Thermodynamics and Thermochemistry

Thermodynamics

Thermodynamics (Greek word thermo means heat and dynamics means motion) is the branch of science which deals with the study of different forms of energy and the quantitative relationships between them.

The complete study of thermodynamics is based upon three generalizations called first, second and third law of thermodynamics. These laws have been arrived purely on the basis of human experience and there is no theoretical proof for any of these laws.

Basic concepts

(1) **System, surroundings and Boundary :** A specified part of the universe which is under observation is called the *system* and the remaining portion of the universe which is not a part of the system is called the *surroundings*.

The system and the surroundings are separated by *real or imaginary boundaries*. The boundary also defines the limits of the system. The system and the surroundings can interact across the boundary.

(2) **Types of systems**

(i) *Isolated system* : This type of system has no interaction with its surroundings. The boundary is sealed and insulated. Neither matter nor energy can be exchanged with surrounding. A substance contained in an ideal thermos flask is an example of an isolated system.

(ii) *Closed system* : This type of system can exchange energy in the form of heat, work or radiations but not matter with its surroundings. The boundary between system and surroundings is sealed but not insulated. For example, liquid in contact with vapour in a sealed tube and pressure cooker.

(iii) *Open system* : This type of system can exchange matter as well as energy with its surroundings. The boundary is neither sealed nor insulated. Sodium reacting with water in an open beaker is an example of open system.

(iv) *Homogeneous system* : A system is said to be homogeneous when it is completely uniform throughout. A homogeneous system is made of one phase only. Examples: a pure single solid, liquid or gas, mixture of gases and a true solution.

(v) *Heterogeneous system* : A system is said to be heterogeneous when it is not uniform throughout, *i.e.*, it consist of two or more phases. Examples : ice in contact with water, two or more immiscible liquids, insoluble solid in contact with a liquid, a liquid in contact with vapour, etc.

(vi) *Macroscopic system* : A macroscopic system is one in which there are a large number of particles (may be molecules, atoms, ions etc.)

(3) **Macroscopic properties of the system**

Thermodynamics deals with matter in terms of bulk (large number of chemical species) behaviour. The properties of the system which arise from the bulk behaviour of matter are called *macroscopic properties*. The common examples of macroscopic properties are pressure, volume, temperature, surface tension, viscosity, density, refractive index, etc.

The macroscopic properties can be subdivided into two types,

(i) *Intensive properties* : The properties which do not depend upon the quantity of matter present in the system or size of the system are called *intensive properties*. Its examples are pressure, temperature, density, specific heat, surface tension, refractive index,

viscosity, melting point, boiling point, volume per mole, concentration etc.

(ii) *Extensive properties* **:** The properties whose magnitude depends upon the quantity of matter present in the system are called *extensive properties*. Its examples are total mass, volume, internal energy, enthalpy, entropy etc. These properties are additive in nature.

Any extensive property if expressed as per mole or per gram becomes an intensive property.

(4) **State of a system and State Variables**

Macroscopic properties which determine the state of a system are referred to as *state variables* or *state functions* or *thermodynamic parameters*. The change in the state properties depends only upon the *initial and final states of the system*, but it is independent of the manner in which the change has been brought about. In other words, the state properties do not depend upon a path followed.

(5) **Thermodynamic equilibrium :** *"A system is said to have attained a state of thermodynamic equilibrium when it shows no further tendency to change its property with time".*

The criterion for thermodynamic equilibrium requires that the following three types of equilibrium exist simultaneously in a system,

(i) *Chemical Equilibrium* **:** A system in which the composition of the system remains fixed and definite.

(ii) *Mechanical Equilibrium* **:** No chemical work is done between different parts of the system or between the system and surrounding. It can be achieved by keeping pressure constant.

(iii) *Thermal Equilibrium* **:** Temperature remains constant *i.e.* no flow of heat between system and surrounding.

(6) **Thermodynamic process :** When the thermodynamic system changes from one state to another, the operation is called a **process**. The various types of the processes are

(i) *Isothermal process* **:** In this process operation is done at constant temperature. $dT = 0$ thus $\Delta E = 0$.

(ii) *Adiabatic process* **:** In this a process there is no exchange of heat takes place between the system and surroundings. The system is thermally isolated, i.e., $dQ = 0$ and its boundaries are insulated.

(iii) *Isobaric process* **:** In this process the pressure remains constant throughout the change i.e., $dP = 0$.

(iv) *Isochoric process* **:** In this process volume remains constant throughout the change, *i.e., dV* = 0.

(v) *Cyclic process* **:** When a system undergoes a number of different processes and finally return to its initial state, it is termed *cyclic process*. For a cyclic process $dE = 0$ and $dH = 0$.

(vi) *Reversible process* **:** A process which occurs infinitesimally slowly, i.e. opposing force is infinitesimally smaller than driving force and when infinitesimal increase in the opposing force can reverse the process, it is said to be *reversible process*.

(vii) *Irreversible process* **:** When the process occurs from initial to final state in single step in finite time and cannot be reversed, it is termed an *irreversible process*. Amount of entropy increases in irreversible process.

Irreversible processes are spontaneous in nature. All natural processes are irreversible in nature

Internal energy, heat and Work

(1) **Internal energy** (E) **:** "*Every system having some quantity of matter is associated with a definite amount of energy. This energy is known as internal energy.*"

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}} + \ldots\ldots$$

(i) *Characteristics of internal energy*

(a) Internal energy of a system is an extensive property.

(b) Internal energy is a state property.

(c) The change in the internal energy does not depend on the path by which the final state is reached.

(d) There is no change in internal energy in a cyclic process.

(e) The internal energy of an ideal gas is a function of temperature only.

(f) Internal energy of a system depends upon the quantity of substance, its chemical nature, temperature, pressure and volume.

(g) The unit of E is ergs in *CGS* or joules in *SI*

$1\ Joule = 10^7\ ergs.$

(ii) *Change in internal energy* (ΔE) **:** It is neither possible nor necessary to calculate the absolute value of internal energy of a system then, $\Delta E = E_f - E_{in}$; ΔE is positive if $E_f > E_{in}$ and negative if $E_f < E_{in}$.

(2) **Heat** (q) **and work** (w) **:** The energy of a system may increase or decrease in several ways but two common ways are *heat and work*.

Heat is a form of energy. It flows from one system to another because of the difference in temperature between them. Heat flows from higher temperature to lower temperature. Therefore, it is regarded as *energy on the move*.

Work is said to be performed if the point of application of force is displaced in the direction of the force. It is equal to the force multiplied by the displacement (distance through which the force acts).

There are three main types of work which we generally come across. These are, Gravitational work, electrical work and mechanical work.

