Class : Chemistry
Class : XI

Kannada

Thermodynamics

- The branch of science which deals with the quantitative relationship between heat and other forms of energies is called thermodynamics.

Thermodynamic Terms

(i) **System** It refers to the part of universe in which observations are carried out.

(ii) **Surroundings** The part of universe other than the system is known as surroundings.

(iii) **Boundary** The wall that separates the system from the surroundings is called boundary.

(iv) **Thermodynamic equilibrium** A system in which the macroscopic properties do not undergo any change with time is called thermodynamic equilibrium.

(v) **Thermal equilibrium** If there is no flow of heat from one portion of the system to another, the system is said to be in thermal equilibrium.

(vi) **Mechanical equilibrium** If no mechanical work is done by one part of the system on another part of the system, it is said to be in mechanical equilibrium. Such a condition exists when pressure remains constant.

Types of Systems

(i) **Open system** The system in which energy and matter both can be exchanged with the surroundings.

(ii) **Closed system** The system in which only energy can be exchanged with the surroundings.

(iii) **Isolated system** The system in which neither energy nor matter can be exchanged with the surroundings.

State of System

When microscopic properties have definite value, the condition existence if the system is known as state of system.

State functions (State variables) When values of a system, independents it of path followed and depend only on initial and firs state, it is known as state function, e.g. $\Delta U, \Delta H, \Delta G$ etc.

Path functions These depend upon the path followed, e.g. Work heat, etc.

Thermodynamic Properties

Intensive Properties

Properties of the system which depend only on the nature of matter but not on the quantity of matter are called intensive properties, e.g., pressure, temperature, specific heat, etc.

Extensive Properties

Properties of the system which are dependent on the quantity od matter are called extensive properties, e.g. internal energy, volume, enthalpy, etc.

Thermodynamic Process

It is the operation which brings change in the state of the system.

Thermodynamic processes are

(i) **Isothermal process** In which temperature remains constant, i.e. $(dT = 0, \Delta U = 0)$.

(ii) **Isochoric process** In which volume remains constant, i.e. $(\Delta V = 0)$.

(iii) **Isobaric process** In which pressure remains constant, i.e. $(\Delta p = 0)$.

(iv) **Adiabatic process** In which heat is not exchanged by system with the surroundings, i.e. $(\Delta q = 0)$.

(v) **Cyclic process** It is a process in which system returns to its original state after undergoing a series of change, i.e. $\Delta U_{\text{cyclic}} = 0; \Delta H_{\text{cyclic}} = 0$.

(vi) **Reversible process** A process that follows the reversible path, i.e. the process which occurs in infinite number of steps in a way that the equilibrium conditions are maintained at each step, and the process can be reversed by infinitesimal change in the state of functions.

(vii) **Irreversible process** The process which cannot be reversed and a amount of energy increases. All natural processes are irreversible.

Internal Energy (E or U):

- It is the total energy within the substance. It is the sum of many types of energies like vibrational energy, translational energy, etc.
- It is an extensive property and state function.
- If absolute value cannot be determined but experimentally change in energy (ΔU) can be determined by
- $\Delta U = U_2 - U_1$ or $\Sigma U_P - \Sigma U_R$
- for exothermic process, $\Delta U = -$ ve, whereas for endothermic process $\Delta' = +$ ve.
- It depends on temperature, pressure, volume and quantity of matter and is independent of the method by which state has been attained.

Zeroth Law of Thermodynamics or Law of Thermal Equilibrium

- The law states that if the two systems are in thermal equilibrium with a third system then they are also in thermal equilibrium with each other. Temperature is used here to know whether the system is in thermal equilibrium or not.

First Law of Thermodynamics

Energy can neither be created nor destroyed although it can be converted from one form to the other.

Mathematically,

$\Delta U = q + W$

where, $\Delta U =$ internal energy change

$q =$ heat added to system

$W =$ work added to system

[Sign convention

(i) q is $+$ve $=$ heat is supplied to the system

(ii) q is-ve = heat is lost by the system

(iii) W is $+$ve $=$ work done on the system

(iv) W is -ve = work done by the system]

Modes of Transference of Energy

Work (W)

- If the system involves gaseous substances and there is a difference of pressure between system and surroundings, work is referred of pressure-volume work (W_{pV}).

