

Thermodynamics and Thermochemistry

Introduction

(1) The branch of science which deals with energy changes during chemical reactions is called **Chemical Energetics**, the branch of science dealing with the quantitative relationships between different forms of energy is known as **Thermodynamics** and the branch dealing with heat changes is called **Thermochemistry**.

Objectives and limitations of thermodynamics

The objectives : (1) To interrelate the various energy changes during physical or chemical transformation.

(2) To predict the feasibility of given change.

(3) To deduce various laws, e.g. phase rule, distribution law, law of mass action etc. thermodynamically.

(4) To systematize the experimental data.

(5) To derive at what conditions, the equilibrium is attained by a change.

The limitations : (1) It's laws are valid for bulk of matter and does not provide information about individual atom.

(2) It predicts feasibility of reaction but fails to suggest rate of reaction.

(3) It fails to explain the systems away from equilibrium.

Terminology of thermodynamics

(1) **System, surroundings and boundary :** The part of the universe chosen for thermodynamic studies is called a **system** and the remaining part of the universe is called in the **surroundings**. Anything which separates system and surroundings is called **boundary**.

(2) **Types of systems :**

(i) A system which can exchange both matter and energy with the surrounding is called **open system**.

(ii) A system which can only exchange energy but not matter with the surroundings is called a **closed system**.

(iii) A system which can neither exchange matter nor energy with the surroundings is called an **isolated system**.

Homogeneous system : A system is supposed to homogeneous if it is uniform throughout *i.e.* all the substances present in it have only one phase.

Heterogeneous system : Not uniform throughout *i.e.*, it has more than one phase.

(3) **Properties of system :** The thermodynamic properties of a system are divided as :

(i) **Intensive properties** : Mass independent properties, e.g. temperature, pressure, viscosity, density, refractive index, surface tension and chemical potential, etc.

(ii) **Extensive properties** : Mass dependent properties, e.g., mass, volume, energy, heat enthalpy and entropy.

Note : □ An extensive property becomes intensive by specifying a unit amount of matter, e.g., mass and volume are extensive but density = M / V is intensive property.

(4) **State variables** : The measurable properties of a system which depend only upon the state of system are known as state variables. e.g. P, V, T , composition; energy etc. The state of the system at a time signify for the fact that the variable factors, e.g. P, V, T etc. (which completely define the state of system) are known.

(5) **Thermodynamic process** : The operations by which the changes from one state to other are made, are known as thermodynamic process. The operations are made in either of the following way :

(i) **Isothermal process** : (a) A process in which temperature of the system remains constant throughout the studies, i.e., $\Delta T = 0$ and also $\Delta E = 0$.

(b) Achieved by thermostatic path.

(ii) **Adiabatic process** : (a) A process during which no exchange of heat takes place in between system and surroundings, i.e., $q = 0$.

(b) Achieved by insulating the system boundaries.

(iii) **Cyclic process** : A process in which initial state of system is regained after a series of operations, i.e., $\Delta E = 0; \Delta H = 0$.

(iv) **Isobaric process** : A process in which pressure of the system remains constant throughout the investigations, i.e., $\Delta P = 0$.

(v) **Isochoric process** : A process in which volume of the system remains constant throughout the investigations, i.e., $\Delta V = 0$.

(vi) **Reversible process** : A reversible process is one in which all changes occurring at any part of the process are exactly reversed, when it is carried out in opposite direction. A reversible process involves :

(a) A slow change during investigations.

(b) Driving force is infinitesimally greater than the opposing force and vice versa.

(c) The process may take place in either direction.

(d) Maximum work is obtained.

(vii) **Irreversible process** : A process whose direction can not be reversed by small change in variables is irreversible process. It involves :

(a) A fast change during investigation.

(b) Driving force is much different than opposing force

(c) The unidirectional process.

(d) Network somewhat lesser than maximum work, is obtained.

Heat, temperature and work

(1) **Heat** is a measure of quantity of energy transferred from one body to other as a result of temperature difference between them.

(2) **Temperature** is a measure of intensity of energy.

