

3. Chemical Thermodynamics and Energetic

System – Part of the universe in which observations are made

Surroundings – Part of universe excluding system

Universe = System + Surroundings

Types of system:

- **Open system:** Exchange of energy and matter takes place between the system and the surroundings
- **Closed system:** No exchange of matter, but exchange of energy can take place between the system and surroundings
- **Isolated system:** No exchange of energy and matter takes place between the system and the surroundings.

The State of System

- State of a thermodynamic system can be described by properties such as its pressure (p), temperature (T), volume (V), composition of the system, etc.
- The values of state functions or state variables depend only on the state of the system and not on how it is reached.

First law of thermodynamics:

“The energy of an isolated system is constant.”

$\Delta U = q + w$ (Mathematical statement)

Work

- If the pressure is not constant at every stage of compression, but changes in a number of finite steps, then

$$W = -\sum p \Delta V$$

- If the pressure is not constant at every stage of compression, but changes in a number of finite steps, then

$$W = -\int_{V_i}^{V_f} p_{\text{ex}} dV$$

- For a reversible isothermal process

$$\begin{aligned}
 W_{\text{rev}} &= - \int_{V_i}^{V_f} nRT \frac{dV}{V} \\
 &= -nRT \ln \frac{V_f}{V_i} \\
 \therefore W_{\text{rev}} &= -2.303 nRT \log \frac{V_f}{V_i}
 \end{aligned}$$

- Work done is zero during free expansion (whether the process is reversible or irreversible).
- For adiabatic change, $q = 0$, $\Delta U = w_{\text{ad}}$

Work

$$\begin{aligned}
 q_{\text{rev}} = -w &= nRT \ln \frac{V_f}{V_i} \\
 &= -2.303 nRT \log \frac{V_f}{V_i}
 \end{aligned}$$

For isothermal irreversible change:

$$\begin{aligned}
 q_{\text{irrev}} = -w &= nRT \ln \frac{V_f}{V_i} \\
 &= -2.303 nRT \log \frac{V_f}{V_i}
 \end{aligned}$$

For isothermal reversible change:

$$\begin{aligned}
 q_{\text{rev}} = -w &= nRT \ln \frac{V_f}{V_i} \\
 &= -2.303 nRT \log \frac{V_f}{V_i}
 \end{aligned}$$

For adiabatic change, $q = 0$:

$$\Delta U = w_{\text{ad}}$$

Enthalpy:

$$\begin{aligned}
 \Delta H &= \Delta U + p\Delta V \\
 \Delta H &= q_p \text{ (at constant pressure)} \\
 \Delta H &= \Delta U = q_v \text{ (at constant volume)} \\
 \Delta H &= \Delta U + \Delta n_g RT
 \end{aligned}$$

ΔH is positive for endothermic reactions and is negative for exothermic reactions.

Extensive property: Value depends on the quantity or size of matter present in the system. Examples: mass, volume, internal energy, enthalpy, heat capacity, etc.

Intensive property: Does not depend on the quantity or size of the matter

Examples: temperature, pressure, density, etc.

Heat capacity:

For an ideal gas, $C_P - C_V = R$

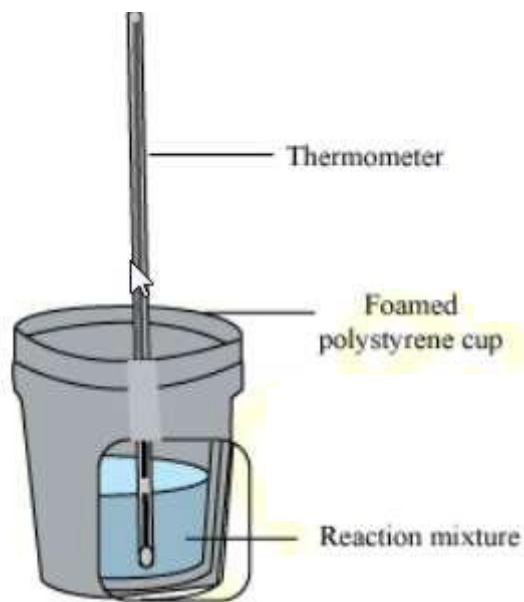
Calorimetry

Measurement of ΔU

- Measured by using a bomb calorimeter
- $q = C_V \Delta T$
Where, C_V is the heat capacity of the bomb calorimeter

