

- **Equilibrium:** It is a state in a process when two opposing processes (forward and reverse) occur simultaneously at the same rate.
- The free energy change at equilibrium state is zero i.e., $\Delta G = 0$.
- **Types of the System:** System are of three types, which are as follows:
 - (i) Open System:** Exchange both matter and energy with the surroundings. For example: Reactant in an open test tube.
 - (ii) Closed System:** Exchange energy but no matter with the surroundings. For example: Reactants in a closed vessel.
 - (iii) Isolated System:** Neither exchange energy nor matter with the surroundings. For example: Reactants in a thermos flask.
- **State of a System:** The variables of functions whose value depend only on the state of a system or they are path independent. For example : pressure (P), volume (V), temperature (T), enthalpy (H), free energy (G), internal energy (U), entropy (S), amount (n) etc.
- **Properties of a System:** The measurable properties of a system are called state variables. They may be further divided into two main types.
 - (i) Extensive property (variable):** It is one whose value depends upon the size of the system. For example, volume, weight, heat, etc.
 - (ii) Intensive property (variable):** It is one whose value is independent of the size of the system. For example, temperature, pressure, refractive index, viscosity, density, surface tension, etc.
- **Thermodynamic Processes :**
 - (i) Isothermal process:** When the temperature of the system remains constant during various operations, then the process is said to be isothermal ($\Delta T = 0$).
 - (ii) Adiabatic process:** In an adiabatic process there is no exchange of heat between the system and the surroundings ($\Delta q = 0$)
 - (iii) Isobaric process:** When the pressure of the system remains constant during various operations, then the process is said to be isobaric ($\Delta P = 0$).
 - (iv) Isochoric process:** When the volume of the system remains constant during various operations, then the process is said to be isochoric $\Delta V = 0$
 - (v) Cyclic process:** When the total internal energy of the system remains constant during various operations, then the process is said to be cyclic ($\Delta U = 0$)
 - (vi) Reversible process:** Process which proceeds infinitely slowly by a series of equilibrium steps.
 - (vii) Irreversible process:** Process which proceeds rapidly and the system does not have chance to achieve equilibrium.

EXOTHERMIC AND ENDOTHERMIC REACTIONS

- Exothermic reactions are those reactions which proceed with the evolution of heat.
- Endothermic reactions are those reactions which proceed with the absorption of heat from the surroundings.

THERMOCHEMICAL EQUATIONS

- Such an **equation** in which information about heat change is included is called a **thermochemical equation**. It is very important in such a case to indicate the physical **state** of the various species involved.

Examples are:



THE FIRST LAW OF THERMODYNAMICS

- **First Law of Thermodynamics:** The energy of an isolated system is constant.

Mathematical Form: $\Delta U = q + w$

where, ΔU = change in internal energy,
 q = heat absorbed by the system, and
 w = work done on the system.

- **Internal Energy (U):** The energy may be defined as the sum of the energies of all the atoms, molecules or ions contained in the system.
- Heat (q) and Work (w) Heat and work are not state functions. This is because the values of both q and w depend upon the way in which the change is carried out.

Sign Conventions for Heat (q) and Work (w):

- (i) $W = +ve$, if work is done on system
- (ii) $W = -ve$, if work is done by system
- (iii) $q = +ve$, if heat is absorbed by the system.
- (iv) $q = -ve$, if heat is evolved by the system.

Work of Expansion/compression:

$$w = -P_{\text{ext}} (V_f - V_i)$$

- **Enthalpy:** It is the measurement of energy in a thermodynamic system. The quantity of **enthalpy** equals to the total content of heat of a system, equivalent to the system's internal energy plus the product of volume and pressure.

$$H = U + pV \text{ or } \Delta H = q_p$$

- **Work done in Isothermal Reversible Expansion of an Ideal Gas :**

$$w_{\text{rev}} = -2.303 nRT \log \frac{V_f}{V_i}$$

$$\text{Or, } w_{\text{rev}} = -2.303 nRT \log \frac{P_i}{P_f}$$

- **Significance of ΔH and ΔU :**
 $\Delta H = q_p$ and $\Delta U = q_v$
- **Relation between ΔH and ΔU :**
 $\Delta H = \Delta U + (n_p - n_r)RT$ for gaseous reaction.

