CONCEPT MAP

THERMODYNAMICS

Branch of science which deals with the study of different forms of energy and the quantitative relationships between them.

Thermodynamic Terms

System

Specified part of the universe which is under investigation

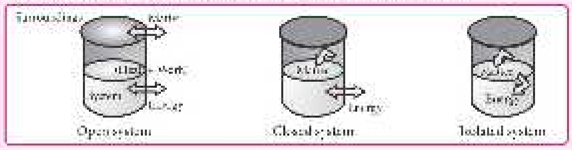
Surroundings

Remaining part of the universe which can interact with the system.

Open system : Can exchange both matter and energy.

Closed system : Can exchange energy but not matter.

Isolated system : Neither matter nor energy can be exchanged.



Open system Closed system Isolated system

Thermodynamic Properties

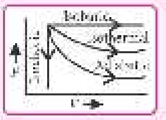
Physical quantities used to define the state of a system.

Intensive Properties : Do not depend upon the quantity or size of matter present in the system. *e.g.*, pressure, temperature, density, surface tension, viscosity, specific heat, melting and boiling points, etc.

Extensive Properties : Depend upon the quantity or size of matter present in the system. *e.g.*, mass, volume, internal energy, entropy, enthalpy, etc.

- Extensive properties are additive but intensive properties are not.

Thermodynamic Processes



Isothermal Process : At constant temperature, $dT = 0$

Isobaric Process : At constant pressure, $dP = 0$

Isochoric Process : At constant volume, $dV = 0$

Adiabatic Process : Completely insulated, $dq = 0$

State Functions

Properties which depend only on the initial and final states of a system *i.e.*, do not depend on the path followed. *e.g.*, pressure, volume, temperature, entropy, enthalpy, internal energy, etc.

Path Functions

Properties which depend upon the path followed *e.g.*, work, heat.

Work : Mode of energy exchanged between the system and the surroundings as a result of pressure difference between them.

- $w_{irreversible} = -P_{ext}(V_f - V_i)$
- $w_{reversible} = -2.303\, nRT \log \frac{V_f}{V_i}$ or $-2.303\, nRT \log \frac{P_i}{P_f}$
- Work done by the system is –ve.
- Work done on the system is +ve.

Heat : Mode of energy exchanged between the system and the surroundings as a result of temperature difference between them.

- Heat given out by the system is –ve.
- Heat absorbed by the system is +ve.
- $q = C\Delta T$; $C_p - C_v = nR$; $\gamma = C_p/C_v$

Have a Look!

- ☞ For isothermal expansion of an ideal gas against vacuum (free expansion), $\Delta U = 0$ as $w = 0$ and $q = 0$.
- ☞ For all isothermal processes involving ideal gas, $\Delta U = 0$.
- ☞ During adiabatic expansion of a real gas and isothermal expansion of an ideal gas, enthalpy remains constant.
- ☞ For elementary substances in the standard state, the standard enthalpy of formation ($\Delta_f H^\circ$) is taken as zero.
- ☞ When a rubber band is stretched, entropy decreases because the macromolecules get uncoiled and hence, arranged in a more ordered manner *i.e.*, randomness decreases.
- ☞ When an egg is boiled, entropy increases because denaturation occurs resulting into a change of proteins from helical form into random coiled form.

Laws of Thermodynamics

First Law of Thermodynamics

- $\Delta U = q + w$
- For adiabatic change, $\Delta U = w_{ad}$ as $q = 0$.
- For isochoric change, $\Delta U = q_v = C_v\Delta T$ as $\Delta V = 0$.

Internal Energy Change (ΔU)

Heat absorbed or evolved by the system at constant volume.

- $\Delta U = U_P - U_R$

Enthalpy Change (ΔH)

Heat absorbed or evolved by the system at constant pressure.

- $\Delta H = q_p = C_p\Delta T$, $\Delta H = \Delta U + P\Delta V$ or $\Delta U + \Delta n_g RT$

Reaction Enthalpy: Enthalpy change accompanying a reaction.

- $\Delta_r H = \Sigma H_P - \Sigma H_R$

Standard Enthalpy of Reaction ($\Delta_r H^\circ$): Enthalpy change of a reaction when all the participating substances are in their standard states.

Standard Enthalpy of Formation ($\Delta_f H^\circ$): Enthalpy change accompanying the formation of one mole of a substance from its constituents in their standard states.

Enthalpy Change during Phase Transformation: Enthalpy change accompanying the conversion of 1 mole of a substance from one state to another.

Hess's Law of Constant Heat Summation

Heat change accompanying a reaction is always same whether the reaction takes place in one step or in multisteps.

$Q = q_1 + q_2 + q_3$

Second Law of Thermodynamics

For a spontaneous process, the entropy of the universe is continuously increasing.

Entropy (S)

Measure of randomness or disorder of the system.

- $\Delta S = \frac{\Delta H}{T}$

- For reversible process, $\Delta S_{total} = 0$
- For irreversible process, $\Delta S_{total} > 0$

Gibbs Free Energy (G)

Net energy available to do useful work.

- $\Delta G = \Delta H - T\Delta S$
- $\Delta G^\circ = -nFE^\circ_{cell}$
- $\Delta G^\circ = -2.303RT \log K$

Criteria for spontaneity

- If $\Delta G < 0$ - process is spontaneous.
- If $\Delta G = 0$ - process is at equilibrium.
- If $\Delta G > 0$ - process is non-spontaneous.

Third Law of Thermodynamics

The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero.