# THERMODYNAMICS

## THERMODYNAMICS PROCESSES

- **Isothermal Process**
  $\Delta T = 0$
- **Isochoric Process**
  $\Delta V = 0$
- **Adiabatic Process**
  $q = 0$
- **Cyclic Process**
  $\Delta U_{cyclic} = 0$

## THERMODYNAMICS PROPERTIES

### INTENSIVE PROPERTIES
**P, T, N**

Properties of the System which are independent of amount of System.

#### STATE FUNCTION
Values of such functions do not depend on the path of the System.
e.g. $\Delta U$, $\Delta H$, $\Delta S$ etc.

### EXTENSIVE PROPERTIES
**V, U, H**

Properties of the System which depend on the amount of the System.

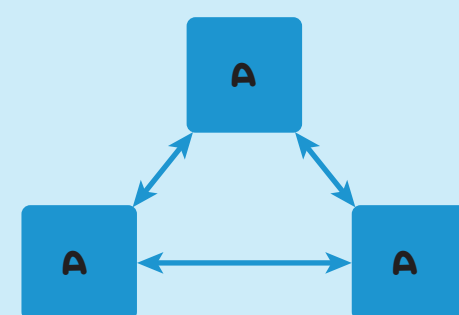#### PATH FUNCTION
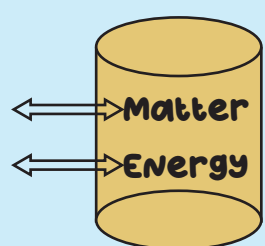Values of such functions depend on the path of the System.
e.g. W and q.

## ZEROTH LAW OF THERMODYNAMICS

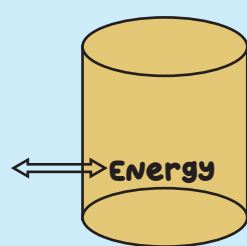If two bodies are in thermal equilibrium with a third one, then they are in thermal equilibrium with each other.

## GIBB'S FREE ENERGY

The net energy available to do useful work and it is a measure of Spontanity.
Standard free energy of a reaction:
$\Delta G^\circ = \Sigma \Delta G^\circ_{Products} - \Sigma \Delta G^\circ_{Reactants}$

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

$\Delta G < 0$, Process is Spontaneous

$\Delta G > 0$, Process is Non-Spontaneous

$\Delta G = 0$, Process is at equilibrium

## GIBB'S ENERGY CHANGE & EQUILIBRIUM

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

| | | |
|---|---|---|
| $\Delta G^\circ = 0$ | $\log K = 0$ | Equilibrium reached. |
| $\Delta G^\circ < 0$ | $\log K > 1$ | Mixture contains mostly products. |
| $\Delta G^\circ > 0$ | $\log K < 1$ | Mixture contains mostly reactants. |

## TYPES OF SYSTEM

**OPEN SYSTEM**
→ Matter
→ Energy

**CLOSED SYSTEM**
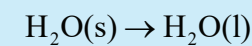→ Energy

**ISOLATED SYSTEM**
Matter
Energy

## ENTHALPY

$\Delta H = \Delta U + \Delta(PV)$
$\Delta H = \Delta U + \Delta n_g RT$

**Enthalpy of reaction** $(\Delta H)$

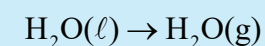$\Delta H = \Sigma \Delta H_{f(Products)} - \Sigma \Delta H_{f(Reactants)}$

$\Delta H = \Sigma B.E._{Reactants} - \Sigma B.E._{Products}$

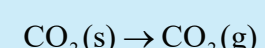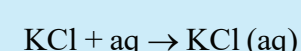| | |
|---|---|
| **Enthalpy of fusion** $(\Delta H^\circ_f)$ $H_2O(s) \rightarrow H_2O(l)$ | Enthalpy change when 1 mole of compound undergoes melting at constant temperature and atmospheric pressure. |
| **Enthalpy of vapourization** $(\Delta H^\circ_{vap})$ $H_2O(\ell) \rightarrow H_2O(g)$ | Enthalpy change when 1 mole of compound undergoes boiling at constant temperature and atmospheric pressure. |
| **Enthalpy of Sublimation** $(\Delta H^\circ_{sub})$ $CO_2(s) \rightarrow CO_2(g)$ | Enthalpy change when 1 mole of solid substance is directly converted into gaseous state at a constant temperature and standard pressure. |
| **Enthalpy of Solution** $(\Delta H^\circ_{sol})$ $KCl + aq \rightarrow KCl(aq)$ | Enthalpy change when 1 mole of substance is dissolved in fixed quantity of solvent. |
| **Bond dissociation enthalpy** $(B.E.)$ $Cl_2(g) \longrightarrow 2Cl(g)$ | It is the enthalpy change to break 1 mole bonds of a particular kind. |

## ISOTHERMAL IRREVERSIBLE WORK

$W_{irr} = -P_{ext}\Delta V$

### ISOTHERMAL REVERSIBLE

$W_{rev} = -2.303nRT \log\left(\frac{V_2}{V_1}\right)$

$W_{rev} = -2.303nRT \log\left(\frac{P_1}{P_2}\right)$

### ADIABATIC REVERSIBLE

$W_{rev} = \frac{nR}{\gamma R}(T_2 - T_1)$

| Sign of $\Delta H$ | Sign of $\Delta S$ | $\Delta G = \Delta H - T\Delta S$ | Spontanity. |
|---|---|---|---|
| Negative | Positive | Always Negative | Spontaneous at all temp. |
| Positive | Negative | Always Positive | Non-Spontaneous at all temperature. |
| Positive | Positive | +ve @ low temp. -ve @ low temp. | Non-Spontaneous at all temperature. Spontaneous at high temperature. |
| Negative | Negative | -ve @ low temp. +ve @ low temp. | Spontaneous at low temperature. Spontaneous at low temperature. |

## SPONTANEITY

It is natural direction of a process.