Mechanical work = Force $\times$ displacement = F.d

Electrical work = potential difference $\times$ charge = V.q

Gravitational work = *mgh*

(i) **Units of heat and work :** The heat changes are measured in calories (cal), Kilo calories (kcal), joules (*J*) or kilo joules (*kJ*)**.** These are related as, 1 *cal* = 4.184 *J;* 1*kcal* = 4.184*kJ*

The *S.I.* unit of heat is joule (*J*) or *kilojoule*. The Joule (*J*) is equal to *Newton – metre* (1 *J*= 1 *Nm*).

Work is measured in terms of ergs or joules. The *S.I.* unit of work is Joule.

$$1 \ Joule = 10^7 \ ergs = 0.2390 \ cal.$$

$$1 \ cal \ > 1 \ joule > 1 \ erg$$

(ii) **Sign conventions for heat and work**

Heat absorbed by the system = q positive

Heat evolved by the system = q negative

Work done on the system = w positive

Work done by the system = w negative.

Zeroth law of thermodynamics

This law forms the basis of concept of temperature. This law can be stated as follows,

"*If a system A is in thermal equilibrium with a system C and if B is also in thermal equilibrium with system C, then A and B are in thermal equilibrium with each other whatever the composition of the system.*"
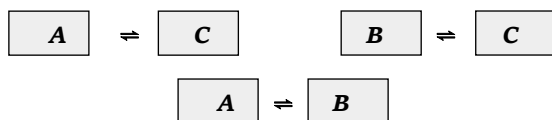
First law of thermodynamics

Helmholtz and Robert Mayer proposed first law of thermodynamics. This law is also known as *law of conservation of energy*. It states that,

"*Energy can neither be created nor destroyed although it can be converted from one form into another.*"

$$E_2 - E_1 = \Delta E = q + w$$

i.e. (Change in internal energy) = (Heat added to the system) +(Work done on the system)

If a system does work (w) on the surroundings, its internal energy decreases. In this case, $\Delta E = q + (-w) = q - w$

i.e.(Change in internal energy)=(Heat added to the system) – (work done by the system)

The relationship between internal energy, work and heat is a mathematical *statement of first law of thermodynamics.*

Enthalpy and Enthalpy change

Heat content of a system at constant pressure is called *enthalpy* denoted by '*H*'.

From first law of thermodynamics, $q = E + PV$ ....(i)

Heat change at constant pressure can be given as

$$\Delta q = \Delta E + P\Delta V$$
..........(ii)

At constant pressure heat can be replaced at enthalpy.

$$\Delta H = \Delta E + P\Delta V$$
.........(iii)

$\therefore \Delta H =$ Heat change or heat of reaction (in chemical process) at constant pressure

$\Delta E =$ Heat change or heat of reaction at constant volume.

In case of solids and liquids participating in a reaction,

$$\Delta H = \Delta E (P\Delta V \approx 0)$$

Difference between ΔH and ΔE is significant when gases are involved in chemical reaction.

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

$$\Delta H = \Delta E + \Delta nRT$$

$$P\Delta V = \Delta nRT$$

Here, $\Delta n = n_P - n_R$

Specific and Molar heat capacity

(1) **Specific heat** (or specific heat capacity) of a substance is the quantity of heat (in *calories, joules, kcal,* or *kilo joules*) required to raise the temperature of 1*g* of that substance through $1^o C$. It can be measured at constant pressure (c_p) and at constant volume (c_v).

(2) **Molar heat capacity** of a substance is the quantity of heat required to raise the temperature of 1 *mole* of the substance by $1^o C$.

$\therefore$ Molar heat capacity = Specific heat capacity $\times$ Molecular weight, *i.e.*, $C_v = c_v \times M$ and $C_p = c_p \times M$.

(3) Since gases on heating show considerable tendency towards expansion if heated under constant pressure conditions, an additional energy has to be supplied for raising its temperature by 1^oC relative to that required under constant volume conditions, *i.e.,*

$C_p > C_v$ or $C_p = C_v + \text{Work done in expansion, } P\Delta V(= R)$

where, C_p = molar heat capacity at constant pressure

C_v = molar heat capacity at constant volume.

(4) **Some useful relations of C_p and C_v**

(i) $C_p - C_v = R = 2\, calories = 8.314\, J$

(ii) $C_v = \dfrac{3}{2}R$ (for monoatomic gas) and $C_v = \dfrac{3}{2} + x$

(for *di* and polyatomic gas), where *x* varies from gas to gas.

(iii) $\dfrac{C_p}{C_v} = \gamma$ (Ratio of molar capacities)

(iv) For monoatomic gas, $C_v = 3\, calories$ whereas, $C_p = C_v + R = 5\, calories$

(v) For monoatomic gas, $(\gamma) = \dfrac{C_p}{C_v} = \dfrac{\frac{5}{2}R}{\frac{3}{2}R} = 1.66$

(vi) For diatomic gas $(\gamma) = \dfrac{C_p}{C_v} = \dfrac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$

(vii) For triatomic gas $(\gamma) = \dfrac{C_p}{C_v} = \dfrac{8R}{6R} = 1.33$

Expansion of an ideal gas

(1) **Isothermal Expansion** : For an isothermal expansion, $\Delta T = 0$; $\Delta E = 0$.

According to first law of thermodynamics,

$$\Delta E = q + w \qquad \therefore q = -w$$

This shows that in isothermal expansion, the work is done by the system at the expense of heat absorbed.

Since for isothermal process, ΔE and ΔT are zero respectively, hence, $\Delta H = 0$

(i) ***Work done in reversible isothermal expansion*** : Consider an ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. The cylinder is not insulated. The external pressure, P_{ext} is equal to pressure of the gas, P_{gas}.

$$P_{ext} = P_{gas} = P$$

If the external pressure is decreased by an infinitesimal amount *dP*, the gas will expand by an infinitesimal volume, *dV*. As a result of expansion, the pressure of the gas within the cylinder falls to $P_{gas} - dP$, *i.e.,* it becomes again equal to the external pressure and, thus, the piston comes to rest. Such a process is repeated for a number of times, *i.e.,* in each step the gas expands by a volume *dV*.
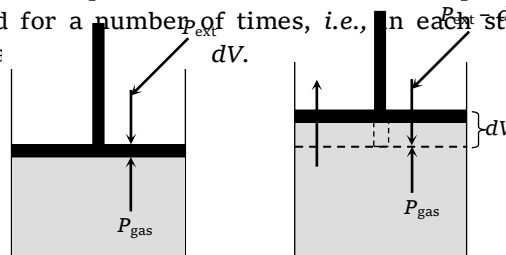

Fig. 10.1

Since the system is in thermal equilibrium with the surroundings, the infinitesimally small cooling produced due to expansion is balanced by the absorption of heat from the surroundings and the temperature remains constant throughout the expansion.

The work done by the gas in each step of expansion can be given as,

$$d_w = -(P_{ext} - dP)dV = -P_{ext}.dV - dP\,.\,dV$$

$dP.dV$, the product of two infinitesimal quantities, is negligible.