(3) **Work** is expressed as the product of two factors. i.e., $W = \text{intensity factor} \times \text{capacity factor}$

Intensity factor is measure of force against which work is done. Capacity factor is the extent for which work is done. i.e. Mechanical work = force \times displacement = $F \times d$

Gravitational work = gravitational force \times height = $mg \times h$

Electrical work = potential difference \times quantity of current = $E \times Q$

Work of expansion = pressure \times change in volume = $P \times \Delta V$

A $-ve$ sign is given for work done by the system.

A $+ve$ sign is given for work done on the system.

The general expression for all types of PV work can be written as $W = -P\Delta V$

For expansion $\Delta V = V_2 - V_1 = +ve$ ($\because V_2 > V_1$)

$\therefore W = -ve$

Thus, work of expansion or work done by the system is $-ve$.

For compression : $\Delta V = V_2 - V_1 = -ve$ ($\because V_2 < V_1$)

$\therefore W = +ve$

Thus, work of compression or work done on the system is $+ve$.

Units of work : $W = \text{dyne cm}$ or erg in C.G.S. = Newton metre or Joule in M.K.S. = calorie

$$1 \text{ cal} = 4.184 \times 10^7 \text{ erg} = 4.184 \text{ J}$$

It is thus, evident that, work heat and energy have same units.

Internal energy and Heat enthalpy

(1) **Internal energy** : Each substance is associated with a definite amount of energy involving the energy depending upon the chemical nature of substance and the conditions of P, V, T . It includes many types of energies such as translational, vibrational, rotational coulombic, potential energy, etc. Therefore, exact magnitude of internal energy cannot be determined. Furthermore, it is a state function and denoted by E and is independent of path. In thermodynamics we deal with the change in internal energy of two states,

$$\Delta E = E_2 - E_1$$

Internal energy is a state function. It is an extensive property.

(2) **Heat enthalpy or heat content** : Enthalpy ' H ' is also a state function and independent of path. It is expressed as $H = E - PV$

Like E , in thermodynamics we deal with change in heat enthalpy ΔH ; $\Delta H = H_2 - H_1$

• **Relation between ΔH and ΔE** : These two are related by $\Delta H = \Delta E + P\Delta V$

at constant volume $\Delta H = \Delta E$ ($\because \Delta V = 0$)

First law of thermodynamics

According to this law, mass and energy of an isolated system remains constant. The law is expressed mathematically as :

$$dq = dE - dW \text{ (for an infinitesimal change) } \dots\dots(1)$$

Where, dE = Change in internal energy, dq = Heat supplied to system, $-dW$ = Work done by the system

Also $q = \Delta E - W \dots\dots(2)$

or $\Delta E = q + W \text{ (for finite change)}$

Some useful formulae based upon 1st law :

(1) **Isothermal process** : $\therefore \Delta t = 0$

\therefore By eq. (2) $q = -W$

i.e., heat given to a system is used in work done by the system.

(2) **Adiabatic process** : $\therefore q = 0$

\therefore By eq. (2) $+\Delta E = W$ or $-\Delta E = -W$

i.e., work is done by the system on the cost of its internal energy.

(3) **Cyclic process** : $\therefore \Delta E = 0$

\therefore By eq. (2) $q = -W$

(4) **Isochoric process.** $\therefore \Delta V = 0$

\therefore By eq. (2) $q_v = \Delta E$

i.e., heat given to a system under constant volume is used up in increasing internal energy.

(5) **Isobaric process** : $\therefore \Delta P = 0$

Consider a system showing increase in volume from V_1 to V_2 at a constant pressure P , during absorption of heat q . The expansion work or work done by the system is $W = -P\Delta V$

Thus by eq. (2) $q_p = \Delta E - (-P\Delta V) = E_2 - E_1 - [-P(V_2 - V_1)] = (E_2 + PV_2) - (E_1 + PV_1)$

$$= H_2 - H_1 \quad (\because H = E + PV)$$

$$q_p = \Delta H$$

i.e., heat given to a system under constant P is used up in increasing heat enthalpy of system.