- (i) $\Delta H = \Delta U$ if $(n_p - n_r)$ is zero; e.g., $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- (ii) $\Delta H > \Delta U$ if $(n_p - n_r)$ is positive; e.g., $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
- (iii) $\Delta H < \Delta U$ if $(n_p - n_r)$ is negative; e.g., $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

STANDARD ENTHALPY OF REACTIONS

- It is defined as the enthalpy change for a reaction, when the reactants and the products are in their standard states. It is denoted by $\Delta_r H^\ominus$.
- **Enthalpy of formation ($\Delta_f H^\ominus$):** The enthalpy change when one mole of a pure compound is formed from its elements in their most stable states is called the enthalpy of formation and is denoted by $\Delta_f H^\ominus$
- **Enthalpy of Combustion ($\Delta_{\text{comb}} H^\ominus$):** Enthalpy of combustion is the enthalpy change (heat evolved) accompanying the complete combustion of 1 mole of a substance in oxygen at a given temperature and 1 bar pressure.
- **Enthalpy of Neutralization ($\Delta_{\text{neut}} H^\ominus$):** Enthalpy of neutralization is the enthalpy change (heat evolved) when one mole of hydrogen ions (H^+) is neutralized by one mole of hydroxyl ions (OH^-) in dilute aqueous medium to form water.
- **Enthalpy of atomization ($\Delta_a H^\ominus$):** It is the change in enthalpy when one mole of a substance is converted into its atoms in gaseous state at a given temperature and 1 bar pressure
- **Enthalpy of transition (phase transformation) ($\Delta_{\text{trs}} H^\ominus$):** It is the change in enthalpy when one mole of substance changes from one phase to another at a constant temperature and under 1 bar pressure
- **Enthalpy of Solution ($\Delta_{\text{sol}} H^\ominus$):** It is the change in enthalpy when one mole of a solute is dissolved in a specific amount of a solvent at a constant temperature and under 1 bar pressure.

- **Enthalpy of ionization ($\Delta_{\text{ion}}H^\ominus$):** It is the change in enthalpy when one mole of a weak electrolyte ionizes completely

in its solution at a constant temperature and under 1 bar pressure.

LAWS OF THERMOCHEMISTRY

- **There are two laws of thermochemistry:** The Lavoisier-Laplace law and the Hess's Law of Constant Heat Summation.
- **Lavoisier–Laplace Law:** When a chemical equation is reversed, the sign of Δ_rH is changed. For example, $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}); \Delta_rH = 180.5 \text{ kJ}$ $2\text{NO}(\text{g}) \rightarrow \text{N}_2(\text{g}) + \text{O}_2(\text{g}); \Delta_rH = -180.5 \text{ kJ}$
- **Hess's Law of Constant Heat Summation:** The total enthalpy change of a reaction remains same whether it takes place in one step or in several steps.
- **Bond Dissociation Enthalpy:** Enthalpy change when one mole of a gaseous covalent bond is broken to form products in gas phase.
- Thermodynamics deals with energy changes in chemical or physical processes and enables us to study these changes quantitatively and to make useful predictions. For these purposes, we divide the universe into the system and the surroundings.

