

# Thermodynamics

**Chemical thermodynamics** is the study of the interrelation of heat and work with chemical reactions or with physical changes of state within the confines of the laws of thermodynamics. Chemical thermodynamics involves not only laboratory measurements of various thermodynamic properties, but also the application of mathematical methods to the study of chemical questions and the *spontaneity* of processes.

## Terminology used in thermodynamics :-

**SYSTEM** : A thermodynamic system is that part of the physical universe the properties of which are under investigation.

**SURROUNDINGS** : The part of the universe other than the system is known as surroundings. Thus universe = system + surroundings In simple case surroundings implies air or water both.

### TYPES OF SYSTEM :

- (i) **Open system** - A system which can exchange matter as well as energy with surroundings.
- (ii) **Closed system** – A system which can exchange energy and not matter with surroundings.
- (iii) **Isolated system** - A system which can exchange neither matter nor energy with surroundings.
- (iv) **Homogeneous system** – A system consisting of one phase only e.g. pure solid, a liquid or a mixture of gases.
- (v) **Heterogeneous system** – It may consists of two or more phases e.g. a solid in contact with liquid etc.

**STATE OF SYSTEM** : A system is in a definite state when each of its properties has a definite value. The properties which arise out of collective behaviour of large number of chemical entities e.g. pressure, volume, temperature, composition, colour, refractive index etc.

**MACROSCOPIC PROPERTIES** : The properties which arise out of collective behaviour of large number of chemical entities e.g. pressure, volume, temperature, composition, colour, refractive index etc.

**EXTENSIVE PROPERTIES** : The properties which depend upon the quantity of the substance or substances present in the system e.g. volume, enthalpy, free energy, entropy, heat capacity. Extensive properties such as the mass, volume and entropy of systems are additive for subsystems.

**INTENSIVE PROPERTIES** : The properties which are independent of the quantity of the substance present in the system e.g. density, molar volume, temperature, melting point, boiling point, freezing point etc.

- Note : Ratio of two extensive properties is intensive. For example, mass and volume are extensive, but their ratio density is intensive.

**STATE VARIABLES AND STATE FUNCTIONS** : These are the macroscopic properties of the system which define the state of system. Any change in state variable changes the state of the system. They depend upon the initial and final state of system. They are temperature, pressure, volume, chemical composition, energy, entropy, free energy.

**INTERNAL ENERGY(U)** : Internal energy U of a system or a body with well-defined boundaries is the total of the kinetic energy due to the motion of molecules and the potential energy associated with the vibrational motion and electric energy of atoms within molecules. The internal energy of an isolated system cannot change, as expressed in the law of conservation of energy, a foundation of the first law of thermodynamics.

The internal energy cannot be measured absolutely. Thermodynamics concerns changes in the internal energy, not its absolute value. The processes that change the internal energy are transfers, into or out of the system, of matter, or of energy, as heat, or by thermodynamic work. These processes are measured by changes in the system's properties, such as temperature, entropy, volume, electric polarization, and molar constitution. The internal energy depends only on the internal state of the system and not on the particular choice from many possible processes (paths) by which energy may pass into or out of the system. It is a state variable, a thermodynamic potential, and an extensive property.

Thermodynamics defines internal energy macroscopically, for the body as a whole. In statistical mechanics, the internal energy of a body can be analyzed microscopically in terms of the kinetic energies of microscopic motion of the system's particles from translations, rotations, and vibrations, and of the potential energies associated with microscopic forces, including chemical bonds.

It is measured in bomb calorimeter, i.e. constant volume calorimeter.

Change in internal energy  $\Delta U = U_{\text{products}} - U_{\text{reactants}} = U_P - U_R$

If  $U_P > U_R$ ,  $\Delta U = +ve$  change is endothermic

If  $U_P < U_R$ ,  $\Delta U = -ve$  change is exothermic

Internal energy depends on temperature, pressure, volume and quantity of matter. In most stable form the internal energy of an element is zero

The unit of energy in the International System of Units (SI) is the joule (J). The internal energy relative to the mass with unit J/kg is the specific internal energy.

