

Chemical Thermodynamics

The word 'thermodynamics' implies flow of heat. It deals with energy changes accompanying all types of physical and chemical processes.

1. **Fundamentals of Thermodynamics** The several terms used in thermodynamics are given below:

- (i) **System and surroundings** The region, where the observation of transformation of heat and work are made is known as system and the remaining area other than system is known as surrounding.

On the basis of exchange of mass and energy, systems are of three types :

- (a) **Isolated system** In which neither matter nor energy can be exchanged with surroundings.
- (b) **Closed system** In which only energy can be exchanged with surroundings.
- (c) **Open system** In which energy and matter both can be exchanged with surroundings.

(ii) **Thermodynamic properties**

- (a) **Intensive properties** Those properties, that depends on nature of matter but do not depend on quantity of the matter, e.g. pressure, temperature, specific heat, melting point, etc.
- (b) **Extensive properties** Those properties, that depends on quantity of the matter present in the system, e.g. internal energy, heat, total moles, volume, enthalpy, entropy, free energy, etc.

(iii) **State and path functions**

- (a) **State functions** The properties which does not depend upon initial and final state of system are known as state functions, e.g. p, V, T, U, G, S, H , etc.
- (b) **Path functions** The properties which depend upon path of the system are known as path functions. e.g. W and q .

2. Types of Thermodynamic Processes The state of a variable can be changed via thermodynamic processes.

These processes are of the following types:

- (i) **Adiabatic process** In this process, the wall isolating the system and the surroundings is called adiabatic wall. For an adiabatic processes, $dq = 0$
- (ii) **Isothermal process** It is the process in which temperature remains fixed. For an isothermal process, $dT = 0$ and thus, $dE = 0$.
- (iii) **Isobaric process** In isobaric process, change in state is brought about at constant pressure, i.e. $dp = 0$.
- (iv) **Isochoric process** In an isochoric process, volume of the system remains constant, i.e. $dV = 0$.
- (v) **Cyclic process** When a system undergoes a number of different states and finally returns to its initial state, the process is called cyclic. dE or $dU = 0$ and $dH = 0$
- (vi) **Reversible process** A reversible system is defined as a system where changes take place infinitesimally slow and the direction of which at any point can be reversed by infinitesimal change in the state of the system.
- (vii) **Irreversible process** An irreversible process is the one in which direction of process cannot be reversed by small change in variables.

3. Work If an object is displaced through a distance dx by a force F , the amount of work done is given by

$$W = F \times dx$$

i.e. it is the product of two factors.

(i) Intensity factor, F (ii) Capacity factor, dx

Work done by the system = - ve

Work done on the system = + ve

Or

In other words, if a system loses energy, work is done by the system and if it gains energy, work is done on the system.

Mechanical work done by a system

(i) **Irreversible process**

$$W_{\text{irrev}} = -p_{\text{ext}} (V_f - V_i)$$

(ii) **Reversible process**

$$W_{\text{rev}} = -2.303nRT \log \frac{V_f}{V_i} = -2.303 nRT \log \frac{p_i}{p_f}$$

4. Heat Capacity In the expression of heat, i.e. $q = \text{coefficient} \times \Delta T$

if coefficient is taken as C , then $q = C\Delta T$

This coefficient C is called the heat capacity, and is defined as the quantity of heat required to raise the temperature of a system by 1° celcius.

The specific heat capacity is denoted by c and can be calculated with the help of following formula:

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

where, q = heat required to raise the temperature by 1°C

c = specific heat capacity, m = mass

ΔT = temperature change (in $^\circ\text{C}$)

If C is the heat capacity of n mole of the system, then its molar heat capacity (C_m) is given by $C_m = C/n$.

5. Internal Energy The total energy within a substance or a system is called its internal energy. It is the sum of electronic energy, nuclear energy, chemical bond energy, potential energy and kinetic energy. Absolute value of internal energy cannot be determined. Internal energy is a state function and an extensive property.