(6) **Work done in irreversible isothermal process** : Suppose an ideal gas expands against external pressure P and its volume changes by an amount dV then work done W can be given by $W = -PdV$

For a finite change V_1 to V_2 ,

Total work done on the system W is derived by $W = -P(V_2 - V_1)$ or $W_{\text{irr}} = -P(V_2 - V_1)$

If $V_2 > V_1$ then W_{irr} is $-ve$, *i.e.*, expansion work or work done by the system.

If $V_2 < V_1$ then W_{irr} is $+ve$ *i.e.*, compression work or work done on the system.

Thus, at constant V ; $W_{\text{irr}} = 0$

(7) **Work done in isothermal reversible process** : Consider a system under isothermal condition, showing reversible expansion of an ideal gas by a volume dV , then

$$\because \Delta E = 0$$

$$\therefore dq = -dW = +PdV \quad (\because dW = -PdV)$$

The total work done during expansion of gas from V_1 to V_2

$$\int dW = \int_{V_1}^{V_2} -PdV = \int_{V_1}^{V_2} -\frac{nRT}{V} \cdot dV$$

$$W_{rev} = -nRT \log_e \frac{V_2}{V_1} = -2.303 nRT \log_{10} \frac{V_2}{V_1} \quad (\because p \propto 1/V)$$

$$\text{Also } W_{rev} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

(8) **Work done in adiabatic reversible process** : Consider a system under adiabatic conditions, showing reversible expansion of an ideal gas by a volume dV , then from I law of thermodynamics, ($\because dq = 0$)

$$W_{rev} = \frac{nR}{\gamma - 1} [T_2 - T_1]$$

If $T_2 > T_1$ then $W_{rev} = +ve$, i.e., work done on the system

If $T_2 < T_1$ then $W_{rev} = -ve$, i.e., work done by the system

Where γ is Poisson's ratio $= \frac{C_p}{C_v}$

Some important results of adiabatic expansions :

$$PV^\gamma = \text{constant} ; TP^{(1-\gamma)} = \text{constant} ; V^{\gamma-1}T = \text{constant}$$

Joule-Thomson effect

The phenomenon of change of temperature produced when a gas is made to expand adiabatically from a region of high pressure to a region of extremely low pressure through a small jet is called Joule-Thomson effect.

(1) The temperature below which a gas becomes cooler on expansion is known as the inversion temperature T_i . Above this temperature gas shows heating effect.

$$T_i = \frac{2a}{Rb} \quad \text{Where } a \text{ and } b \text{ called vander Waal's constant.}$$

(2) Joule-Thomson effect is zero for an ideal gas in which vander Waals' forces of attraction are negligible and there is no expenditure of energy in overcoming these forces of attraction.

$$\text{Joule-Thomson coefficient } \mu_{JT} \text{ is given by, } \mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial H}{\partial P} \right)_T / C_p$$

$\mu_{JT} = 0$ for an ideal gas, $\mu_{JT} = -ve$ for heating effect, $\mu_{JT} = +ve$ for cooling effect.

Thermochemistry

It is concerned with heat changes accompanying physical and chemical transformations. It is also termed as chemical energetics. It is based on first law of thermodynamics. If E_1 and E_2 represent total energies associated with reactants and products respectively, three cases may arise :

- (1) $E_1 = E_2$ neither heat is evolved nor absorbed. such reactions are very rare.
- (2) $E_1 > E_2$ the difference ($E_1 - E_2$) of energy will be evolved, i.e., heat is evolved.
- (3) $E_1 < E_2$ the difference ($E_2 - E_1$) of energy will be absorbed i.e., heat is absorbed.

The thermochemical equation

(1) A thermochemical equation represents the thermal changes as well as chemical changes taking place during the course of reaction, e.g., $C + O_2 \longrightarrow CO_2$; $\Delta H = -94.3kcal$

(2) A thermochemical equation is treated as an algebraic equation for all practical purposes, e.g., it may be added, subtracted, multiplied or divided as the case may be.

(3) A thermochemical equation should always be written in mole and never in gm.