Internal energy and heat capacity:

$$\Delta U = C_{v,m} \times \Delta T$$

$$= \frac{C \times \Delta T \times M}{W}, \text{ where}$$

C = Heat capacity of calorimeter,

$C_{v,m}$  = Molar heat capacity

$\Delta T$  = Rise in temperature

M = Molecular mass of the substance

W = Mass of the substance taken

#### **Different modes of energy transfer between system and surroundings :**

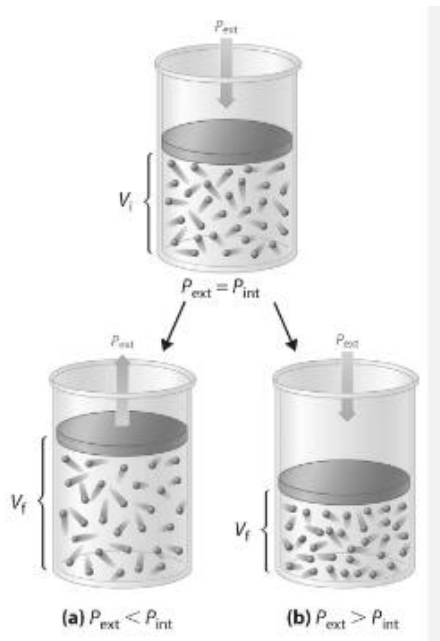
Exchange of energy between system and surroundings can take place by

- (a) Heat
- (b) Work
- (c) Electrical Energy
- (d) Radiations

**Heat (q):** We can also change the internal energy of a system by transfer of heat from the surroundings to the system or vice-versa without expenditure of work. This exchange of energy, which is a result of temperature difference is called heat, q. The q is positive when heat is transferred from the surroundings to the system and q is negative when heat is transferred from

system to the surroundings. Heat may be defined as **energy in transit** from a high temperature object to a lower temperature object. An object does not possess "heat", i.e. heat is not the property of a system. Heat is an extensive property and it is a path function.

**Work:** Let us consider the case of mechanical work or pressure-volume work.



For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is  $V_i$  and pressure of the gas inside is  $p_{int}$ .

If external pressure is  $p_{ext}$  which is greater than  $p$ , piston is moved inward till the pressure inside becomes equal to  $p_{ext}$ .

Let this change be achieved in a single step and the final volume be  $V_f$ . During this compression, suppose piston moves a distance,  $l$  and is cross-sectional area of the piston is  $A$ ,

then, volume change

$$= l \times A = \Delta V = (V_f - V_i)$$

We know,

$$\text{Pressure} = \frac{\text{force}}{\text{area}}$$

Therefore,

$$\text{force on the piston} = p_{ext} \times A$$

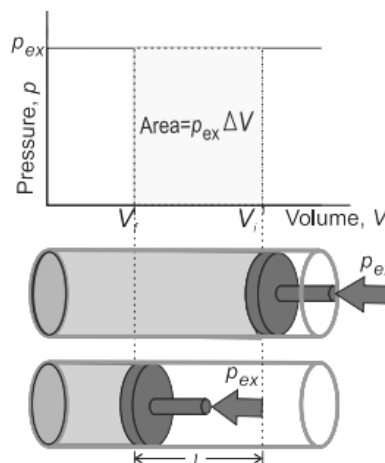
If  $w$  is the work done on the system by movement of the piston then

$$w = \text{force} \times \text{distance} = p_{ext} \cdot A \cdot l$$

$$= p_{ext} \cdot (-\Delta V)$$

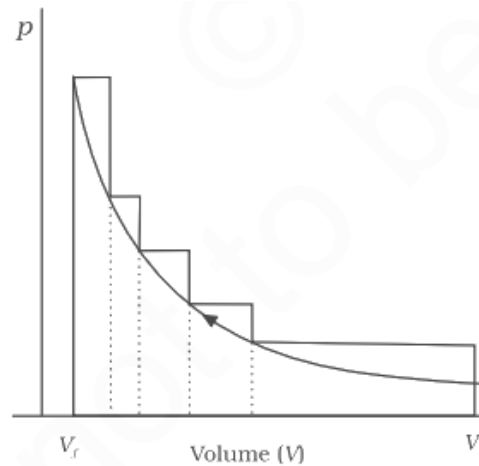
$$= -p_{ext} \Delta V$$

$$= -p_{ext} (V_f - V_i)$$



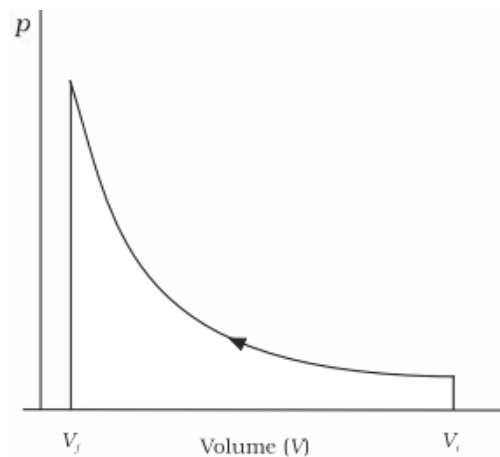
The negative sign of this expression is required to obtain conventional sign for  $w$ , which will be positive. It indicates that in case of compression work is done on the system. Here  $(V_f - V_i)$  will be negative and negative multiplied by negative will be positive. Hence the sign obtained for the work will be positive.