Expression for Pressure-Volume Work

(i) Work done in irreversible expansion against constant pressure p under isothermal conditions

$$q = -W_{pV} = p_{ext}\,\Delta V$$

(ii) Work done in reversible expansion under isothermal conditions

$$q = -W_{rev} = 2.303nRT\log\left(\frac{V_2}{V_1}\right)$$

$$\text{or } q = -W_{rev} = 2.303nRT\log\frac{p_1}{p_2}$$

(iii) Work done in reversible expansion under adiabatic conditions

$$W_{rev} = \frac{nR}{\gamma-1}(T_2 - T_1)$$

where, γ = Poisson's ratio

(Under adiabatic conditions $TV^{\gamma-1}$ = constant)

(iv) Work done in irreversible expansion under adiabatic conditions

$$W_{irrev} = -p_{ext} \times nR\left[\frac{p_1T_2 - p_2T_1}{p_1p_2}\right]$$

(v) When an ideal gas expands in vacuum then

$$p_{ext} = 0$$

- Work done is maximum in reversible conditions.

  Units: CGS system - erg

  SI system - joule
- Work and heat both appear only at the boundary of the system during a change in state.

Heat (q)

- It occurs when there is a difference of temperature between system and surroundings. It is a random form of energy and path dependent. Its units are joule or calorie.

Heat Capacity of a System

Heat capacity (C) of a system is defined as the amount of heat required p raise the temperature of a system by 1°C.

Molar Heat Capacity

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

Specific Heat Capacity

It is the heat capacity of 1 g of substance of the system.

$q = mc\Delta T$

where, m = mass of substance, c = specific heat or specific heat capacity

Molar heat capacity, at constant pressure, $C_p = c_p \times M$

Molar heat capacity, at constant volume, $C_V = c_V \times M$

(c_p and c_V are specific heats at constant pressure and constant volume respectively and M is molecular weight of gas)

$c_p - c_V = R$ (R = Molar gas constant)

$$C_p - C_V = \frac{R}{M}$$

- The molar heat capacity at constant volume, $C_V = \left(\frac{3}{2}\right)R$

  The molar heat capacity at constant pressure,

  $C_p = \left(\frac{3}{2}\right)R + R = \left(\frac{5}{2}\right)R$
- Poisson's ratio,

  $\gamma = \frac{C_p}{C_V} = \left(\frac{5}{3}\right) = 1.66$

  $\gamma = 1.66$ for monoatomic gas

  $\gamma = 1.40$ for diatomic gas

  $\gamma = 1.33$ for triatomic gas

Measurement of ΔH and ΔU : Calorimetry

(a) For gaseous reactions Reactions involving gases are carried out in a bomb calorimeter at constant volume.

$\Delta U = -$ (Heat absorbed by bomb calorimeter)

(b) For reaction in solution Reactions involving solution are carried out at constant pressure inside a coffee-cup calorimeter.

$\Delta_r H = (mc\Delta T)_{\text{calorimeter}} + (mc\Delta T)_{\text{solution}}$.

Enthalpy (H)

- It is the sum of internal energy and pV-energy of the system. It is a state function and extensive property.

  Mathematically,

  $H = U + pV$
- Like U, absolute value of H also cannot be known, ΔH is determined experimentally.
- $\Delta H = H_2 - H_1$ or $\Delta H = \Sigma H_P - \Sigma H_R$
- For exothermic reaction (the reaction in which heat is evolved), $\Delta H = -$ve, whereas for endothermic reaction (the reaction in which heat is absorbed), $\Delta H = +$ ve.

  Relationship between ΔH and ΔU

  $\Delta H = \Delta U + p\Delta V$ or $\Delta H = \Delta U + \Delta n_{(g)}RT$
- Here, $\Delta n_g =$ change in the number of gas moles.

Enthalpy Change or Reaction Enthalpy ($\Delta_r H$)

- It is the change in enthalpy that accompanies a chemical reaction represented by a balanced chemical equation.

  $\Delta_r H = \Sigma H_{(P)} - \Sigma H_{(R)}$
- Enthalpy of reaction expressed at the standard state conditions is called standard enthalpy of reaction $(\Delta H^{\ominus})$.

  Factors affecting enthalpy of reaction are

  (i) Physical state of reactants and products.

  (ii) Allotropic forms of elements involved.

  (iii) Chemical composition of reactants and products.

  (iv) Amount of reactants.

