KALINGA INSTITUTE OF INDUSTRIAL TECHNOLOGY (KIIT)

(Deemed to be University)

School of Applied Sciences (Chemistry)

Course Handout

Subject Code-CH1007

Chapter-1

Thermodynamics & Equilibrium

Lecture-1: Introduction, Concept of internal energy, enthalpy and entropy

Thermodynamics (**thermochemistry**)-is the study of energy flow during a chemical reaction. Thermodynamics was developed to know the most efficient way of converting heat into work!

Thermodynamics allows you to predict whether or not a reaction will occur (feasibility). Thermodynamics can predict spontaneity of a reaction but says nothing about the rate of a reaction.
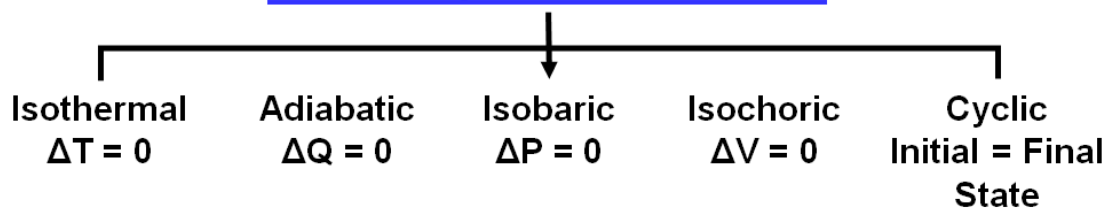
The System and the Surroundings; A system in thermodynamics refers to that part in which observations in thermodynamic changes are made and remaining part of universe constitutes the surroundings.
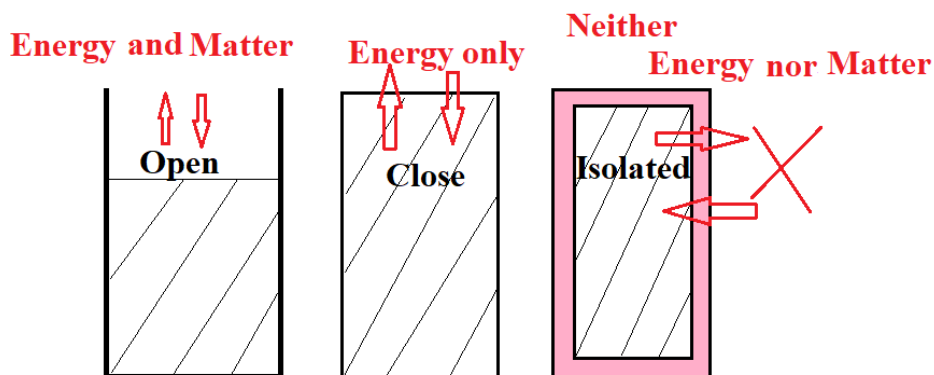
There **are seven important thermodynamic parameters** (state functions): *P (pressure), V (volume), T (temperature), H (enthalpy), S (entropy), U (internal energy) and G (Gibbs free energy)*

A **Thermodynamic process** is when a system undergoes a series of changes.

Thermodynamic Processes

| Isothermal	Adiabatic	Isobaric	Isochoric	Cyclic
$\Delta T = 0$	$\Delta Q = 0$	$\Delta P = 0$	$\Delta V = 0$	Initial = Final State

Properties of the Thermodynamics System:

Extensive property (depend on system mass)	Intensive property (independ on system mass)
Volume, Number of moles, Mass, Internal energy, enthalpy, entropy, free energy, heat capacity	Refractive index, Surface tension, density, temperature, Boiling point, Freezing point, molar volume

Dividing the system in half does not change the value of an intensive property.

How do we determine the energy changes in a thermodynamic process? (Work and Energy)

(a) **Work (w)**-Path function, (J/kJ), j/mol or kJ/mol if expressed for 1 mol

$$w = \int -P_{ex}\, dV \quad \text{..................................... ....1}$$
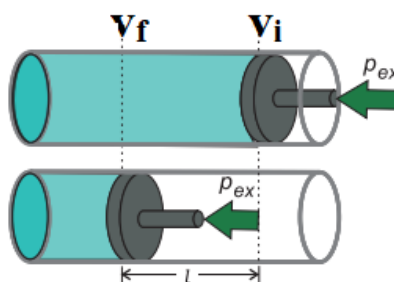
Here, $dV = (V_f - V_i) = (-)$ ve. Hence $w = (+)$ ve. Work is performed on the system.

Work done by system w is (- ve), work performed on the system w is (+ ve)

(b) **Heat (Q)**-Path function, (J/kJ), j/mol or kJ/mol if expressed for 1 mol

Form of energy change when there is temperature difference. Can be calculate from heat capacity of a material $dQ = CdT$

Heat capacity (C), C_v and C_p, $C_P - C_v = R$

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(c) **Enthalpy (H)**- State function, (J/kJ), j/mol or kJ/mol if expressed for 1 mol

Heat content of a system or a substance.

$$H = U + PV \text{...}2$$

$dH = (dQ)_p$, Heat absorbed/desorbed by the system at constant pressure P is change in enthalpy.

$$dH = nC_p \, dT \text{...}3$$

(d)   **Internal energy (U)**- State function, (J/kJ), Total energy of the system.

Change in internal energy can be measured, not the internal energy.