If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to  $-\sum p\Delta V$ .



If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount,  $dV$ . In such a case we can calculate the work done on the gas by the relation

$$w = - \int_{V_i}^{V_f} p_{ext} dV$$



Here,  $p_{ext}$  at each stage is equal to  $(p_{int} + dp)$  in case of compression. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e.,  $p_{ext} = (p_{int} - dp)$ . In general case we can write,  $p_{ext} = (p_{int} \pm dp)$ . Such processes are called **reversible processes**.

A process or change is said to be **reversible**, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as **irreversible processes**.

We can relate work to internal pressure of the system under reversible conditions as follows:

$$\begin{aligned} w_{rev} &= - \int_{V_i}^{V_f} p_{ext} dV \\ &= - \int_{V_i}^{V_f} (p_{int} \pm dp) dV \end{aligned}$$

Since  $dp \times dV$  is very small we can write

$$w_{rev} = - \int_{V_i}^{V_f} p_{int} dV$$

Now, the pressure of the gas ( $p_{int}$  which we can write as  $p$  now) can be expressed in terms of its volume through gas equation. For  $n$  mol of an ideal gas i.e.,  $pV = nRT$

$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal reversible process),

$$w_{rev} = - \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

$$\Rightarrow w = -nRT \ln \frac{v_f}{v_i}$$

$$\Rightarrow w = -2.303nRT \log \frac{v_f}{v_i}$$

**Free expansion:** Expansion of a gas in vacuum ( $p_{\text{ext}} = 0$ ) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

**Processes and their types:** The operation by which a system changes from one state to another state is called process.

**Thermodynamic processes:**

1. **Isothermal process ( $\Delta T = 0$ )** : During each stage of process, the temperature remains constant. If the process is exothermic heat is given out to surroundings, If the process is endothermic heat is absorbed from surroundings.
2. **Adiabatic process ( $dq=0$ )** : No heat leaves or enter the system, temperature of a system rises in exothermic process, temperature falls in endothermic process.
3. **Isobaric process ( $\Delta P = 0$ )** : Pressure remains constant, only volume changes.
4. **Isochoric process ( $\Delta V = 0$ )** : Volume remains constant but pressure changes.
5. **Cyclic process ( $\Delta E = 0$ )** : After undergoing a number of changes, the system returns to its original state. In cyclic process  $\Delta E = 0$ ;  $\Delta H = 0$ ;  $\Delta S = 0$ .
6. **Reversible process** : If the driving force is only infinitesimally greater than the opposing force and process can be reversed at any instant, it is known as reversible process.
7. **Irreversible process** : It does not take place infinitesimally slow.

**Thermodynamic Equilibrium** : When there is no change in macroscopic properties with time. The types are :

- (i) **Thermal equilibrium** : The temperature of the system remains constant throughout and no heat flows from one part to another part of system.
- (ii) **Mechanical equilibrium** : The pressure remains constant and no mechanical work is done by one part of system on another part.
- (iii) **Chemical equilibrium** : The composition of various phases remains the same.

**FIRST LAW OF THERMODYNAMICS :**

- (i) Law of equivalence of different forms of energies
- (ii) Energy can neither be created nor destroyed but can be transformed from one form to another.
- (iii) Total energy of universe is conserved (fixed, constant).

**MATHEMATICAL EXPRESSION OF FIRST LAW** : If  $q$  is the amount of heat absorbed by the system and  $w$  is the work done on the system, the change in internal energy,

$$\Delta U = q + w$$

$$\Delta U = q + P\Delta V \text{ (if work is only pressure-volume work)}$$

**Note** :  $q$  and  $w$  are not state functions but the sum of the two ( $q + w$ ) which represents  $\Delta U$  is a state function.

**Application of First Law for different thermodynamic processes:**

- (i) when  $w = 0$ ,  $\Delta U = q$ .

If heat is absorbed by system, internal energy increases. If heat is lost by system, internal energy decreases.

- (ii) when  $q = 0$ ,  $\Delta U = W$ .

If work is done on the system, internal energy increases. If work is done by the system, internal energy decreases. In adiabatic process work is done by the system at the expense of internal energy.

(iii) when  $\Delta U = 0$ ,  $q = -w$ .

Heat absorbed by the system is equal to work done by the system

(iv) Cyclic process,  $\Delta U = 0$ ,  $q = -w$ .

Work done by the system is equal to heat absorbed.