Exothermic and Endothermic reaction

For a given chemical change, $A + B \longrightarrow C + D$

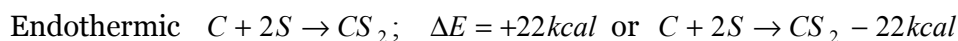
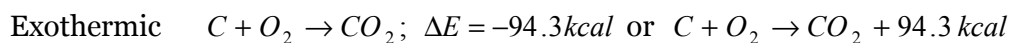
Change in internal energy during reaction (ΔE) = Internal energy of products – internal energy of reactants

$$i.e., \Delta E = \Sigma E_p - \Sigma E_R$$

if $\Delta E = +ve$; the reaction is endothermic

if $\Delta E = -ve$; the reaction is exothermic

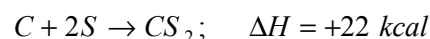
The exothermic and endothermic nature are expressed as :



Heat of reaction

(1) **Heat of reaction :** It is defined as, the amount of heat absorbed or released or the change in internal energy or the change in heat enthalpy during the complete course of reaction as represented by balanced chemical equation e.g., $C + O_2 \rightarrow CO_2$; $\Delta E = -94.3kcal$

i.e., 12 gm C reacts with 32 gm O_2 to give 44 gm CO_2 along with 94.3 kcal of heat evolution,



i.e., 12 gm C reacts with 64gm S to give 76gm CS_2 along with 22.0 kcal of heat absorption.

(2) Factor's influencing heats of reaction

(i) **Condition of constant P or V :** Heat changes at constant volume are expressed in ΔE .

Heat changes at constant pressure are expressed in ΔH .

Also for a change $\Delta H = \Delta E + P\Delta V$ (1)

where P is the pressure and ΔV is change in volume.

Also ΔH and ΔE are related together as

$$\Delta H = \Delta E + \Delta nRT \quad \text{.....(2)}$$

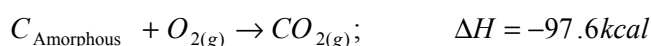
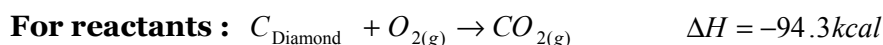
Where ΔH and ΔE are change in enthalpy and change in internal energy for a given change respectively.

Δn = Mole of products – Mole of reactants, R = Molar gas constant, T = Temperature in Kelvin

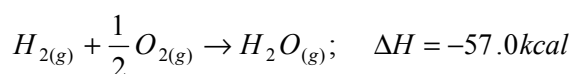
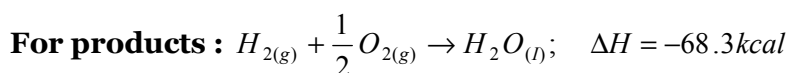
Note : □ While using eq. (2) for numerical one should keep in mind that for Δn

- Count only gaseous phase molecules.
- If $\Delta n = 0$; $\Delta H = \Delta E$.
- Δn may be +ve or –ve integer or fraction.
- Put R in the same units in which ΔH and ΔE are given.
- Normally reactions are carried out at constant pressure and therefore, heat changes are to be taken as ΔH unless stated otherwise.

(ii) **Physical nature of reactants and products :**



where C_D and C_A are diamond and amorphous form of C.



Therefore, it is necessary to write physical state of reactants and products while writing thermochemical equation.

(iii) **Temperature :** The variation of ΔH or ΔE with temperature is expressed in terms of **Kirchhoff's equation** as, $\Delta H_2 - \Delta H_1 = \Delta C_p(T_2 - T_1)$ or $\Delta E_2 - \Delta E_1 = \Delta C_v(T_2 - T_1)$

Where ΔH_2 and ΔE_2 are heats of reaction at temperature T_2

ΔH_1 and ΔE_1 are heats of reaction at temperature T_1

$\Delta C_p = C_p$ of products – C_p of reactants

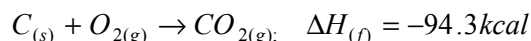
$\Delta C_v = C_v$ of products – C_v of reactants

C_p and C_v are molar specific heats at constant P and V respectively.