  (v) Temperature.

Various Forms of Enthalpy of Reaction

Enthalpy of Formation $(\Delta, \mathrm{H}^{\circ})$

It is the heat change when one mole of compound is obtained from constituent elements. Enthalpy of formation at standard state known as standard enthalpy of formation $(\Delta, \mathrm{H}^{\circ})$ and is taken a zero by convention.

Enthalpy of Combustion $(\Delta_{\mathrm{C}}\mathrm{H}^{\circ})$

It is the enthalpy change taking place when one mole of a compound undergoes complete combustion in the presence of oxygen $(\Delta_{\mathrm{C}}\mathrm{H})$. $\Delta_{\mathrm{C}}\mathrm{H}$ is always negative, because process of combustion is exotherng

Enthalpy of Solution $(\Delta_{\mathrm{sol}}\,\mathrm{H}^{\circ})$

It is the enthalpy change when one mole of a substance is dissolved in large excess of solvent, so that on further dilution no appreciable heat change occur.

So,

$\Delta_{\mathrm{sol}}\,\mathrm{H}^{\circ} = \Delta_{\mathrm{lattice}}\,\mathrm{H}^{\circ} + \Delta_{\mathrm{hyd}}\,\mathrm{H}^{\circ}$

Enthalpy of Hydration $\left(\Delta_{\mathrm{hyd}}\,\mathrm{H}^{\circ}\right)$

It is the enthalpy change when one mole of anhydrous or partially hydrated salt combines with required number of moles of water to form a specific hydrate undergoes complete combustion. It is an exothermic process.

Enthalpy of Fusion $(\Delta_{\mathrm{fus}}\,\mathrm{H}^{\circ})$

It is the enthalpy change that accompanies melting of one mole of solid substance.

Enthalpy of Vaporisation $\left(\Delta_{\mathrm{vap}}\,\mathrm{H}^{\circ}\right)$

It is the enthalpy change that accompanies conversion of one mole of liquid substance completely into vapours.

Enthalpy of Neutralisation $(\Delta_{\mathrm{n}}\mathrm{H}^{\circ})$

- It is the enthalpy change that takes place when 1 g-equivalent of an acid (or base) is neutralised by 1 g-equivalent of a base (or acid) in dilute solution.
- Enthalpy of neutralisation of strong acid and strong base is always constant, i.e. 57.1 kJ.
- Enthalpy of neutralisation of strong acid and weak base or weak acid and strong base is not constant and numerically less than 57.1 kJ due to the fact that here the heat is used up in ionisation of weak acid or weak base. This is known as enthalpy of ionisation of weak acid/or base.

Enthalpy of Transition $(\Delta_1\mathrm{H}^{\circ})$

It is the enthalpy change when one mole of the substance undergoes transition from one allotropic form to another.

Enthalpy of Atomisation $(\triangle_{\mathrm{a}}\,\mathrm{H}^{\circ})$

It is the enthalpy change occurring when one mole of the molecule breaks into its atoms.

Enthalpy of Dilution

It is the enthalpy change, when one mole of a substance is diluted from one concentration to another.

Enthalpy of Sublimation (Δ_{sub} H°)

It is the enthalpy change, when one mole of a solid substance sublimes.

Lattice Enthalpy

It is the enthalpy change, when one mole of an ionic compound dissociates into its ions in gaseous state.

Bond Enthalpy (Δ_{bond} H°)

Enthalpy is required to break a bond and energy is released when bond is formed. For this, two different terms are used in thermodynamics.

(a) **Bond dissociation enthalpy** The enthalpy change is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form product in the gas phase.

(b) **Mean bond enthalpy** The average value of dissociation energies of polyatomic molecule.

Some factors affecting the bond enthalpy:

(i) Size of atoms

(ii) Electronegativity

(iii) Bond length

(iv) Number of bonding electrons

Joule-Thomson Effect

- The phenomenon of cooling of a gas when it is made to expand adiabatically from a region of high pressure to a region of extremely low pressure is known as Joule-Thomson effect. This effect is zero when an ideal gas expands in vacuum.
- When an ideal gas undergoes expansion under adiabatic condition in vacuum, no change takes place in its internal energy, i.e. $\left(\frac{\partial E}{\partial V}\right)_T = 0$ where, $\left(\frac{\partial E}{\partial V}\right)_T$ is called the internal pressure.