**Enthalpy, H** : We know that the heat absorbed at constant volume is equal to change in the internal energy i.e.,  $\Delta U = q_v$ . But most of chemical reactions are carried out not at constant volume, but in flasks or test tubes under constant atmospheric pressure. We need to define another state function which may be suitable under these conditions.

We may write equation  $\Delta U = q + w$  as

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

at constant pressure, where  $q_p$  is heat absorbed by the system and  $-p\Delta V$  represent expansion work done by the system.

Let us represent the initial state by subscript 1 and final state by 2. We can rewrite the above equation as

$$U_2 - U_1 = q_p - p(V_2 - V_1)$$

On rearranging, we get

$$q_p = (U_2 + pV_2) - (U_1 + pV_1)$$

Now we can define another thermodynamic function, the enthalpy H [Greek word enthalpien, to warm or heat content] as :

$$H = U + pV$$

so, the above equation becomes

$$q_p = H_2 - H_1 = \Delta H$$

Although  $q$  is a path dependent function,  $H$  is a state function because it depends on  $U$ ,  $p$  and  $V$ , all of which are state functions. Therefore,  $\Delta H$  is independent of path. Hence,  $q_p$  is also independent of path.

For finite changes at constant pressure, we can write

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

Since  $p$  is constant, we can write

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

It is important to note that when heat is absorbed by the system at constant pressure, we are actually measuring changes in the enthalpy.

We know,  $\Delta H = q_p$ . when heat is absorbed by the system at constant pressure, we actually measure changes in the enthalpy.

$\Delta H$  is negative for exothermic reactions which evolve heat during the reaction and  $\Delta H$  is positive for endothermic reactions which absorb heat from the surroundings.

The difference between  $\Delta H$  and  $\Delta U$  is not usually significant for systems consisting of only solids and / or liquids. Solids and liquids do not suffer any significant volume changes upon heating. The difference, however, becomes significant when gases are involved.

Let us consider a reaction involving gases. If  $V_A$  is the total volume of the gaseous reactants,  $V_B$  is the total volume of the gaseous products,  $n_A$  is the number of moles of gaseous reactants and  $n_B$  is the number of moles of gaseous products, all at constant pressure and temperature, then using the ideal gas law, we write,

$$pV_A = n_A RT \text{ and } pV_B = n_B RT$$

Thus,

$$pV_B - pV_A = n_B RT - n_A RT = (n_B - n_A) RT$$

$$\text{or } p(V_B - V_A) = (n_B - n_A) RT$$

$$\text{or } p \Delta V = \Delta n_g RT$$

Here,  $\Delta n_g$  refers to the number of moles of gaseous products minus the number of moles of gaseous reactants.

Substituting the value of  $p\Delta V$ , we get

$$\Delta H = \Delta U + \Delta n_g RT$$

**FACTORS AFFECTING THE  $\Delta H$  :**

- (i) Physical state of reactants and products
- (ii) Quantities of reactants and products
- (iii) Allotropic forms
- (iv) Temperature
- (v) Conditions of constant P and Constant V at a particular temperature.

**Heat Capacity:** Let us see how to measure heat transferred to a system. This heat appears as a rise in temperature of the system in case of heat absorbed by the system. The increase of temperature is proportional to the heat transferred.

$$q \propto \Delta T$$

$$\Rightarrow q = \text{coeff} \times \Delta T$$

The magnitude of the coefficient depends on the size, composition and nature of the system.

We can also write it as  $q = C \Delta T$

The coefficient, C is called the heat capacity.

Thus, we can measure the heat supplied by monitoring the temperature rise, provided we know the heat capacity.

When C is large, a given amount of heat results in only a small temperature rise. Water has a large heat capacity i.e., a lot of energy is needed to raise its temperature.

C is directly proportional to amount of substance. The **molar heat capacity** of a substance

$$C_m = \frac{C}{n}$$

It is the quantity of heat needed to raise the temperature of one mole by one degree celsius (or one kelvin).

**Specific heat**, also called specific heat capacity(c) is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin).

For finding out the heat, q, required to raise the temperatures of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change,  $\Delta T$  as

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

**The relationship between  $C_p$  and  $C_v$  for an ideal gas:**

At constant volume, the heat capacity, C is denoted by  $C_v$  and at constant pressure, this is denoted by  $C_p$ . Let us find the relationship between the two.

$$\text{At constant volume as } q_v = C_v \times \Delta T = \Delta U$$

$$\text{At constant pressure as } q_p = C_p \times \Delta T = \Delta H$$

The difference between  $C_p$  and  $C_v$  can be derived for an ideal gas as:

$$\begin{aligned} \text{For a mole of an ideal gas, } \Delta H &= \Delta U + \Delta(pV) \\ &= \Delta U + \Delta(RT) \end{aligned}$$

$$\therefore \Delta H = \Delta U + R\Delta(T)$$

On putting the values of  $\Delta H$  and  $\Delta U$ , we have

$$C_p \times \Delta T = C_v \times \Delta T + R\Delta(T)$$

$$\therefore C_p = C_v + R$$

$$\therefore C_p - C_v = R$$

### ENTHALPY CHANGE, $\Delta_r H$ OF A REACTION : REACTION ENTHALPY:

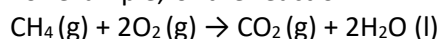
The enthalpy change accompanying a reaction is called the reaction enthalpy.