Measurement of ΔH

- The calorimeter used for measuring heat change at constant pressure



- At constant pressure, $\Delta H = q_p$

Reaction enthalpy or enthalpy change of a reaction, $\Delta_r H$

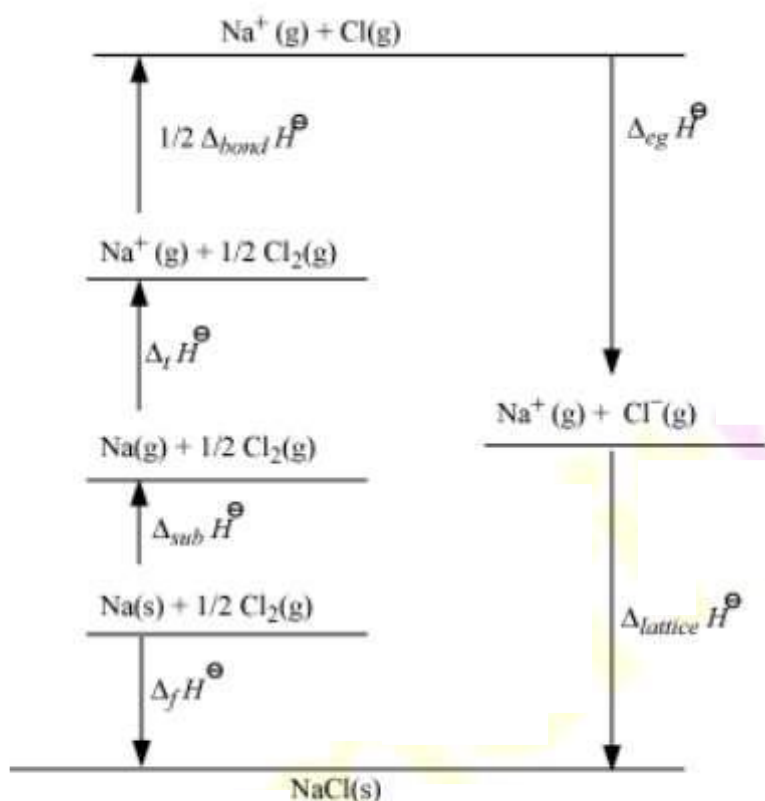
$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \dots$$

Hess's law of constant heat summation:

When a reaction takes place in several steps, its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 + \dots$$

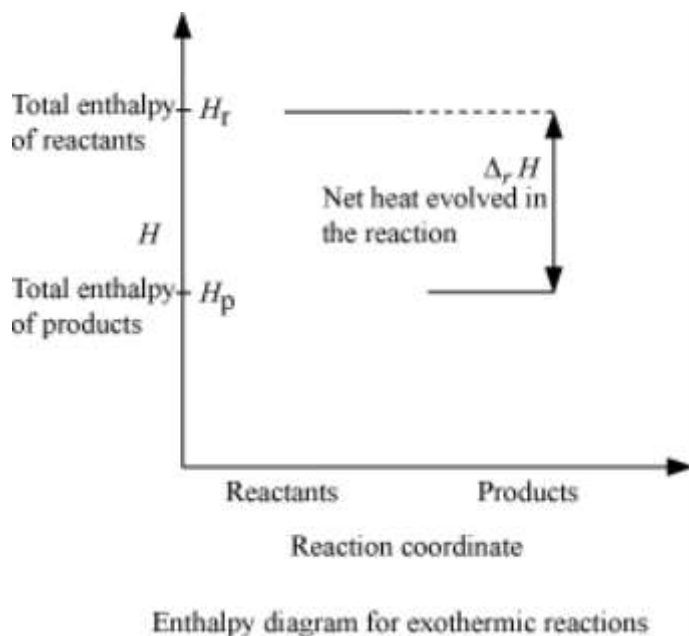
Lattice enthalpy: Enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.



Enthalpy diagram for lattice enthalpy of NaCl
(Born – Haber Cycle)

Spontaneity:

- Enthalpy



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

$$\Delta S = 0 \text{ (at equilibrium)}$$

- **Entropy:**

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

$$\Delta S = 0 \text{ (at equilibrium)}$$

For a spontaneous process:

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

For an isolated system, $\Delta U = 0, \Delta S > 0$

Thus, entropy change distinguishes a spontaneous change while energy change does not.

- **Gibbs energy:**

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

$$\Delta_r G = 0 \text{ (at equilibrium)}$$

For spontaneous reactions, ΔG is negative.

For non-spontaneous reaction, ΔG is positive.

$$\Delta G = -RT \ln K$$