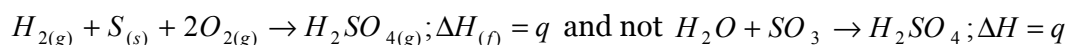
(3) Other terms used for heats of reactions :

(i) **Heat of formation** : It is defined as the change in heat enthalpy or change in internal energy when **one mole** of a substance is formed from its **initial components**, e.g.

(a) CO_2 has C and O atoms therefore, heat of formation of CO_2 is



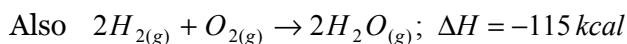
(b) H_2SO_4 has H , S and O atoms therefore, heat of formation of H_2SO_4 is



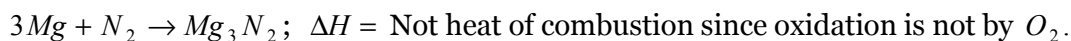
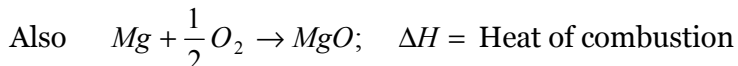
(ii) **Heat of Combustion** : It is defined as the change in heat enthalpy or change in internal energy when **one mole** of a substance is **completely oxidized** in air (O_2), e.g.,



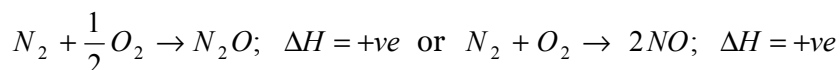
Heat of combustion of C is given by eq. (1) and not by $C + \frac{1}{2}O_2 \rightarrow CO$, since C is not completely oxidized in this case.



but heat of combustion of H_2 is $-115/2$, i.e. since 1 mole H_2 be taken



Note : \square Heats of combustion's are always exothermic except oxidation of N as :



\square In $F_2 + \frac{1}{2}O_2 \rightarrow F_2O$; $\Delta H = +ve$; here O_2 is oxidized and not F_2 , which is reduced.

(iii) **Heat of solution** : It is defined as the change in heat enthalpy or change in internal energy when 1 mole of the solute is dissolved in excess of solvent so that further dilution does not bring any heat change. further on dissolution of an electrolyte in water;

(a) Heat of ionisation (ΔH_i) is required to separate ions from each other, i.e. $\Delta H_i = +ve$.

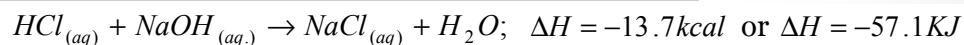
(b) Heat of hydration is given out during hydration of ions, i.e., $\Delta H_h = -ve$.

Therefore, $\Delta H_s = \Delta H_i + \Delta H_h$



if $\Delta H_i < \Delta H_h$ then $\Delta H_s = -ve$

(iv) **Heat of neutralization** : It is defined as the change in heat enthalpy or change in internal energy when 1gm equivalent of an acid reacts completely with 1gm equivalent of base in dilute solution. Dilute solution refers for complete ionisation of acids and bases for e.g.,

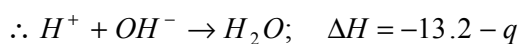
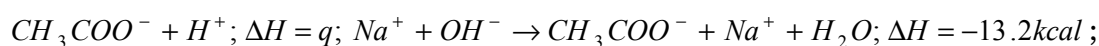


In dilute solutions, $H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O; \quad \Delta H = -13.7kcal$

or $H^+ + OH^- \rightarrow H_2O; \quad \Delta H = -13.7kcal$

i.e., heat of neutralization is also defined as heat of formation of water from H^+ and OH^- ions.

In case of weak acids or weak bases the observed value is little lower because a part of it is used in dissociating weak acid or weak base which is not at all completely ionised at dilute solution conditions. These are, however, completely ionised at infinite dilution, e.g.,



$$\therefore -13.2 - q = -13.7; \quad \Delta H = \text{less than } 57.1 KJ$$

$\therefore q = 0.5 kcal$; where q is heat of dissociation of weak acid.