$\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$

$$= \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}}$$

Here symbol  $\sum$  (sigma) is used for summation and  $a_i$  and  $b_i$  are the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation.

For example, for the reaction



$$\Delta_r H = [H_m(\text{CO}_2, \text{g}) + 2H_m(\text{H}_2\text{O}, \text{l})] - [H_m(\text{CH}_4, \text{g}) + 2H_m(\text{O}_2, \text{g})]$$

where  $H_m$  is the molar enthalpy.

### Standard enthalpy of reactions( $\Delta H^0$ ):

The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

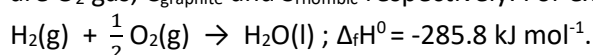
The standard state of a substance at a specified temperature is its pure form at 1 bar.

### Enthalpy changes during phase transformations:

- **Standard enthalpy of fusion** : The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion,  $\Delta_{\text{fus}} H^0$ . For example,  $\text{H}_2\text{O}(\text{s}) \rightarrow \text{H}_2\text{O}(\text{l})$ ,  $\Delta_{\text{fus}} H^0 = +6.0 \text{ kJ mol}^{-1}$ .
- **Standard enthalpy of vaporization**: Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization,  $\Delta_{\text{vap}} H^0$ . For example,  $\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$ ,  $\Delta_{\text{vap}} H^0 = +40.79 \text{ kJ mol}^{-1}$ .
- **Standard enthalpy of sublimation**(  $\Delta_{\text{sub}} H^0$ ) is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1bar). For example,  $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$ ,  $\Delta_{\text{sub}} H^0 = +25.2 \text{ kJ mol}^{-1}$ .

**Standard enthalpy of formation ( $\Delta_f H^0$ ):** The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation.

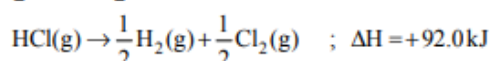
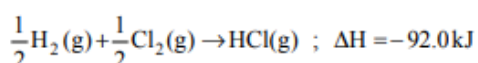
The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure. For example, the reference state of dihydrogen is  $\text{H}_2$  gas and those of dioxygen, carbon and sulphur are  $\text{O}_2$  gas,  $\text{C}_{\text{graphite}}$  and  $\text{S}_{\text{rhombic}}$  respectively. For example,



By convention, standard enthalpy for formation,  $\Delta_f H^0$ , of an element in reference state, i.e., its most stable state of aggregation is taken as zero.

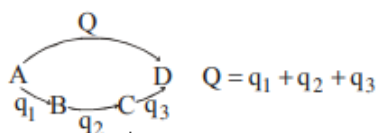
### THE LAWS OF THERMOCHEMISTRY :

**(1) Lavoisier and Laplace law** : The heat evolved or absorbed in the course of a chemical reaction is equal to the heat absorbed or evolved when the reaction is reversed.

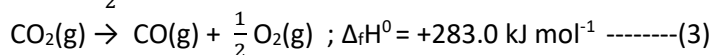
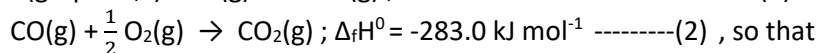
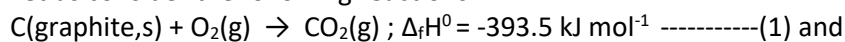


**(2) Hess's law of constant heat summation** : Law is based upon the first law of thermodynamics and states that if a chemical change can be made to take place in two or more ways involving one or more steps, the net amount of heat change in the complete process is the same regardless of the method employed.

