)$

$\quad = -20,000 + 24,000 = 4,000$ calmol^{-1} (non-spontaneous)

$\Delta G = 20 \times 10^3 - 300 \times 30$

$\quad = 20,000 - 9,000 = 11,000$ calmol^{-1} (non-spontaneous)

$\Delta G = 20 \times 10^3 - 300 \times (-30) = 20,000 + 9,000$

$\quad = 29,000$ calmol^{-1} (non-spontaneous)

Correct option (a)