Joule-Thomson Coefficient

- The number of degrees of temperature change produced pet atmospheric drop in pressure at constant enthalpy when a gas is allowed to expand through a porous plug is called Joule-Thomson coefficient. It is given as

$$\mu = \frac{dT}{dp}$$

- where, μ = Joule-Thomson coefficient, dT = change in temperature
- dp = change in pressure.

Inversion Temperature

- The temperature below which a gas becomes cooler on expansion is known as the inversion temperature. It is given as

$$T_i = \frac{2a}{Rb}$$

- where, a and b = van der Waals' constant.

At inversion temperature T_i, the Joule Thomson coefficient $\mu = 0$, i.e. the gas is neither heated nor cooled.

Laws of Thermochemistry

Lavoisier Laplace Law

The enthalpy change during a reaction is equal in magnitude to the enthalpy change in the reverse process but it is opposite in sign.

Hess's Law of Constant Heat Summation

The standard enthalpy of a reaction, which takes place in several steps, is the sum of the standard enthalpies of the intermediate reactions into which the overall reactions may be divided at the same temperature. According to Hess's law

- $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$
- Applications of Hess's law are
  (a) In determination of heat of formation.
  (b) In determination of heat of transition.
  (c) In determination of heat of hydration.
  (d) To calculate bond energies.

Trouton's Rule

According to this rule, "The ratio of enthalpy of vaporisation and normal boiling point of a liquid is approximately equal to 88 J per mol per kelvin, i.e.

$\frac{\Delta H_{vap}}{T} = 88\ J/mol/K$

Dulong and Petit Law

This law states "The product of specific heat and molar mass of any metallic element is equal to $6.4 cal/mol/^\circ C$, i.e.

Specific heat $\times$ molar mass $= 6.4 cal/mol/^\circ C$

Kirchhoff's Equation

$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$ and $\Delta C_V = \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1}$

Clausius-Clapeyron Equation

$-2.303 \log \frac{p_2}{p_1} = \frac{\Delta H_V}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

where, $\Delta H_V =$ molar heat of vaporisation.

- **Spontaneous Process**

The physical or chemical process which proceeds by its own in a particular direction under given set of conditions without outside help is called spontaneous process. It cannot be reversed.

All natural processes are spontaneous process.

Spontaneous process where no initiation is needed

(i) Sugar dissolves in water.

(ii) Evaporation of water.

(iii) Nitric oxide (NO) reacts with oxygen.

where some initiation Spontaneous process is required

(i) Coal keeps on burning once initiated.

(ii) Heating of $CaCO_3$ to give calcium oxide and CO_2 is initiated by heat.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Entropy (S)

It is the measure of degree of randomness or disorder of the molecules It is a state function and extensive property.

Units : $JK^{-1}\ mol^{-1}$

The change in entropy during a process is mathematically given as

$$\Delta, S^\circ = \Sigma S^\circ(\text{ products }) - \Sigma S^\circ(\text{ reactants }) = \frac{q_{rev}}{T} = \frac{\Delta H}{T}$$

- where, q_{rev} = heat absorbed by the system in reversible manner
- $T =$ temperature
- $4\ \Delta S > 0$, Increase in randomness, heat is absorbed,

  $\triangle S < 0$, Decrease in randomness, heat is evolved.

  Entropy of even elementary substances are not zero.

  Entropy change of an ideal gas is given by
- $\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)$

Entropy Change During Phase Transition

The change of matter from one state to another state is called phase transition.

The entropy changes at the time of phase transition:

- $\Delta S_{melting} = \frac{\Delta H_{fusion}}{T_m}$

  $T_m =$ melting point of substance
- $\Delta S_{vaporisation} = \frac{\Delta H_{vaporisation}}{T_b}$

  $T_b =$ boiling point of substance
- $\Delta S_{sublimation} = \frac{\Delta H_{sublimation}}{T_{sub}}$

  $T_{sub} =$ sublimation temperature

Enthalpy Criterion of Spontaneous Process

All the processes which are accompanied by decrease of energy (exothermic reactions, having negative value of ΔH) occur spontaneously. It fails when some endothermic reactions occur spontaneously.

Entropy Criterion of Spontaneous Process

A process is spontaneous if and only if the entropy of the universe increases.