The total amount of work done by the isothermal reversible expansion of the ideal gas from volume V_1 to volume V_2 is, given as, $w = -nRT \log_e \dfrac{V_2}{V_1}$ or

$$w = -2.303\, nRT \log_{10} \dfrac{V_2}{V_1}$$

At constant temperature, according to Boyle's law,

$P_1 V_1 = P_2 V_2$ or $\dfrac{V_2}{V_1} = \dfrac{P_1}{P_2}$ So, $w = -2.303\, nRT \log_{10} \dfrac{P_1}{P_2}$

Isothermal compression work of an ideal gas may be derived similarly and it has exactly the same value with positive sign.

$$w_{compression} = 2.303\, nRT \log \dfrac{V_1}{V_2} = 2.303\, nRT \log \dfrac{P_2}{P_1}$$

(ii) ***Work done in irreversible isothermal expansion*** : Two types of irreversible isothermal expansions are observed, *i.e.,* (a) Free expansion and (b) Intermediate expansion. In free expansion, the external pressure is zero, *i.e.,* work done is zero when gas expands in vacuum. In intermediate expansion, the external pressure is less than gas pressure. So, the work done when volume changes from V_1 to V_2 is given by

$$w = -\int_{V_1}^{V_2} P_{ext} \times dV = -P_{ext}(V_2 - V_1)$$

Since P_{ext} is less than the pressure of the gas, the work done during intermediate expansion is numerically less than the work done during reversible isothermal expansion in which P_{ext} is almost equal to P_{gas}.

(2) **Adiabatic Expansion :** In adiabatic expansion, no heat is allowed to enter or leave the system, hence, $q = 0$.

According to first law of thermodynamics,
$$\Delta E = q + w \quad \therefore \quad \Delta E = w$$

work is done by the gas during expansion at the expense of internal energy. In expansion, ΔE decreases while in compression ΔE increases.

The molar specific heat capacity at constant volume of an ideal gas is given by

$$C_v = \left(\frac{dE}{dT}\right)_v \text{ or } dE = C_v.dT$$

and for finite change $\Delta E = C_v \Delta T$ So, $w = \Delta E = C_v \Delta T$

The value of ΔT depends upon the process whether it is reversible or irreversible.

(i) *Reversible adiabatic expansion* : The following relationships are followed by an ideal gas under reversible adiabatic expansion.

$$PV^\gamma = \text{constant}$$

where, P = External pressure, V = Volume

$$\gamma = \frac{C_p}{C_v}$$

where, C_p = molar specific heat capacity at constant pressure, C_v = molar specific heat capacity at constant volume.

$$\left(\frac{T_1}{T_2}\right)^\gamma = \left(\frac{P_1}{P_2}\right)^{\gamma-1} = \left(\frac{P_2}{P_1}\right)^{1-\gamma}$$

knowing γ, P_1, P_2 and initial temperature T_1, the final temperature T_2 can be evaluated.

(ii) *Irreversible adiabatic expansion* : In free expansion, the external pressure is zero, *i.e,* work done is zero. Accordingly, ΔE which is equal to w is also zero. If ΔE is zero, ΔT should be zero. Thus, in free expansion (adiabatically), $\Delta T = 0$, $\Delta E = 0$, $w = 0$ and $\Delta H = 0$.

In intermediate expansion, the volume changes from V_1 to V_2 against external pressure, P_{ext}.

$$w = -P_{ext}(V_2 - V_1) = -P_{ext}\left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1}\right)$$

$$= -P_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right) \times R$$

or $w = C_v(T_2 - T_1) = -RP_{ext}\left(\frac{T_2P_1 - T_1P_2}{P_1P_2}\right)$

Spontaneous and Non-spontaneous processes

A process which can take place by itself under the given set of conditions once it has been initiated if necessary, is said to be a *spontaneous process*. In other words, a spontaneous process is a process that can occur without work being done on it. The spontaneous processes are also called *feasible* or *probable processes*.

On the other hand, the processes which are forbidden and are made to take place only by supplying energy continuously from outside the system are called *non-spontaneous processes*. In other words, non spontaneous processes can be brought about by doing work.

Examples of Spontaneous and Non-spontaneous processes

(1) The diffusion of the solute from a concentrated solution to a dilute solution occurs when these are brought into contact is spontaneous process.

(2) Mixing of different gases is spontaneous process.

(3) Heat flows from a hot reservoir to a cold reservoir is spontaneous process.

(4) Electricity flows from high potential to low potential is spontaneous process.

(5) Expansion of an ideal gas into vacuum through a pinhole is spontaneous process.

All the above spontaneous processes becomes non-spontaneous when we reverse them by doing work.

Spontaneous process and Enthalpy change : A spontaneous process is accompanied by decrease in internal energy or enthalpy, *i.e.,* work can be obtained by the spontaneous process. It indicates that only exothermic reactions are spontaneous. But the melting of ice and evaporation of water are endothermic processes which also proceeds spontaneously. It means, there is some other factor in addition to enthalpy change (ΔH) which explains the spontaneous nature of the system. This factor is entropy.

Second law of thermodynamics

All the limitations of the first law of thermodynamics can be remove by the second law of thermodynamics. This law is generalisation of certain experiences about heat engines and refrigerators. It has been stated in a number of ways, but all the statements are logically equivalent to one another.

(1) **Statements of the law**

(i) *Kelvin statement* : *"It is impossible to derive a continuous supply of work by cooling a body to a*

temperature lower than that of the coldest of its surroundings.”

(ii) *Clausius statement* : *“It is impossible for a self acting machine, unaided by any external agency, to transfer heat from one body to another at a higher temperature or Heat cannot itself pass from a colder body to a hotter body, but tends invariably towards a lower thermal level.”*

(iii) *Ostwald statement* : *“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.”*

(iv) *Carnot statement* : *“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.”*

(2) **Proof of the law** : No rigorous proof is available for the second law. The formulation of the second law is based upon the observations and has yet to be disproved. No deviations of this law have so far been reported. However, the law is applicable to cyclic processes only.

The Carnot cycle

Carnot, a *French engineer*, in 1824 employed merely theoretical and an imaginary reversible cycle known as carnot cycle to demonstrate the maximum convertibility of heat into work.

The system consists of one mole of an ideal gas enclosed in a cylinder fitted with a piston, which is subjected to a series of four successive operations.

For cyclic process, the essential condition is that net work done is equal to heat absorbed. This condition is satisfied in a carnot cycle.

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2} = \text{Thermodynamic efficiency}$$

Thus, the larger the temperature difference between high and low temperature reservoirs, the more the heat converted into work by the heat engine.

Since $\frac{T_2 - T_1}{T_2} < 1$, it follows that $w < q_2$. This means

that only a part of heat absorbed by the system at the higher temperature is transformed into work. The rest of the heat is given out to surroundings. The efficiency of the heat engine is always less then 1. This has led to the following enunciation of the second law of thermodynamics.