Thermodynamic System

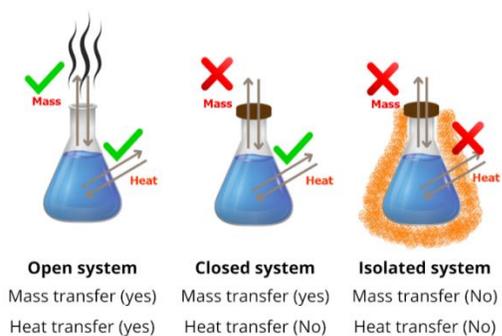


Fig 9.2 Thermodynamic Systems

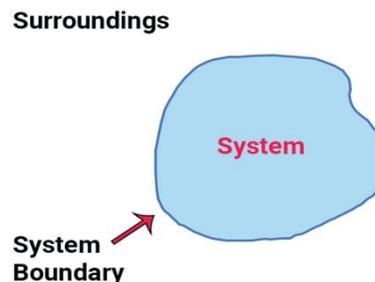
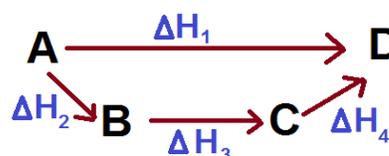


Fig 9.1 System and Surrounding

- **Hess's Law:** The enthalpy change in a chemical or physical process is the same whether the process is carried out in one step or in several steps.



$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

- Hess's law is one of the important outcomes of the first law of thermodynamics.

Applications of Hess's Law:

- It helps in calculating the enthalpies of formation of those compounds which cannot be determined experimentally.
- It helps in determining the enthalpy of allotropic transformation like $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$
- It helps in calculating the enthalpy of hydration.
- For Polyatomic gaseous molecules; Bond Enthalpy = Average of the bond dissociation enthalpies of the bonds of the same type.

Check Yourself

1. Third law of thermodynamics provides a method to evaluate which property?

- (A) Absolute Energy
(B) Absolute Enthalpy
(C) Absolute Entropy
(D) Absolute Free Energy

2. One mole of which of the following has the highest entropy?

- (A) Liquid Nitrogen (B) Hydrogen Gas
(C) Mercury (D) Diamond

3. The enthalpy of vaporisation of a substance is 8400 J mol^{-1} and its boiling point is -173°C . The entropy change for vaporisation is:

- (A) $84 \text{ J mol}^{-1}\text{K}^{-1}$ (B) $21 \text{ J mol}^{-1}\text{K}^{-1}$
(C) $49 \text{ J mol}^{-1}\text{K}^{-1}$ (D) $12 \text{ J mol}^{-1}\text{K}^{-1}$

4. The species which by definition has ZERO standard molar enthalpy of formation at 298 K is

- (A) $\text{Br}_{2(\text{g})}$ (B) $\text{Cl}_{2(\text{g})}$
(C) $\text{H}_2\text{O}_{(\text{g})}$ (D) $\text{CH}_{4(\text{g})}$

5. Which of the following is true for the reaction? $\text{H}_2\text{O} (\text{l}) \leftrightarrow \text{H}_2\text{O} (\text{g})$ at 100°C and 1 atm pressure

- (A) $\Delta S = 0$ (B) $\Delta H = T \Delta S$
(C) $\Delta H = \Delta U$ (D) $\Delta H = 0$

Stretch Yourself

1. Why is it advised to add ethylene glycol to water in a car radiator in hill station?

2. An aqueous solution of 2% non-volatile exerts a pressure of 1.004 Bar at the normal boiling point of the solvent. What is the molar mass of the solute?

3. Explain why does an azeotropic mixture distill without any change in composition?

Test Yourself

Question: Out of NH_3 and CO_2 which gas will be adsorbed more readily on the surface of activated charcoal and why?

Answer: NH_3 gas will be adsorbed more readily on activated charcoal. It has higher critical temperature than CO_2 and is an easily liquefiable gas. Its Van der Waals forces are stronger.



Answers

Check Yourself

Answer: 1(C); 2(B); 3(A); 4(B); 5(A)

Stretch Yourself

1. NH_3 has higher critical temperature than CO_2 , *i.e.*, NH_3 is more liquefiable than CO_2 . Hence, NH_3 has greater intermolecular forces of attraction and hence will be adsorbed more readily.
2. Do it by yourself.
3. River water is a colloidal solution of clay and sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in the sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.
4. Dialysis is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane
5. Hydrated ferric oxide sol $\text{AlCl}_3/\text{Al}^{3+}$