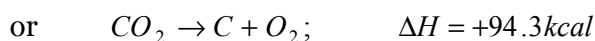
(v) **Heat of fusion** : Heat absorbed in converting one mole of solid into the liquid at its melting point.

(vi) **Heat of vaporisation** : Heat absorbed in converting one mole of a liquid into its vapours at its boiling point.

(vii) **Heat of sublimation** : Heat absorbed in converting one mole of solid directly into its vapour.

Law of thermochemistry

(1) **Lavoisier and Laplace law**: The heat enthalpy change or internal energy change in a chemical reaction is equal but opposite to that of heat change, when heat reaction is reversed, e.g.,

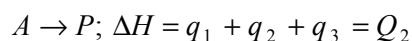


(2) **Hess's law of constant heat summation** : Whether a reaction is made by method or by other, in one step or in several steps, the total change in heat enthalpy or internal energy remains constant throughout the complete course of reaction, e.g.,

I Method



II Method



Therefore, according to Hess's law, $Q_1 = Q_2$

The law has been verified theoretically, however experimental verification is not possible.

Application of Hess's law

(i) To determine heat of transition i.e., conversion of one allotropic modification to another.

(ii) To determine heat of intermediate steps in a reaction.

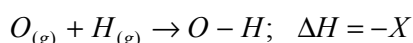
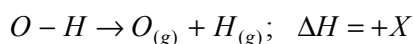
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(iii) To calculate heat of reactions of known or unknown reactions.

(iv) To calculate bond energies.

Bond energy

The change in heat enthalpy when a bond is broken into (or produced from), isolated gaseous atoms.

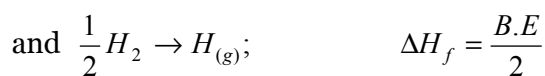
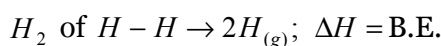


Thus, bond energy is +ve when bond is broken up and bond energy is -ve when bond is formed.

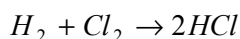
Note : □ Bond energy values are normally given by +ve sign for breaking up of bond.

□ Bond energy data is normally expressed per mole.

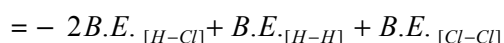
□ For like atoms bonds.



□ For solving bond energy numericals say



$\Delta H = B.E.$ data of formation of bond + $B.E.$ data of dissociation of bond

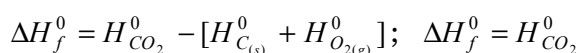
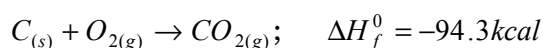


Since bond formation is always exothermic.

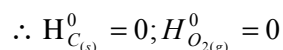
Standard heat of formation and heat enthalpy

(1) Standard heat enthalpy H^0 of a substance is its heat enthalpy at $25^\circ C$ and $1 \text{ atm } P$.

(2) Consider formation of a substance say CO_2 from its components at $25^\circ C$ and $1 \text{ atm } P$.



Since H^0 values for pure elements has been assumed to be zero



i.e., standard heat of formation of a substance = standard heat enthalpy of that substance.

Spontaneous process

The physical or chemical process which occurs in a particular set of conditions either of its own or after proper initiation is known as **spontaneous process**. All natural processes are spontaneous processes. Spontaneous process cannot reverse of their own.

A process that does not occur of its own i.e., a process which does not have any natural tendency to occur is termed as **non-spontaneous processes**. Lifting of water to higher level with the help of electric motor is a non-spontaneous processes.

Driving force : It is the force which makes the process to occur by itself. It is the resultant of two basic tendencies :

- Tendency to attain a state of minimum energy.
- Tendency to attain a state of maximum randomness.

Entropy (S) is a state function and is a measure of degree or disorder or randomness of system. More is the disorder in system, higher is its entropy. It is normally expressed in terms of change in entropy.