It is impossible to convert heat into work without compensation.

Entropy and Entropy change

(1) **Definition :** Entropy is a thermodynamic state quantity which is a measure of randomness or disorder of the molecules of the system.

Entropy is represented by the symbol “S”. It is difficult to define the actual entropy of a system. It is more convenient to define the change of entropy during a change of state.

The entropy change of a system may be defined as the integral of all the terms involving heat exchanged (q) divided by the absolute temperature (T) during each infinitesimally small change of the process carried out reversibly at constant temperature.

$$\Delta S = S_{final} - S_{initial} = \frac{q_{rev}}{T}$$

If heat is absorbed, then $\Delta S = +ve$ and if heat is evolved, then $\Delta S = -ve$.

(2) **Units of entropy :** Since entropy change is expressed by a heat term divided by temperature, it is expressed in terms of *calorie per degree, i.e.,* cal deg^{-1} . In *SI* units, the entropy is expressed in terms of joule per degree Kelvin, i.e., JK^{-1} .

(3) **Characteristics of entropy :** The important characteristics of entropy are summed up below

(i) Entropy is an extensive property. Its value depends upon the amount of the substance present in the system.

(ii) Entropy of a system is a state function. It depends upon the state variables (T, p, V, n).

(iii) The change in entropy in going from one state to another is independent of the path.

(iv) The change in entropy for a cyclic process is always zero.

(v) The total entropy change of an isolated system is equal to the entropy change of system and entropy change of the surroundings. The sum is called *entropy change of universe*.

$$\Delta S_{\text{universe}} = \Delta S_{sys} + \Delta S_{Surr}$$

(a) In a reversible process, $\Delta S_{universe} = 0$ and, therefore

$$\Delta S_{sys} = -\Delta S_{Surr}$$

(b) In an irreversible process, $\Delta S_{universe} > 0$. This means that there is increase in entropy of universe is spontaneous changes.

(vi) Entropy is a measure of unavailable energy for useful work.

Unavailable energy = Entropy × Temperature

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

$$S = k \log_e W \text{ and } S = 2.303 \, k \log_{10} W$$

where, k is Boltzmann's constant

(4) **Entropy changes in system & surroundings and total entropy change for Exothermic and Endothermic reactions :** Heat increases the thermal motion of the atoms or molecules and increases their disorder and hence their entropy. In case of an exothermic process, the heat escapes into the surroundings and therefore, entropy of the surroundings increases on the other hand in case of endothermic process, the heat enters the system from the surroundings and therefore. The entropy of the surroundings decreases.

In general, there will be an overall increase of the total entropy (or disorder) whenever the disorder of the surroundings is greater than the decrease in disorder of the system. The process will be *spontaneous only when the total entropy increases*.

(5) **Entropy change during phase transition :** The change of matter from one state (solid, liquid or gas) to another is called *phase transition*. Such changes occur at definite temperature such as melting point (solid to liquid). boiling point (liquid to vapours) etc, and are accompanied by absorption or evolution of heat.

When a solid changes into a liquid at its fusion temperature, there is absorption of heat (latent heat). Let ΔH_f be the molar heat of fusion. The entropy change will be

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

Similarly, if the latent heat of vaporisation and sublimation are denoted by ΔH_{vap} and ΔH_{sub}, respectively, the entropy of vaporisation and sublimation are given by

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \quad \text{and} \quad \Delta S_{sub} = \frac{\Delta H_{sub}}{T_s}$$

Since $\Delta H_f, \Delta H_{vap}$ and ΔH_{Sub} are all positive, these processes are accompanied by increase of entropy and the reverse processes are accompanied by decrease in entropy.

(6) **Entropy change for an ideal gas :** In going from initial to final state, the entropy change, ΔS for an ideal gas is given by the following relations,

(i) When T and V are two variables,

$$\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \, .$$ Assuming C_v is constant

(ii) When T and p are two variables,

$$\Delta S = nC_P \ln \frac{T_2}{T_1} - nR \ln \frac{p_2}{p_1} \, .$$ Assuming C_p, is constant

(a) Thus, for an *isothermal process* (T constant),

$$\Delta S = nR \ln \frac{V_2}{V_1} \, or = -nR \ln \frac{p_2}{p_1}$$

(b) For *isobaric process* (p constant),
$$\Delta S = n C_p \ln \frac{T_2}{T_1}$$

(c) For *isochoric process* (V constant),
$$\Delta S = n C_v \ln \frac{T_2}{T_1}$$

(d) *Entropy change during adiabatic expansion* : In such process $q=0$ at all stages. Hence $\Delta S = 0$. Thus, reversible adiabatic processes are called *isoentropic process*.

Free energy and Free energy change

Gibb's free energy (G) is a *state function* and is a measure of maximum work done or useful work done from a reversible reaction at constant temperature and pressure.

(1) **Characteristics of free energy**

(i) The free energy of a system is the enthalpy of the system minus the product of absolute temperature and entropy *i.e.,* $G = H - TS$

(ii) Like other state functions E, H and S, it is also expressed as ΔG. Also $\Delta G = \Delta H - T\Delta S_{system}$ where ΔS is entropy change for system only. This is *Gibb's Helmholtz equation*.

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

(iv) For a spontaneous process decrease in free energy is noticed *i.e.,* $\Delta G = -ve$.

(v) At absolute zero, $T\Delta S$ is zero. Therefore if ΔG is – *ve*, ΔH should be – *ve* or only exothermic reactions proceed spontaneously at absolute zero.

(vi) $\Delta G_{system} = T\Delta S_{universe}$, where $\Delta H = 0$

(vii) The standard free energy change,

$\Delta G^o = -2.303 \, RT \log_{10} K,$ where K is equilibrium constant.

(a) Thus if $K > 1,$ then $\Delta G^o = -ve$ thus reactions with equilibrium constant $K>1$ are thermodynamically spontaneous.

(b) If $K<1,$ then $\Delta G^o = +ve$ and thus reactions with equilibrium constant $K<1$ are thermodynamically spontaneous in reverse direction.

(2) **Criteria for spontaneity of reaction** : For a spontaneous change $\Delta G = -ve$ and therefore use of

$\Delta G = \Delta H - T\Delta S$, provides the following conditions for a change to be spontaneous.