## ENTROPY

This is the measure of the degree of randomness or disorder of the system.

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

$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings}$

Entropy changes during phase transformation

$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T}$, $\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$

$\Delta_{sub} S = \frac{\Delta_{subs}H}{T}$

Entropy change of a reaction.

$\Delta_r S^\circ = \Sigma s^\circ_{products} - \Sigma s^\circ_{reactants}$

## WORK (W)

Work is a mode of energy transfer when temperature difference is not involved.

$W = -P_{ext}\Delta V$

## HEAT (q)

Exchange of energy due to temperature differnece.

## INTERNAL ENERGY (U)

Total energy within the substance

## FIRST LAW OF THERMODYNAMICS

Law of conservation of energy total energy of an isolated system is constant.

Mathematically, $\Delta U = q + w$

## SIGN CONVENTION

Heat absorbed by the system = +ve

Heat evolved by the system = -ve

Work done by the system = -ve

Work done on the system = +ve

## FREE EXPANSION

When an ideal gas expands in vacuum then, $P_{ext} = 0$.

$\therefore w = 0$

## SECOND LAW OF THERMODYNAMICS

The Total entropy of the universe is always increasing in the course of every spontaneous or natural change.

$\Delta S_{Total} > 0$

## THIRD LAW OF THERMODYNAMICS

The Entropy of a perfectly crystalline substance at 0 K or absolute zero Temperature to be zero.

## Molar HEAT CAPACITY

Amount of heat required to raise the temperature of a 1 mole Substance.

Molar heat capacity $\Rightarrow q_v = N_v RT$
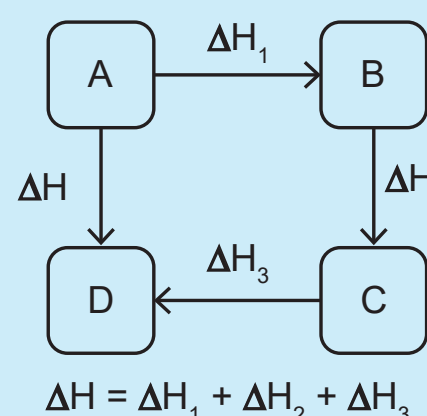
Specific heat capacity $\Rightarrow q_p = nC_p RT$
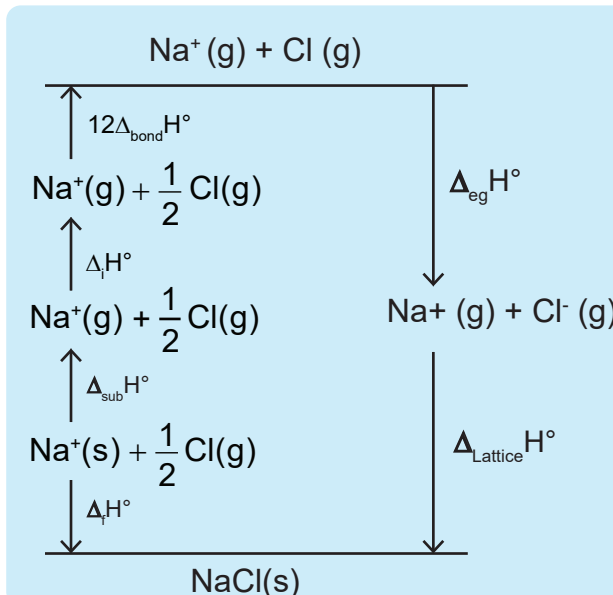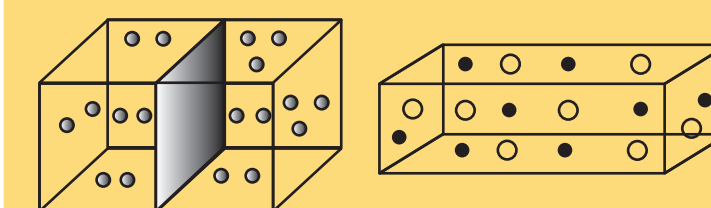
### MEYERS'S FORMULA
$C_p - C_v = R$

### POISSON'S RATIO
$\frac{C_p}{C_v} = \gamma$

## HESS' LAW CONSTANT HEAT SUMMATION

$A \xrightarrow{\Delta H_1} B$
$A \xrightarrow{\Delta H} D$
$B \xrightarrow{\Delta H_2} C$
$D \xleftarrow{\Delta H_3} C$

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

## EORN HABER CYCLE

$Na^+(g) + Cl(g)$

$\xrightarrow{12\Delta_{bond}H^\circ}$

$Na^+(g) + \frac{1}{2}Cl(g)$ — $\Delta_{eg}H^\circ$ → $Na^+(g) + Cl^-(g)$

$\Delta_f H^\circ$

$Na^+(g) + \frac{1}{2}Cl(g)$

$\Delta_{sub}H^\circ$

$Na^+(s) + \frac{1}{2}Cl(g)$ — $\Delta_{Lattice}H^\circ$

$\Delta_f H^\circ$

$NaCl(s)$

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