If $U_1 < U_2$, energy is absorbed, hence ΔU is positive. If $U_1 > U_2$, energy is released, hence ΔU will be negative. During an isothermal process, $\Delta U = 0$ for an ideal gas.

6. First Law of Thermodynamics Energy can neither be created nor be destroyed but can be converted from one form to another. That's why, it is also called law of conservation of energy. The mathematical expression of first law of the thermodynamics is

$$\Delta U = q + W$$

If work done is work of expansion, then $W = -p\Delta V$ where p is external pressure and ΔV is change in volume.

Hence, $\Delta U = q - p\Delta V$; $q = \Delta U + p\Delta V$

Neither q nor W is a state function but $q + W$ is a state function for ideal gas. For isothermal expansion as $\Delta U = 0$, thus $q = -W$.

7. **Enthalpy** It is the sum of internal energy and the product of pressure-volume work. It is an extensive property and represented by the symbol H .

$$\therefore H = U + pV \Rightarrow \Delta U + p\Delta V = \Delta H$$

If $\Delta V = 0$, so $\Delta H = \Delta E$ and as $\Delta H = q_p$

Then, $\Delta E = q_v$

Here, q_v = heat supplied at constant volume

q_p = heat supplied at constant pressure

Relation between ΔH and ΔU

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

This equation is helpful for calculating ΔH from ΔU and vice-versa.

If, **Case I** $\Delta n_g = 0$, then $\Delta H = \Delta U$,

Case II $\Delta n_g < 0$, then $\Delta H < \Delta U$,

Case III $\Delta n_g > 0$, then $\Delta H > \Delta U$,

8. **Measurement of ΔU and ΔH : Calorimetry.**

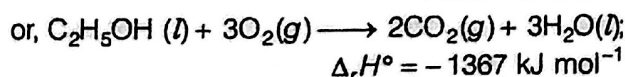
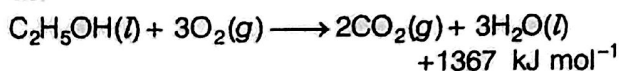
From the temperature change, the heat (i.e. q_v or U) is calculated by the expression,

$$q_v = c \cdot m \cdot \Delta T = C \cdot \Delta T = \frac{C \cdot \Delta T \cdot M}{m_i}$$

(M = molar mass, m_i = mass)

Since, the bomb-calorimeter is sealed, its volume remains the same, (i.e. $\Delta V = 0$) and hence, no work is done on/by the system.

9. **Thermochemical Equations** A balanced chemical equation in which the value of enthalpy of reaction (ΔH°) is also mentioned is called a thermochemical equation. The thermochemical equation for the combustion of ethanol is written as:



Negative sign of enthalpy of reaction shows the exothermic nature of the reaction.

10. **Enthalpy Change, $\Delta_r H$ of a Reaction or Reaction Enthalpy**

Enthalpy change of a reaction can be calculated by the following expression:

$\Delta_r H$ = sum of enthalpies of products – sum of enthalpies of reactants

$$\Delta_r H = \sum_i x_i H_p - \sum_j y_j H_R$$

where, x_i and y_j = stoichiometric coefficients of products and reactants respectively in a balanced equation.

Σ = sigma used for summation

H_p = enthalpy of formation of products

H_R = enthalpy of formation of reactants

Enthalpy change during phase transformations

- (i) **Enthalpy of fusion ($\Delta_{\text{fus}} H^\circ$)** The enthalpy change occurring when 1 mole of a solid substance in its standard state melts completely into its liquid form is called standard or molar enthalpy of fusion.
- (ii) **Enthalpy of vaporisation ($\Delta_{\text{vap}} H^\circ$)**, The enthalpy change when one mole of a liquid is converted into vapour at its boiling temperature and under standard pressure (1 bar) is called enthalpy of vaporisation or molar enthalpy of vaporisation.
- (iii) **Enthalpy of sublimation ($\Delta_{\text{sub}} H^\circ$)** The enthalpy change when one mole of a solid substance sublimates, i.e. converted into its vapours without melting at a temperature below its melting point (and at 1 bar pressure) is called the enthalpy of sublimation or molar enthalpy of sublimation.