(1) For a reaction change (ΔS) is given by, $\Delta S = \Sigma S_{\text{products}} - \Sigma S_{\text{Reactants}}$

$$(2) \Delta S = \frac{q_{\text{rev}}}{T} = \frac{W_{\text{rev}}}{T} = \frac{nRT \log_e \frac{V_2}{V_1}}{T} = nR \log_e \frac{V_2}{V_1} = 2.303 nR \log_{10} \frac{V_2}{V_1} = 2.303 nR \log_{10} \frac{P_1}{P_2}$$

Where, q_{rev} is the heat supplied to a system at temperature $T^\circ (K)$ under reversible conditions.

(3) At constant P , $q_{\text{rev}} = \Delta H_{\text{rev}}$, $\Delta S = \frac{\Delta H_{\text{rev}}}{T}$

i.e., entropy change of fusion : $\Delta S_f = \frac{\Delta H_f}{T}$ Where T is freezing point

and entropy change of vaporization : $\Delta S_v = \frac{\Delta H_v}{T}$ Where T is boiling point

(4) Entropy of one mole of a substance in pure state at one atmosphere and $25^\circ C$ is termed as standard entropy, S° .

For a reaction in standard state, $A \rightarrow B$, $\Delta S^\circ = S_B^\circ - S_A^\circ$

(5) Entropy, S , is related to thermodynamic probability, W by the relation :

$$S = k \log_e W \text{ or } S = 2.303 k \log_{10} W \text{ Where } k \text{ is Boltzmann's constant.}$$

(6) At absolute zero temperature, a solid is supposed to have highly ordered state, i.e., $W=1$ and hence $S=0$, i.e., $\lim_{T \rightarrow 0} S = 0$; **This is zeroth law of thermodynamics.**

Free energy F or G

Free energy (F or G) is also a state function and is a measure of maximum work done. It is expressed as

$$G = H - TS \text{ or } \Delta G = \Delta H - T \Delta S \text{ at constant}$$

Standard free energy change (ΔG°):

(1) $\Delta G^\circ = -2.303 RT \log_{10} K$

(2) At equilibrium $\Delta G = 0$

(3) The decrease in free energy ($-\Delta G$) is given as : $-\Delta G = W_{\text{net}} = 2.303 nRT \log_{10} \frac{V_2}{V_1}$

(4) ΔG_f^0 for free elemental state = 0 .

(5) $\Delta G_f^0 = G_{\text{Reactants}}^0$

• **Conditions for spontaneity of reaction :** For a spontaneous change $\Delta G = -ve$. Thus following results can also be evaluated for spontaneous process.

ΔH	ΔS		$\Delta H - T\Delta S$	Nature
$-ve$	$+ve$	\therefore	$\Delta G = -ve$	Spontaneous
$+ve$	$-ve$	\therefore	$\Delta G = +ve$	Non spontaneous
$+ve$	$+ve$	if	$\Delta H < T\Delta S; \Delta G = -ve$	Spontaneous
$-ve$	$-ve$		$\Delta G = -ve$	Spontaneous
		if	$\Delta H > T\Delta S$ i.e., T is low	
			$\Delta G = +ve$	Non spontaneous
		if	$\Delta H < T\Delta S$ i.e., T is high	

Second law of thermodynamics

(1) It is impossible to transfer heat from a cold to hot reservoir without doing some work. (Clausius)

(2) It is impossible to obtain work by cooling a body below its lowest temperature. (Kelvin)

(3) It is impossible to construct a machine functioning in cycle which can convert heat completely into equivalent amount of work without producing changes elsewhere, i.e., perpetual motions are not allowed. (Ostwald)

(4) Entropy of the universe is always increasing.

(5) It is impossible to take heat from a hot reservoir and convert it completely into work by a cyclic process without transferring a part of it to a cold reservoir.

(6) Carnot cycle having efficiency η

$$\eta = \frac{W}{Q_2} = \frac{T_2 - T_1}{T_2} = \frac{Q_2 - Q_1}{Q_2}$$

Where Q_2 is the heat absorbed from the source at T_2 and $-Q_1$ is the heat lost to the sink at T_1 . From equation

$$\eta = 1 - \frac{T_1}{T_2} = 1 - \frac{Q_1}{Q_2}$$

Thus "It is impossible to convert heat into equivalent amount of work without compensation".