Table :10.1 Criteria for spontaneity of reaction

ΔH	ΔS	ΔG	Reaction characteristics	Example
–	+	Always negative	Reaction is spontaneous at all temperatures	$2O_{3(g)} \rightarrow 3O_{2(g)}$
+	–	Always positive	Reaction is non spontaneous at all temperatures	$3O_{2(g)} \rightarrow 2O_{3(g)}$
–	–	Negative at low temperature but positive at high temperature	Reaction is spontaneous at low temperature but becomes non spontaneous at high temperature	$CaO_{(s)} + CO_{2(g)} \rightarrow CaCO_{3(s)}$
+	+	Positive at low temperature but negative at high temperature	Reaction is non spontaneous at low temperature but becomes spontaneous at high temperature	$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$

Third law of thermodynamics

This law was first formulated by German chemist *Walther Nernst* in 1906. According to this law,

"The entropy of all perfectly crystalline solids is zero at the absolute zero temperature. Since entropy is a measure of disorder, it can be interpreted that at absolute zero, a perfectly crystalline solid has a perfect order of its constituent particles."

The most important application of the third law of thermodynamics is that it helps in the calculation of absolute entropies of the substance at any temperature *T*.

$$S = 2.303\, C_p \log T$$

Where C_p is the heat capacity of the substance at constant pressure and is supposed to remain constant in the range of 0 to *T*.

Limitations of the law

(1) Glassy solids even at 0°K has entropy *greater than zero*.

(2) Solids having mixtures of *isotopes* do not have zero entropy at 0°K. For example, entropy of solid chlorine is not zero at 0°K.

(3) Crystals of *CO, N₂O, NO, H₂O*, etc. do not have perfect order even at 0°K thus their entropy is not *equal to zero*.

Thermochemistry

"Thermochemistry is a branch of physical chemistry which is concerned with energy changes accompanying chemical transformation. It is also termed as chemical energetics. It is based on the first law of thermodynamics."

Exothermic and Endothermic reactions

(1) **Exothermic reactions :** The chemical reactions which proceed with the *evolution of heat* energy are called exothermic reactions. The heat energy produced during the reactions is indicated by writing +q or more precisely by giving the actual numerical value on the products side. In general exothermic reactions may be represented as,

$A + B \rightarrow C + D + q$ (heat energy)

In the exothermic reactions the *enthalpy of the products will be less than the enthalpy of the reactants*, so that the enthalpy change is negative as shown below

$\Delta H = H_p - H_r$; $H_p < H_r$; $\Delta H = -ve$

*Examples* : (i) $C(s) + O_2(g) \rightarrow CO_2(g) + 393.5 kJ$

(at constant temperature and pressure)

or $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393.5 kJ$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$; $\Delta H = -285.8 kJ$

(iii) Fermentation is also an example of exothermic reaction.

(2) **Endothermic reactions :** The chemical reactions which proceed with the absorption of heat energy are called endothermic reactions. Since the heat is added to the reactants in these reactions, the heat absorbed is indicated by either putting (–) or by writing the actual numerical value of heat on the reactant side

$A + B \rightarrow C + D - q$ (heat energy)
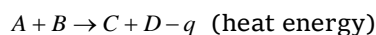
The heat absorbed at constant temperature and constant pressure measures enthalpy change. Because of the absorption of heat, the enthalpy of products will be more than the enthalpy of the reactants. Consequently, ΔH will be positive $(+ve)$ for the endothermic reactions.

$\Delta H = H_p - H_r$; $H_p > H_r$; $\Delta H = +ve$

Example : (i) $N_2(g) + O_2(g) \rightarrow 2NO(g)$; $\Delta H = +180.5 kJ$

(ii) $C(s) + 2S(s) \rightarrow CS_2(l)$ $\Delta H = +92.0 kJ$

(iii) Preparation of ozone by passing silent electric discharged through oxygen is the example of endothermic reaction.

(iv) Evaporation of water is also the example of endothermic reaction.

For exothermic reaction : ΔH or $\Delta E = -ve$

For endothermic reaction : ΔH or $\Delta E = +ve$

Heat of reaction or Enthalpy of reaction

Heat of reaction is defined as the amount of heat evolved or absorbed when quantities of the substances indicated by the chemical equation have completely reacted. The heat of reaction (or enthalpy of reaction) is actually the difference between the enthalpies of the products and the reactants when the quantities of the reactants indicated by the chemical equation have completely reacted. Mathematically,
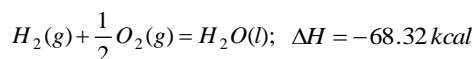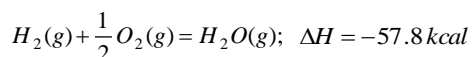
Enthalpy of reaction (heat of reaction) $= \Delta H = \Sigma H_P - \Sigma H_R$

(1) **Factors which influence the heat of reaction** : There are a number of factors which affect the magnitude of heat of reaction.

(i) *Physical state of reactants and products* : Heat energy is involved for changing the physical state of a chemical substance. For example in the conversion of water into steam, heat is absorbed and heat is evolved when steam is condensed. Considering the following two reactions

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g); \quad \Delta H = -57.8\,kcal$$

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l); \quad \Delta H = -68.32\,kcal$$

It is observed that there is difference in the value of ΔH if water is obtained in gaseous or liquid state. ΔH value in second case is higher because heat is evolved when steam condenses. Hence, physical sate always affects the heat of reaction.

(ii) *Allotropic forms of the element* : Heat energy is also involved when one allotropic form of an element is converted into another. Thus, the value of ΔH depends on the allotropic form used in the reaction. For example, the value of ΔH is different when carbon in the form of diamond or in amorphous form is used.

C (diamond) $+ O_2(g) \rightarrow CO_2(g); \quad \Delta H = -94.3\,kcal$

C (amorphous) $+ O_2(g) \rightarrow CO_2(g); \quad \Delta H = -97.6\,kcal$
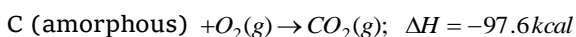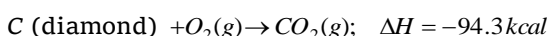
The difference between the two values is equal to the heat absorbed when 12*g* of diamond is converted into 12*g* of amorphous carbon. This is termed as *heat of transition*.

(iii) *Temperature* : Heat of reaction has been found to depend upon the temperature at which reaction is occurring. The variation of the heat of reaction with temperature can be ascertained by using *Kirchhoff's equation*.

$$\frac{\Delta H_{T_2} - \Delta H_{T_1}}{T_2 - T_1} = \Delta C_P$$

Kirchhoff's equation at constant volume may be given as,

$$\frac{\Delta E_{T_2} - \Delta E_{T_1}}{T_2 - T_1} = \Delta C_v$$

(iv) *Reaction carried out at constant pressure or constant volume* : When a chemical reaction occurs at constant volume, the heat change is called the internal energy of reaction at constant volume. However, most of the reactions are carried out at constant pressure; the enthalpy change is then termed as the enthalpy of reaction at constant pressure. The difference in the values is negligible when solids and liquids are involved in a chemical change. But, in reactions which involve gases, the difference in two values is considerable.