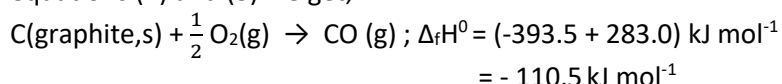




Let us consider the following reactions:



We can combine the above two reactions in such a way so as to obtain the desired reaction. Adding equations (1) and (3) we get,



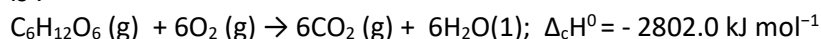
**Applications of Hess's law :** It is used in the

- (i) Calculation of heats of reactions
- (ii) Determination of heat changes of slow reactions
- (iii) Calculation of enthalpies of formation
- (iv) Calculation of bond energies

#### ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS:

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

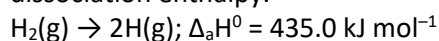
For example, combustion of glucose gives out 2802.0 kJ/mol of heat, for which the overall equation is :



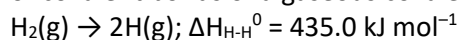
Our body also generates energy from food by the same overall process as combustion, although the final products are produced after a series of complex bio-chemical reactions involving enzymes.

**Enthalpy of atomization ( $\Delta_a H^\circ$ ):** The enthalpy change that accompanies the total separation of all atoms in a chemical substance (either an element or a compound) is called enthalpy of atomization. All bonds in the compound are broken in atomization and none are formed, so enthalpies of atomization are always positive. The associated standard enthalpy is known as the standard enthalpy of atomization.

In case of diatomic molecules, like dihydrogen, the enthalpy of atomization is also the bond dissociation enthalpy.



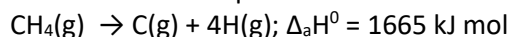
**Bond Enthalpy ( $\Delta_{\text{bond}} H^\circ$ ):** The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.



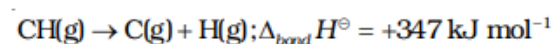
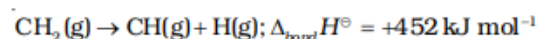
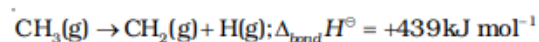
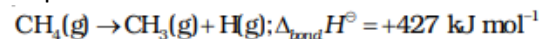
Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules.

In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

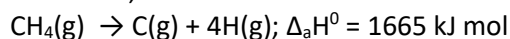
**Polyatomic Molecules:** Let us now consider a polyatomic molecule like methane,  $\text{CH}_4$ . The overall thermochemical equation for its atomization reaction is given below:



In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ :



Therefore,



In such cases we use mean bond enthalpy of C – H bond.

For example in  $\text{CH}_4$ ,  $\Delta_{\text{C-H}} H^\ominus$  is calculated as:

$$\begin{aligned} \Delta_{\text{C-H}} H^\ominus &= \frac{1}{4}(\Delta_a H^\ominus) = \frac{1}{4}(1665 \text{ kJ mol}^{-1}) \\ &= 416 \text{ kJ mol}^{-1} \end{aligned}$$

We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in  $\text{CH}_3\text{CH}_2\text{Cl}$ ,  $\text{CH}_3\text{NO}_2$  etc, but it does not differ in a great deal.

The standard enthalpy of reaction,  $\Delta_r H^\ominus$  is related to bond enthalpies of the reactants and products in gas phase reactions as:

$$\Delta_r H^\ominus = \sum \text{bond enthalpies}_{\text{reactants}} - \sum \text{bond enthalpies}_{\text{products}}$$

### Enthalpy of Solution ( $\Delta_{\text{sol}} H^\ominus$ ):

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But solvation of these ions (hydration in case solvent is water) also occurs at the same time.

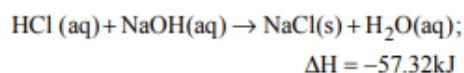
The enthalpy of solution of  $\text{AB}(\text{s})$ ,  $\Delta_{\text{sol}} H^\ominus$ , in water is, therefore, determined by the selective values of the lattice enthalpy,  $\Delta_{\text{lattice}} H^\ominus$  and enthalpy of hydration of ions,  $\Delta_{\text{hyd}} H^\ominus$  as

$$\Delta_{\text{sol}} H^\ominus = \Delta_{\text{lattice}} H^\ominus + \Delta_{\text{hyd}} H^\ominus$$

For most of the ionic compounds,  $\Delta_{\text{sol}} H^\ominus$  is positive and the dissociation process is endothermic.

Therefore the solubility of most salts in water increases with rise of temperature.

**Heat of neutralization :** It is defined as the enthalpy change ( $\Delta H$ ) accompanying the neutralization of one gram equivalent of the acid by a base in dilute solution at that temperature



Heat of neutralization of every strong acid by a strong base is identical. When acid or alkali is weak the heat of neutralization is different because the reaction involves the dissociation of the weak acid or the weak alkali.

### Limitations of the First Law of Thermodynamics:

1. The first law of thermodynamics fails to give the feasibility of the process or change of state that the system undergoes.
2. It fails to explain the direction of heat flow.
3. It doesn't say the process is a spontaneous or non-spontaneous process.

### HEAT ENGINE :

Machine which converts heat into work is called heat engine.