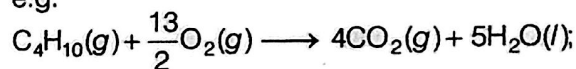
11. **Enthalpies for Different Types of Reactions**

Depending upon the type of reactions, the enthalpies can be of following types:

- (i) **Standard enthalpy of combustion ($\Delta_c H^\circ$)**

The amount of heat evolved when one mole of the substance is burnt completely in oxygen or air and all the reactants and products are in their standard states, is called the standard enthalpy of combustion.

e.g.



$$\Delta_c H^\circ = -2658.0 \text{ kJ mol}^{-1}$$

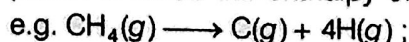
Calorific value

Mathematically, calorific value = $\frac{\Delta_c H}{\text{mass}}$

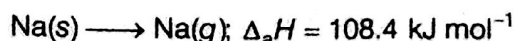
- (ii) **Enthalpy of formation, ($\Delta_f H^\circ$)** It is the enthalpy change taking place when 1 mole of the substance is formed from its elements. Enthalpy of reaction can be calculated from enthalpies of formation as

$$\Delta H_r = \Sigma \Delta_f H^\circ_{\text{products}} - \Sigma \Delta_f H^\circ_{\text{reactants}}$$

- (iii) **Enthalpy of atomisation, ($\Delta_a H^\circ$)** The enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase is called the enthalpy of atomisation.



$$\Delta_a H = 165 \text{ kJ mol}^{-1}$$



- (iv) **Bond enthalpy ($\Delta_{\text{bond}} H^\circ$) or bond dissociation enthalpy**, The enthalpy change accompanying the breaking of one mole of covalent bonds of a gaseous covalent compound to give products in the gas phase, is called the bond dissociation enthalpy.

Mean bond enthalpy From the bond enthalpy it is possible to calculate enthalpy change of a reaction by using the expression.

$$\Delta_r H^\circ = \sum \text{Bond enthalpies}_{\text{reactants}} - \sum \text{Bond enthalpies}_{\text{products}}$$

or
$$\Delta_r H^\circ = \sum \Delta_f H^\circ_{\text{bonds of products}} - \sum \Delta_f H^\circ_{\text{bonds of reactants}}$$

(A) **Enthalpy of solution ($\Delta_{\text{sol}} H^\circ$)** The enthalpy change when one mole of solute is dissolved completely in specified amount of solvent or water is called enthalpy of solution

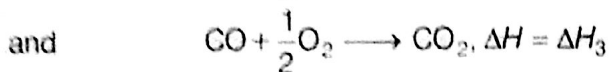
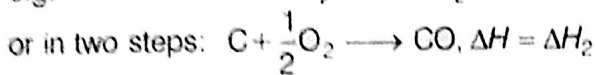
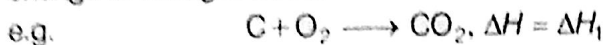
The enthalpy of solution is also given as,

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

(B) **Enthalpy of dilution ($\Delta_{\text{dil}} H^\circ$)** The enthalpy change associated with the dilution process of a component in a solution at constant pressure.

12. Hess's Law of Constant Heat Summation

The total amount of heat absorbed or evolved is same whether the reaction takes place in one step or in number of steps, i.e. it depends only on the initial reactants and final products and does not depend upon the path by which this change is brought about.