$\Delta E + \Delta nRT = \Delta H$ or $q_v + \Delta nRT = q_p$

$\Delta E = q_v =$ heat change at constant volume;

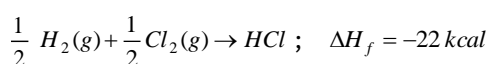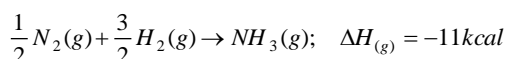$\Delta E \quad \Delta H = q_p =$ heat change at constant pressure,

$\Delta n =$ total number of moles of gaseous product - total number of moles of gaseous reactants.

(2) **Types of heat of reaction**

(i) *Heat of formation* : It is the quantity of heat evolved or absorbed (*i.e.* the change in enthalpy) when one mole of the substance is formed from its constituent elements under given conditions of temperature and pressure. It is represented by ΔH_f. When the temperature and pressure are as 25°*C* and 1 atmospheric pressure. The heat of formation under these conditions is *called standard heat of formation*. It is usually represented by ΔH_f^0.
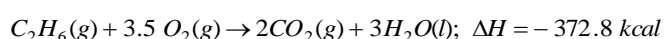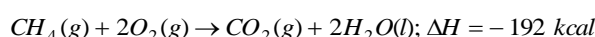
The standard heat of formation of 1 mole of $NH_3(g)$ and 1 mole of $HCl(g)$.

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightarrow NH_3(g); \quad \Delta H_{(g)} = -11\,kcal$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl; \quad \Delta H_f = -22\,kcal$$

It may be calculated by

$$\Delta H^0 = [\Sigma \Delta H^0_{(products)} - \Sigma \Delta H^0_{(Reactants)}]$$

(ii) *Heat of combustion* : It is the amount of heat evolved or absorbed (*i.e.* change in enthalpy) when one mole of the substance is completely burnt in air or oxygen. For example

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \Delta H = -192\ kcal$

$C_2H_6(g) + 3.5\ O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l); \Delta H = -372.8\ kcal$

It may be calculated by

$$\Delta H^0 = [\Sigma \Delta H^0_{f(Products)} - \Sigma H^0_{f(Reactants)}]$$

The enthalpy or heat of combustion have a number of applications. Some of these are described below,

(a) *Calorific value of foods and fuels* : Energy is needed for the working of all machines. Even human body is no exception. Coal, petroleum, natural gas etc. serve as the principal sources of energy for man-made machines, the food which we eat serves as a source of energy to our body.

The energy released by the combustion of foods or fuels is usually compared in terms of their combustion energies per gram. It is known as *calorific value*. The amount of heat produced in calories or Joules when one gram of a substance (food or fuel) is completely burnt or oxidised.

When methane burns, 890.3 kJ mol^{-1} of energy is released.

$$\underset{\substack{1 \text{ mole}(16g)}}{CH_4(g)} + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l); \ \Delta H_{CH_4} = -890.3 \, kJ$$
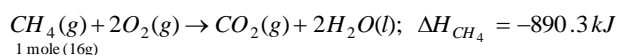
So, the calorific value of methane =

$$-\frac{890.3}{16} = -55.6 \, kJ/g$$

(b) *Enthalpies of formation* : Enthalpies of formation of various compounds, which are not directly obtained, can be calculated from the data of enthalpies of combustions easily by the application of Hess's law.

$$\text{Heat of reaction} = \Sigma \, \text{Heat of combustion of reactants}$$
$$- \Sigma \, \text{Heat of combustion of products.}$$

(iii) **Heat of neutralisation :** It is the amount of heat evolved (i.e., change in enthalpy) when one equivalent of an acid is neutralised by one equivalent of a base in fairly dilute solution, e.g., *Neutralisation reactions are always exothermic reaction and the value of ΔH is $(-ve)$.*

$$HCl(aq.) + NaOH \, (aq.) \rightarrow NaCl(aq.) + H_2O$$
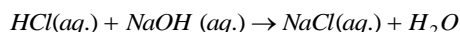
$$\Delta H = -13.7 \, kcal$$

The heat of neutralisation of a strong acid against a strong base is always constant (13.7 $kcal$ or 57 $kJ \, mole^{-1}$). It is because in dilute solutions all strong acids and bases ionise completely and thus the heat of neutralisation in such cases is actually the heat of formation of water from H^+ and OH^- ions, *i.e.,*

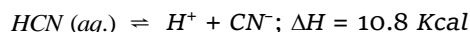$$H^+ + OH^- \rightarrow H_2O; \Delta H = -13.7 \, kcal$$
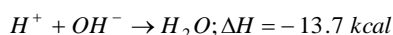
In case of neutralisation of a weak acid or a weak base against a strong base or acid respectively, since a part of the evolved heat is used up in ionising the weak acid or base, it is always less than 13.7 $kcal \, mole^{-1}$ (57 $kJ \, mole^{-1}$). For example,

$$HCN \, (aq.) + NaOH \, (aq.) \rightarrow NaCN(aq.) + H_2O$$
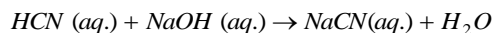
$$\Delta H = -2.9 \, kcal$$

$$HCN \, (aq.) \rightleftharpoons H^+ + CN^-; \Delta H = 10.8 \, Kcal$$

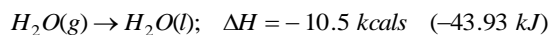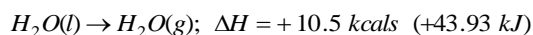10.8 $KCal$ of heat is absorbed for ionisation of HCN it is heat of dissociation or ionisation

(iv) **Heat of solution :** *It is the amount of heat evolved or absorbed (i.e., change in enthalpy) when one mole of the solute is dissolved completely in excess of the solvent (usually water).* For example,

$$NH_4Cl(s) + H_2O(l) \rightarrow NH_4Cl(aq.); \ \Delta H = +3.90 \, kcal$$

$$BaCl_2(s) + H_2O(l) \rightarrow BaCl_2(aq.); \ \Delta H = -2.70 \, kcal$$

(v) **Heat of hydration :** *It is the amount of heat evolved or absorbed (i.e change in enthalpy) when* 1 *mole of an anhydrous or a partially hydrated salt combines with the required number of moles of water to form a specific hydrate.* For example,

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO_4 \cdot 5H_2O(s); \ \Delta H = -18.69$$
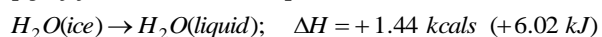
(vi) **Heat of vapourisation :** When a liquid is allowed to evaporate, it absorbs heat from the surroundings and evaporation is accompanied by increase in enthalpy. For example: 10.5 $k \, cals$ is the increase in enthalpy when one mole of water is allowed to evaporate at $25^o C$. When the vapours are allowed to condense to liquid state, the heat is evolved and condensation of vapour is accompanied by decrease in enthalpy.