**EFFICIENCY OF HEAT ENGINE :** The fraction of the heat absorbed, converted into work is called the efficiency of machine

$$\eta = \frac{W}{Q} = \frac{\text{Work done}}{\text{Heat absorbed}}$$

**CARNOT CYCLE :** It is a process where a system after undergoing a number of successive changes returns to its original state. It consists of four different operations.

- (i) Isothermal reversible expansion
- (ii) Adiabatic reversible expansion
- (iii) Isothermal reversible compression
- (iv) Adiabatic reversible compression

### Efficiency of Carnot Engine:

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

Since  $\frac{T_2 - T_1}{T_2}$  is always less than unity, hence efficiency  
is always less than unity

**SPONTANEOUS PROCESS :** A process which has an urge or a natural tendency to occur either of its own or after proper initiation under a given set of conditions. It is irreversible process and may only be reversed by some external agents.

### (i) Spontaneous processes that need no initiation:

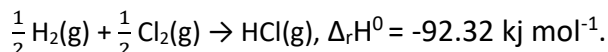
- (a) Evaporation of water.
- (b) Dissolution of sugar.
- (c) Intermixing of gases.

### (ii) Spontaneous processes that need initiation:

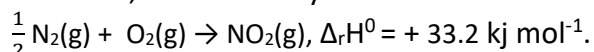
- (a) combination of hydrogen and oxygen. These gases may be mixed at room temperature and left for many years without observing any perceptible change. However the reaction occurs instantaneously when electric discharge is applied on the mixture.
- (b) Burning of coal.

### Driving forces (criterion) for spontaneity of a process:

(i) **Enthalpy a criterion for spontaneity** : During the flow of water downhill or fall of a stone on to the ground, there is a net decrease in potential energy in the direction of change. So we can say that a chemical reaction is spontaneous in a given direction in which there is decrease in energy. This is true for many exothermic reactions like



However, there are many endothermic reactions which are spontaneous like,



Therefore, it becomes obvious that while decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases. So Enthalpy is not the sole criterion for spontaneity of a process.

(ii) **Entropy and spontaneity**: Let us consider diffusion of two gases into each other in a closed container which is isolated from the surroundings. During this process  $\Delta H = 0$  i.e., there is no change in enthalpy, but still the process is spontaneous.

We may now formulate another postulate: in an isolated system, there is always a tendency for the systems' energy to become more disordered or chaotic and this could be a criterion for spontaneous change!

To explain this, we introduce another thermodynamic function, entropy denoted as  $S$ . The above mentioned disorder is the manifestation of entropy. One can think of entropy as a measure of the degree of randomness or disorder in the system. The greater the disorder in an isolated system, the higher is the entropy.

Entropy, like any other thermodynamic property such as internal energy  $U$  and enthalpy  $H$  is a state function and  $\Delta S$  is independent of path.

Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. Thus heat ( $q$ ) has randomizing influence on the system.

However, the distribution of heat also depends on the temperature at which heat is added to the system. A system at higher temperature has greater randomness in it than one at lower temperature. Thus, temperature is the measure of average chaotic motion of particles in the system.

Heat added to a system at lower temperature causes greater randomness than when the same quantity of heat is added to it at higher temperature. This suggests that the entropy change is inversely proportional to the temperature.  $\Delta S$  is related with  $q$  and  $T$  for a reversible reaction as :

$$\Delta S = \frac{q_{rev}}{T}$$

The total entropy change ( $\Delta S_{total}$ ) for the system and surroundings of a spontaneous process is given by

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

When a system is in equilibrium, the entropy is maximum, and the change in entropy,  $\Delta S = 0$ .

We can say that entropy for a spontaneous process increases till it reaches maximum and at equilibrium the change in entropy is zero. Since entropy is a state property, we can calculate the change in entropy of a reversible process by

$$\Delta S_{sys} = \frac{q_{sys,rev}}{T}$$

We find that both for reversible and irreversible expansion for an ideal gas, under isothermal conditions,  $\Delta U = 0$ , but  $\Delta S_{total}$  i.e.,  $\Delta S_{system} + \Delta S_{surr}$  is not zero for irreversible process. Thus,  $\Delta U$  does not discriminate between reversible and irreversible process, whereas  $\Delta S$  does.

(iii) **Gibbs energy and spontaneity**: We have seen that for a system, it is the total entropy change,  $\Delta S_{total}$  which decides the spontaneity of the process. But most of the chemical reactions fall

into the category of either closed systems or open systems. Therefore, for most of the chemical reactions there are changes in both enthalpy and entropy. Therefore, neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for these systems.