Then, $\Delta H_1 = \Delta H_2 + \Delta H_3$

13. Entropy It is the measure of degree of randomness or disorder in an isolated system and is represented by the symbol S. Greater the degree of randomness, higher is the entropy. Entropy is also a state function, i.e. depends only on initial and final states of a system, so entropy change can be given as,

$$\Delta S = S_2 - S_1 = \sum S_{\text{products}} - \sum S_{\text{reactants}}$$

14. Entropy Change for Various Processes

Consider an isothermal reversible process in which, let the system absorbs q amount of heat from surroundings at temperature, T . The increase in the entropy of the system will be

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

When the reversible process is adiabatic, there will be no heat exchange between system and surroundings,

i.e.
$$q = 0$$

$$\therefore \Delta S_{\text{system}} = 0$$

$$\Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

Entropy change in irreversible processes

$$\therefore \Delta S_{\text{system}} = - \frac{q}{T_1}, \Delta S_{\text{surroundings}} = + \frac{q}{T_2}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$= \frac{q}{T_1} + \frac{q}{T_2} = q \left[\frac{T_1 - T_2}{T_1 T_2} \right]$$

But $T_1 > T_2$

$$\therefore T_1 - T_2 = +ve \text{ or } \Delta S_{\text{total}} > 0$$

Entropy change during phase transitions

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

$$\Delta S_{\text{vaporisation}} = S_{\text{vap}} - S_{\text{liq}} = \frac{\Delta H_{\text{vaporisation}}}{T_b}$$

$$\Delta S_{\text{sublimation}} = S_{\text{vap}} - S_{\text{sol}} = \frac{\Delta H_{\text{sublimation}}}{T_{\text{sub}}}$$

15. Spontaneity A physical or chemical change that occurs by its own, i.e. without the assistance of external source, is called spontaneous process or natural process or feasible process or probable process.

16. Second Law of Thermodynamics It can be stated as "for a spontaneous process in an isolated system, the change in entropy is positive."

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

17. Gibbs Energy and Spontaneity The maximum amount of energy available to a system during a process, that can be converted into useful work is called free energy or Gibbs free energy or Gibbs energy.

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

The above equation is called **Gibbs Helmholtz equation** or simply **Gibbs equation**.

In this equation,

ΔG = change in free energy

ΔH = enthalpy change

ΔS = change in entropy

T = absolute temperature

At a given temperature and pressure,

(i) If ΔG is negative (< 0), the process is spontaneous.

(ii) If ΔG is positive (> 0), the process is non-spontaneous.

(iii) If ΔG is zero, the process is in equilibrium state.

Standard free energy change

$$\Delta_r G^\circ = \left[\begin{array}{l} \text{Sum of the standard free energies} \\ \text{for formation of products} \end{array} \right]$$

$$- \left[\begin{array}{l} \text{Sum of the standard free energies} \\ \text{for formation of reactants} \end{array} \right]$$

$$= \sum \Delta_r G^\circ_{\text{(products)}} - \sum \Delta_r G^\circ_{\text{(reactants)}}$$

18. Standard Free Energy of Formation Free energy change when 1 mole of the compound is made from its elements in their standard states is called standard molar free energy of formation of a compound.

Efficiency of a fuel cell =
$$\frac{\Delta G}{\Delta H}$$

Relation between Gibbs free energy and equilibrium constant

$$\Delta G = \Delta G^\circ + RT \ln Q \quad [\because Q = \text{reaction quotient}]$$

At equilibrium, $\Delta G = 0$

and $Q = K$

Hence, $\Delta G^\circ = -RT \ln K$

$$\Delta G^\circ = -2.303 RT \log K$$

The above equation is helpful in predicting the spontaneity of the reaction. e.g.

(i) If $\Delta G^\circ < 0$, $-\Delta G^\circ/RT = +ve$ and $e^{-\Delta G^\circ/RT} > 1$ and hence, $K > 1$.

It means that the reaction occurs spontaneously.

(ii) If $\Delta G^\circ > 0$; $-\Delta G^\circ/RT = -ve$
and $e^{-\Delta G^\circ/RT} < 1$ and hence $K < 1$.

It means that the reaction is non-spontaneous.

19. Third Law of Thermodynamics

According to this law, "the entropy of a perfectly crystalline substance approaches zero as the absolute zero of temperature is approached". It forms on the basis from which entropies at other temperatures can be measured.

$$\lim_{T \rightarrow 0} S = 0$$

In case of CO and NO molecules in solid state, there is randomness even at 0 K due to their dipole moment, hence, entropy in such cases is not zero even at 0 K.