The evaporation and condensation can be represented as,

$$H_2O(l) \rightarrow H_2O(g); \ \Delta H = +10.5 \, kcals \ (+43.93 \, kJ)$$

$$H_2O(g) \rightarrow H_2O(l); \ \Delta H = -10.5 \, kcals \ (-43.93 \, kJ)$$

Thus the change in enthalpy when a liquid changes into vapour state or when vapour changes into liquid state is called *heat of vapourisation*.

(vii) **Heat of fusion :** When a solid is allowed to melt, it changes into liquid state with the absorption of heat (increase in enthalpy) and when a liquid is allowed to freeze, it changes into solid with the evolution of heat (decrease in enthalpy). The change in enthalpy of such type of transformations is called *enthalpy of fusion*. For example,

$$H_2O(ice) \rightarrow H_2O(liquid); \ \Delta H = +1.44 \, kcals \ (+6.02 \, kJ)$$

$$H_2O \, (liquid) \rightarrow H_2O \, (ice); \ \Delta H = -1.44 \, kcals \ (-6.02 \, kJ)$$

(viii) ***Heat of precipitation :*** It is defined as the amount of heat liberated in the precipitation of one mole of a sparingly soluble substance when solutions of suitable electrolytes are mixed, for example

$$Ba^{2+} + SO_4^{2-}(aq) \rightarrow BaSO_4(s): \Delta H = -4.66\, kcal$$

(ix) ***Heat of sublimation :*** Sublimation is a process in which a solid on heating changes directly into gaseous state below its melting point.

Heat of sublimation of a substance is the amount of heat absorbed in the conversion of 1 mole of a solid directly into vapour phase at a given temperature below its melting point.

$$I_2(s) \rightarrow I_2(g)\,; \quad \Delta H = +62.39\, kJ$$

Most solids that sublime are molecular in nature e.g. iodine and naphthalene etc.

$$\Delta H_{sub.} = \Delta H_{fusion} + \Delta H_{vaporisation}$$

(3) **Experimental determination of the heat of reaction :** The heat evolved or absorbed in a chemical reaction is measured by carrying out the reaction in an apparatus called *calorimeter*. The principle of measurement is that heat given out is equal to heat taken, *i.e.,* $Q = (W + m) \times s \times (T_2 - T_1)$,

Where Q is the heat of the reaction (given out), W is the water equivalent of the calorimeter and m is the mass of liquid in the calorimeter and s its specific heat, T_2 is the final temperature and T_1 the initial temperature of the system. Different types of calorimeters are used but two of the common types are,

(i) Water calorimeter and (ii) Bomb calorimeter

Bomb calorimeter : This is commonly used to find the heat of combustion of organic substances.

Since the reaction in a bomb calorimeter proceeds at constant volume, the heat of combustion measured is ΔE

$$\Delta E = \frac{(W + m)(t_2 - t_1) \times s}{w_1} \times M\, kcal$$

Where M is the molecular mass of the substance, w_1 is the weight of substance taken, W is the water equivalent of calorimeter, m is the mass of liquid in the calorimeter and s is the specific heat of liquid.

ΔH can be calculated from the relation, $\Delta H = \Delta E + \Delta nRT$

Laws of thermochemistry

(1) **Levoisier and Laplace law :** According to this law enthalpy of decomposition of a compound is numerically equal to the enthalpy of formation of that compound with opposite sign, For example,

$$C(s) + O_2 \rightarrow CO_2(g); \Delta H = -94.3\, kcal$$

$$CO_2(g) \rightarrow C(s) + O_2(g); \Delta H = +94.3 kcal$$
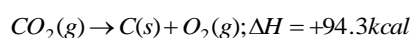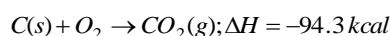
(2) **Hess's law** (the law of constant heat summation) **:** This law was presented by Hess in 1840. According to this law "*If a chemical reaction can be made to take place in a number of ways in one or in several steps, the total enthalpy change (total heat change) is always the same, i.e. the total enthalpy change is independent of intermediate steps involved in the change.*" The enthalpy change of a chemical reaction depends on the initial and final stages only. Let a substance A be changed in three steps to D with enthalpy change from A to B, ΔH_1 calorie, from B to $C, \Delta H_2$ calorie and from C to $D, \Delta H_3$ calorie. Total enthalpy change from A to D will be equal to the sum of enthalpies involved in various steps, Total enthalpy change $\Delta H_{steps} = \Delta H_1 + \Delta H_2 + \Delta H_3$

Now if D is directly converted into A, let the enthalpy change be ΔH_{direct}. According to Hess's law $\Delta H_{steps} + \Delta H_{direct} = 0$, i.e. ΔH_{steps} must be equal to ΔH_{direct} numerically but with opposite sign. In case it is not so, say ΔH_{steps} (which is negative) is more that ΔH_{direct} (which is positive), then in one cycle, some energy will be created which is not possible on the basis of first law of thermodynamics. Thus, ΔH_{steps} must be equal to ΔH_{direct} numerically.
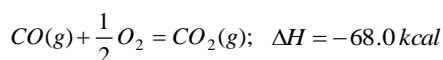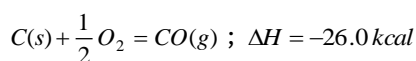
(i) ***Experimental verification of Hess's law***

(a) *Formation of carbon dioxide from carbon*

First method : carbon is directly converted into $CO_2(g)$.

$$C(s) + O_2(g) = CO_2(g); \Delta H = -94.0\, kcal$$
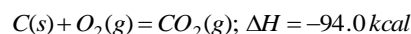
Second method : Carbon is first converted into $CO(g)$ and then $CO(g)$ into $CO_2(g)$, i.e. conversion has been carried in two steps,

$$C(s) + \frac{1}{2}O_2 = CO(g)\,; \ \Delta H = -26.0\, kcal$$

$$CO(g) + \frac{1}{2}O_2 = CO_2(g); \ \Delta H = -68.0\, kcal$$

Total enthalpy change $C(s)$ to $CO_2(g)$; $\Delta H = -94.0\, kcal$

(b) *Formation of ammonium chloride from ammonia and hydrochloric acid:*

First   method

$NH_3(g) + HCl = NH_4Cl(g); \Delta H = -42.2\,kcal$

$NH_4Cl(g) + aq = NH_4Cl(aq); \Delta H = +4.0\,kcal$

$NH_3(g) + HCl(g) + aq = NH_4Cl(aq); \quad \Delta H = -38.2\,kcal$

Second method

$NH_3(g) + aq = NH_3(aq); \quad \Delta H = -8.4\,kcal$

$HCl(g) + aq = HCl(aq); \Delta H = -17.3\,kcal$

$NH_3(aq) + HCl(aq) = NH_4Cl(aq); \quad \Delta H = -12.3\,kcal$

$NH_3(g) + HCl(g) + aq = NH_4Cl(aq); \quad \Delta H = -38.0\,kcal$
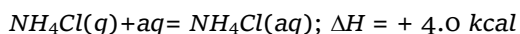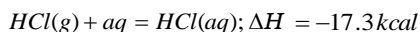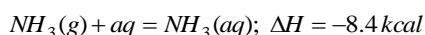
(ii) *Applications of Hess's law*

(a) For the determination of enthalpies of formation of those compounds which cannot be prepared directly from the elements easily using enthalpies of combustion of compounds.