(i) $\eta = 1$ (100% efficiency) only when $T_1 = 0K$ (i.e. $-273^\circ C$) which is not practically possible.

(ii) Greater the difference between T_2 and T_1 greater is the value of η . Hence superheated steam (under high pressure) is used in an engine with a boiler.

Gibb's-Helmholtz equations

It interrelates ΔG and ΔH at constant pressure :

$$\Delta G = \Delta H + T \left[\frac{\delta(\Delta G)}{\delta T} \right]_p \quad \text{or} \quad \frac{\Delta G - \Delta H}{T} = \left[\frac{\delta(\Delta G)}{\Delta T} \right]_p \quad \text{or} \quad -\Delta S = \left[\frac{\delta(\Delta G)}{dT} \right]_p$$

$$\Delta S = nF \left[\frac{\delta E_{\text{cell}}}{\delta T} \right]_p \quad (\because \Delta G = -nEF)$$

Thus temperature coefficient of the emf of a cell is, $\left[\frac{\delta E_{\text{cell}}}{dT} \right]_p \frac{\Delta S}{nF}$

Temperature dependence of vapour state or The Clapeyron-Clausius equation

Variation of the vapour pressure for the liquid \rightleftharpoons gas equilibrium is given by Clapeyron-Clausius equation.

$$\log P = -\frac{\Delta H_v}{2.303 R} \left(\frac{1}{T} \right) + K$$

Equation is, represents the equation of a straight line. Hence the plot of $\log P$ vs $\frac{1}{T}$ yields a straight line with slope = $-\frac{\Delta H_v}{2.303 R}$ and intercept = K . This enables the evaluation of ΔH_v , the **latent heat of vaporisation**.

If vapour pressures P_1 and P_2 at temperature T_1 and T_2 are known then by equation.

$$\log P = \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Third law of thermodynamics

The entropy of a substance at absolute zero (zero *Kelvin*) is taken to be zero. The importance of law lies in calculating absolute entropies of pure substances at different temperatures. This is possible by knowing the values of heat capacities (C_p) at number of temperature between $0K$ and TK .

$$\Delta S = \int_0^T C_p d \log T = 2.303 \int C_p d \log T$$

The plot of C_p vs $\log T$ gives the value of integral. It should be noted that this law is true only for the substances which exist in perfect crystalline form at $0K$. However, if there are imperfections at $0K$, then entropy will be larger than zero.

Limitations :

- (1) Glassy solids even at $0K$ has entropy greater than zero.
- (2) Solids having mixtures of isotopes do not have zero entropy at $0K$. For example entropy of solid chlorine is not zero
- (3) Crystals of CO , N_2O , NO , H_2O etc. do not have perfect order even at $0K$ thus their entropy is not equal to zero.

Some important points

(1) Since molar heat capacities of solids are approx. equal to one another, *i.e.*, ΔC_p or $\Delta C_v = 0$.

Therefore, ΔH of reactions involving only solids do not change appreciably with temperature $\frac{C_p}{C_v} = \gamma$

(2) The value of γ depends upon the atomicity of gaseous molecules. Thus

$\gamma = 1.66$, for monoatomic gases (*He, Ne, Ar*)

$\gamma = 1.40$, for diatomic gases (*O₂, H₂, N₂, Cl₂*)

$\gamma = 1.33$, for triatomic gases (*SO₂, O₃, CO₂*)

(3) 1 cal > 1 joule > 1 erg.

(4) Sign conventions :

If work is done on the system, $W + ve$.

If work is done by the system, $W - ve$

If heat is absorbed by the system, q or $\Delta H + ve$

If heat is given out by the system, q or $\Delta H - ve$

If energy is absorbed by the system *i.e.*, internal energy increases, $\Delta E + ve$

If energy is released *i.e.* *I.E.* of the system decreases $\Delta E - ve$

(5) For organic compounds belonging to the same homologous series, enthalpy of combustion increases with increase in molecular mass, but calorific value decreases

(6) A metallic element with higher atomic mass has a lower specific heat and vice versa (**Dulong and Petit's rule**)

(7) Graphical representation of four thermodynamic processes is as follows :