For a process to be spontaneous

- $(\Delta S_{universe} > 0$ or $\Delta S_{syst} + \Delta S_{surr} > 0)$
- At equilibrium state, $\Delta S = 0$.

- **Limitations of $\triangle S$ criterion and need for another term** We cannot find entropy change of surroundings during chemical changes. So we need another parameter for spontaneity viz Gibbs' energy of system (G).

- **Second Law of Thermodynamics**

  The entropy of the universe is always increasing in the course of every spontaneous or natural change.

  Or

- All spontaneous processes or natural changes are thermodynamically irreversible without the help of an external work, i.e., heat cannot flow itself from a colder to hotter body.

Gibbs Energy or Gibbs Free Energy

- It is the energy available for a system at some conditions and by which useful work can be done. It is a state function and extensive property, Mathematically,
- $G = H - TS$
- Change in Gibbs energy during the process is given by Gibbs Helmholtz equation.
- $(\Delta G = G_2 - G_1 = \Delta H - T\Delta S)$
- where, $\Delta G =$ Gibbs free energy, $H =$ enthalpy of system

  $TS =$ random energy,

  $\Delta G_{system} = -T\Delta S_{total}$ [In hypothetical system where $\Delta H = 0$]
- The Gibbs energy criterion of spontaneity

  $\Delta G > 0$, process is non-spontaneous

  $\Delta G < 0$, process is spontaneous

  $\Delta G = 0$, process is in equilibrium state.

Effect of Temperature on Spontaneity

S. No.	**Sign of ΔH**	**Sign of ΔS**	**$\Delta G = \Delta H - T\Delta S$**	**Remarks**
1	Negative	Positive	Always negative	Spontaneous at all temperatures
2	Positive	Negative	Always positive	Non-spontaneous at all temperatures
3	Positive	Positive	Positive at low temperature Negative at high temperature	Non-spontaneous at low temperature Spontaneous at high temperature
4	Negative	Negative	Negative at low temperature Positive at high temperature	Spontaneous at low temperature Non-spontaneous at high temperatures

- Now an exothermic reaction which is non-spontaneous at high temperature may become spontaneous at low temperature. Similarly, endothermic reactions which are non-spontaneous at low temperature may become spontaneous at high temperature.

Standard Free Energy Change (ΔG°)

- It is the change in free energy which takes places when the reactants are converted into products at the standard states, i.e. (1 atm and 298 K)
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
- $\Delta G^\circ = \Sigma \Delta G^\circ_{f\,(Products)} - \Sigma \Delta G^\circ_{f\,(Reactant)}$
- where, $\Delta G^\circ_f =$ standard energy of formation

  Standard energy of formation of all free elements is zero.

Gibbs Energy Change and Equilibrium

Criterion for equilibrium,

- Now, relation
- $A + B \rightleftharpoons C + D$
- $\Delta G = 0$
- $\Delta G = \Delta G^\circ + RT\ln Q$
- $0 = \Delta G^\circ + RT\ln K$
- $\Delta G^\circ = -RT\ln K$
- $\Delta G^\circ = -2.303RT\log K$
- or

  $\Rightarrow$ We also know that
- $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -RT\ln K$

Relation between ΔG° and EMF of the Cell

- $\Delta G^\circ = -nFE^\circ_{cell}$
- where, $n =$ number of electrons lost or gained
- n = number
- F = Faraday or $96500C$
- E^o_{cell} = standard electrode potential

Third Law of Thermodynamics

- This law was formulated by Nernst in 1906. According to this law, "The entropy of a perfectly crystalline substance at zero K or absolute zero is taken to be zero".
- We can find absolute entropies of pure substances at different temperature.
- $\Delta S = \int_0^T C_p d\ln T = 2.303 \int_0^T C_p d\log T$
- where, $C_p =$ heat capacities
- $T =$ temperature between 0 K and T K.
- This law is only applicable for perfectly crystalline substances. If there is imperfection at 0 K, the entropy will be larger than zero.

Carnot Cycle

- It is an imaginary cycle which demonstrates the maximum conversion of heat into work. It involves four processes

  (i) isothermal reversible expansion;

  (ii) adiabatic reversible expansion;

  (iii) isothermal reversible compression;

  (iv) adiabatic reversible compression.

- The efficiency of a heat engine in a Carnot cycle,

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{q_2 - q_1}{q_2} = \frac{w}{q_2}$$

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