(b) For the determination of enthalpies of extremely slow reactions.

(c) For the determination of enthalpies of transformation of one allotropic form into another.

(d) For the determination of bond energies.

$\Delta H_{reaction} = \Sigma$ Bond energies of reactants – Σ Bond energies of products.
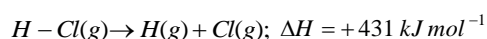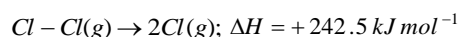
(e) For the determination of resonance energy.

(f) For the determination of lattice energy.

Bond energy or Bond enthalpies

When a bond is formed between atoms, energy is released. Obviously same amount of energy will be required to break the bond. The energy required to break the bond is termed *bond dissociation energy*. The more precise definition is,

"*The amount of energy required to break one mole of bond of a particular type between the atoms in the gaseous state, i.e., to separate the atoms in the gaseous state under 1 atmospheric pressure and the specified temperature is called bond dissociation energy.*"

For example, $H - H(g) \rightarrow 2H(g); \Delta H = +433\,kJ\,mol^{-1}$

$Cl - Cl(g) \rightarrow 2Cl(g); \Delta H = +242.5\,kJ\,mol^{-1}$

$H - Cl(g) \rightarrow H(g) + Cl(g); \Delta H = +431\,kJ\,mol^{-1}$

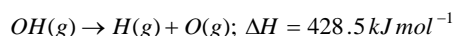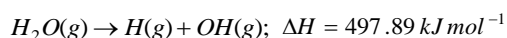The bond dissociation energy of a diatomic molecule is also called *bond energy*. However, the bond dissociation energy depends upon the nature of bond and also the molecule in which the bond is present. When a molecule of a compound contains more than one bond of the same kind, the average value of the dissociation energies of a given bond is taken. *This average bond dissociation energy required to break each bond in a compound is called bond energy.*

Bond energy is also called, the heat of formation of the bond from gaseous atoms constituting the bond with reverse sign.

$H(g) + Cl(g) \rightarrow H - Cl(g); \Delta H = -431\,kJ\,mol^{-1}$
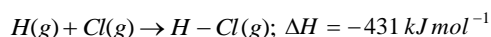
Bond energy of $H - Cl = -$ (enthalpy of formation) $= -(-431) = +431\,kJ\,mol^{-1}$

Consider the dissociation of water molecule which consists of two $O - H$ bonds. The dissociation occurs in two stages.

$H_2O(g) \rightarrow H(g) + OH(g); \Delta H = 497.89\,kJ\,mol^{-1}$

$OH(g) \rightarrow H(g) + O(g); \Delta H = 428.5\,kJ\,mol^{-1}$

The average of these two bond dissociation energies gives the value of bond energy of $O - H$.

Bond energy of $O - H$ bond

$= \dfrac{497.8 + 428.5}{2} = 463.15\,kJ\,mol^{-1}$

Similarly, the bond energy of $N - H$ bond in NH_3 is equal to one – third of the energy of dissociation of NH_3 and those of $C - H$ bond in CH_4 is equal to one – fourth of the energy of dissociation of CH_4.

Bond energy of $C - H = \dfrac{1664}{4} = 416\,kJ\,mol^{-1}$

$[CH_4(g) \rightarrow C(g) + 4H(g); \Delta H = 1664\,kJ\,mol^{-1}]$
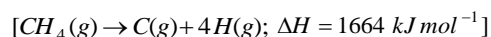
Applications of bond energy

(1) Heat of a reaction $= \Sigma$ Bond energy of reactants – Σ Bond energy of products.

(2) **Determination of resonance energy :** When a compound shows resonance, there is considerable difference between the heat of formation as calculated from bond energies and that determined experimentally.

Resonance energy = Experimental or actual heat of formation – Calculated heat of formation.

Tips & Tricks

✎ Joule thomson coeffient $\mu = \left(\dfrac{\partial T}{\partial p}\right)_H$

For cooling $\mu = +ve$

For Heating $\mu = -ve$

Neither cooling nor heating $\mu = 0$

✎ The temperature at which a real gas shows neither cooling nor heating effect on adiabatic expansion (*i.e.*, $\mu = 0$) is called inversion temperature.

✎ Hydrogen has highest calorific value.

✎ $13.7\, Kcal/mol = 57\, KJ/mol$ (be cause of $1\,cal$ =4.2 Joule)

✎ Enthalpy of fusion of ice per mole is $6 KJ$.

✎ Order of bond energy in halogen $Cl_2 > Br_2 > F_2 > I_2$.

✎ Heat of vapourisation of water per mole is 10.5 *KCal*.

✎ The heat of reaction is independent of the time consumed in the process.

Ordinary Thinking

Objective Questions

Basic concepts

1. Internal energy of an ideal gas depends on
   (a) Volume   (b) Temperature
   (c) Pressure   (d) None of these

2. Any series of operations so carried out that at the end, the system is back to its initial state is called
   (a) Boyle's cycle   (b) Reversible process
   (c) Adiabatic process   (d) Cyclic process

3. One calorie is equal to   [CPMT 1988]
   (a) 0.4184 *Joule*   (b) 4.184 *Joule*
   (c) 41.84 *Joule*   (d) 418.4 *Joule*

4. The total internal energy change for a reversible isothermal cycles is
   (a) Always 100 calories per degree
   (b) Always negative

   (c) 0
   (d) Always positive

5. A well stoppered thermos flask contains some ice cubes. This is an example of a   [AIIMS 1992]
   (a) Closed system
   (b) Open system
   (c) Isolated system
   (d) Non-thermodynamic system

6. Identify the intensive quantity from the following
   [IIT JEE 1993]
   (a) Enthalpy and temperature
   (b) Volume and temperature
   (c) Enthalpy and volume
   (d) Temperature and refractive index

7. Which of the following units represents the largest amount of energy [CPMT 1989; MP PET 2000]
   (a) Electron volt   (b) Erg
   (c) Joule   (d) Calorie

8. Energy equivalent to one erg, one joule and one calorie is in the order   [NCERT 1980; CPMT 1997]
   (a) $1\,erg > 1\,joule > 1\,calorie$ (b) $1\,erg > 1\,calorie > 1\,joule$
   (c) $1\,calorie > 1\,joule > 1\,erg$ (d) $1\,joule > 1\,calorie > 1\,erg$