For this purpose, we define a new thermodynamic function the Gibbs energy or Gibbs function,  $G$ , as

$$G = H - TS$$

Gibbs function,  $G$  is an extensive property and a state function.

The change in Gibbs energy for the system,  $\Delta G_{sys}$  can be written as

$$\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys} - S\Delta T_{sys}$$

At constant temperature,  $\Delta T = 0$

$$\therefore \Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$$

Usually the subscript 'system' is dropped and we simply write this equation as

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

Now let us consider how  $\Delta G$  is related to reaction spontaneity. We know

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$$

If the system is in thermal equilibrium with the surrounding, then the temperature of the surrounding is same as that of the system. Also, increase in enthalpy of the surrounding is equal to decrease in the enthalpy of the system.

Therefore, entropy change of surroundings

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

$$\therefore \Delta S_{total} = \Delta S_{system} + \left(-\frac{\Delta H_{sys}}{T}\right)$$

Rearranging the above equation:

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

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

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

$$\text{Thus, } -(\Delta H_{sys} - T\Delta S_{system}) > 0$$

$$\text{or, } -\Delta G > 0$$

$$\text{or, } \Delta G = \Delta H - T\Delta S < 0$$

$\Delta H$  is the enthalpy change of a reaction,  $T\Delta S$  is the energy which is not available to do useful work. So  $\Delta G$  is the net energy available to do useful work and is thus a measure of the 'free energy'. For this reason, it is also known as the free energy of the reaction.

$\Delta G$  gives a criteria for spontaneity at constant pressure and temperature.

- (i) If  $\Delta G$  is negative ( $< 0$ ), the process is spontaneous.
- (ii) If  $\Delta G$  is positive ( $> 0$ ), the process is non spontaneous.

**Note :** If a reaction has a positive enthalpy change and positive entropy change, it can be spontaneous when  $T\Delta S$  is large enough to outweigh  $\Delta H$ . This can happen in two ways;

- (a) The positive entropy change of the system can be 'small' in which case  $T$  must be large.
- (b) The positive entropy change of the system can be 'large', in which case  $T$  may be small.

The former is one of the reasons why reactions are often carried out at high temperature.

**GIBBS ENERGY CHANGE AND EQUILIBRIUM :** Let us examine the free energy changes in reversible reactions. 'Reversible' under strict thermodynamic sense is a special way of carrying out a process such that system is at all times in perfect equilibrium with its surroundings. When applied to a chemical reaction, the term 'reversible' indicates that a given reaction can proceed in either direction simultaneously, so that a dynamic equilibrium is set up. At equilibrium the free energy of

the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy.

So, the criterion for equilibrium  $A + B \rightleftharpoons C + D$  ; is  $\Delta_r G = 0$

Gibbs energy for a reaction in which all reactants and products are in standard state,  $\Delta_r G^0$  is related to the equilibrium constant of the reaction as follows:

$$0 = \Delta_r G^0 + RT \ln K$$

$$\text{or, } \Delta_r G^0 = - RT \ln K$$

$$\text{or, } \Delta_r G^0 = -2.303 RT \log K$$

$$\text{or, } \Delta_r G^0 = \Delta_r H^0 - T \Delta_r S^0 = - RT \ln K$$

For strongly endothermic reactions, the value of  $\Delta_r H^0$  may be large and positive. In such a case, value of K will be much smaller than 1 and the reaction is unlikely to form much product.

In case of exothermic reactions,  $\Delta_r H^0$  is large and negative, and  $\Delta_r G^0$  is likely to be large and negative too. In such cases, K will be much larger than 1. We may expect strongly exothermic reactions to have a large K, and hence can go to near completion.

$\Delta_r G^0$  also depends upon  $\Delta_r S^0$ , if the changes in the entropy of reaction is also taken into account, the value of K or extent of chemical reaction will also be affected, depending upon whether  $\Delta_r S^0$  is positive or negative.

#### **SECOND LAW OF THERMODYNAMICS :**

The entropy of the universe increases in every spontaneous (natural) change. The entropy of the universe is continuously increasing. Other statements of second law of thermodynamics

(i) **Clausius** : Heat cannot itself pass from a colder body to a hotter body.

(ii) **Kelvin** : It is impossible to get a continuous supply of work from a body or engine which can transfer heat from a single heat reservoir.

(iii) **Planck** : It is impossible to construct a device which will work in a single complete cycle and convert heat into work without producing any change in the surroundings.

**ZEROth LAW OF THERMODYNAMICS** : If two bodies have separately equality of temperature with a third body, they also have equality of temperature with each other.

**THIRD LAW OF THERMODYNAMICS** : At absolute zero temperature, the entropy of a perfectly crystalline substance is taken as zero. This law was formulated by Nernst in 1906.