$dU = (dQ)_v$. Heat absorbed/desorbed by the system at constant volume V is change in internal energy.

$$dU = nC_v dT \text{...}4$$

(e) **Entropy (S)- State function**, (J/kJ), randomness in a system, measure of spontaneity of a system. Change in entropy can be measured, not the entropy.

$$dS_{rev} = \int \frac{dQ}{T} \text{..}5$$

For reversible process, $\Delta S_{system} + \Delta S_{surrounding} = 0$

For irreversible process, $\Delta S_{system} + \Delta S_{surrounding} > 0$

Review Questions-

1   What will be internal energy change of a system if q amount of heat is taken out from a system and no work is performed? What kind of system it can be?

2   What will be internal energy change of a system if q amount of heat is supplied and w amount of work is performed by it?

3   2 litres of an ideal gas expands isothermally to 10 litres against vacuum, how much heat is absorbed and how much work is done in the expansion?

4   2 litres of an ideal gas expands isothermally to 10 litres against 1 atm external pressure, how much heat is absorbed and how much work is done in the expansion?

5   Calculate the change in internal energy and enthalpy when 32 g of O_2 is heated from 0 ℃ to 100 ℃.

Lecture-2: Entropy calculations involving ideal gases (expansion, mixing etc.)

$$dS = \int \frac{dQ}{T} \quad\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.6$$

From 1st law of thermodynamics- $dU = dQ - PdV$

$$\text{Then, } \Delta S = \int \frac{dU + pdV}{T} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.7$$

and applying $dU = nC_v dT$, solution leads to

$$\Delta S = nC_v ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \quad \text{for (T, V) variable}\dots\dots\dots\dots\dots\dots.8$$

$$\Delta S = nC_p ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} \quad \text{for (T, P) variable}\dots\dots\dots\dots\dots\dots\dots.9$$

Entropy of mixing (ΔS)mix-
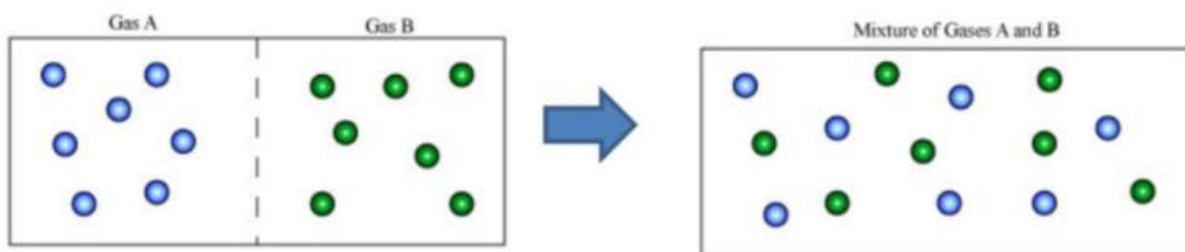
$$\Delta S = nRln\frac{V_f}{V_i} \qquad \text{(at constant T and P)}\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.10$$

$$(\Delta S)_{mix} = \Delta S_A + \Delta S_B$$

$$\Delta S_A = n_A Rln\frac{n_A + n_B}{n_A} \text{ and } \Delta S_B = n_B Rln\frac{n_A + n_B}{n_B}$$

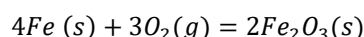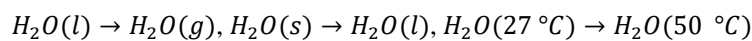$$(\Delta S)_{mix} = -nR\sum \chi_i ln\chi_i \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.11$$

χ_i is mole fraction, and

$$\chi_i = \frac{n_i}{n_T} \qquad \text{(n is mole number)}$$

Review Question-

1. Show that entropy of mixing is maximum when $\chi_1 = \chi_2 = 0.5$.

2. 2 mol of mono-atomic gas expand from a state (25 °C, 1atm) to another (50 °C, 0.5atm). Calculate ΔS.

3. Which of the following transition will leads to increase in entropy;

$$H_2O(l) \rightarrow H_2O(g), H_2O(s) \rightarrow H_2O(l), H_2O(27 \,°C) \rightarrow H_2O(50 \,°C)$$

$$4Fe\,(s) + 3O_2(g) = 2Fe_2O_3(s)$$

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Lecture-3: Concept of free energy (A and G), Gibb's-Helmholtz equation, conditions of spontaneity and equilibrium

Free energy is the available energy in a system in a given set of thermodynamic conditions that can be extracted to perform work.

(a) **Helmholtz work function** (A)- The useful work obtainable from a closed thermodynamic system at a constant temperature and volume.

$$A = f(V, T)$$
$$A = U - TS$$

(b) **Gibb's free energy (G)**- It is the energy available to do non-PV work in a thermodynamically-closed system at constant pressure and temperature.

$$G = f(P, T)$$
$$G = H - TS$$
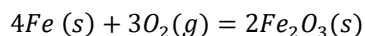$$G = G^0 + RTlnQ_p \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.12$$
$$\Delta G = nRTln\frac{P_2}{P_1}\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.13$$

(c) **Gibb's Helmholtz relation-**

$$\Delta G = \Delta H + T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..14$$

Review Question-

1. Derive $dG = VdP - SdT, dA = dG + pdV$
2. 5mol of ideal gas expand isothermally from 1l to 10l at 27 °C. Calculate change in free energy.
3. We all know rusting of iron is spontaneous;

$$4Fe\ (s) + 3O_2(g) = 2Fe_2O_3(s)$$

even though the entropy is decreasing. Give your reasoning.

Lecture-4: Derivation and applications of van't Hoff isotherm and isochore

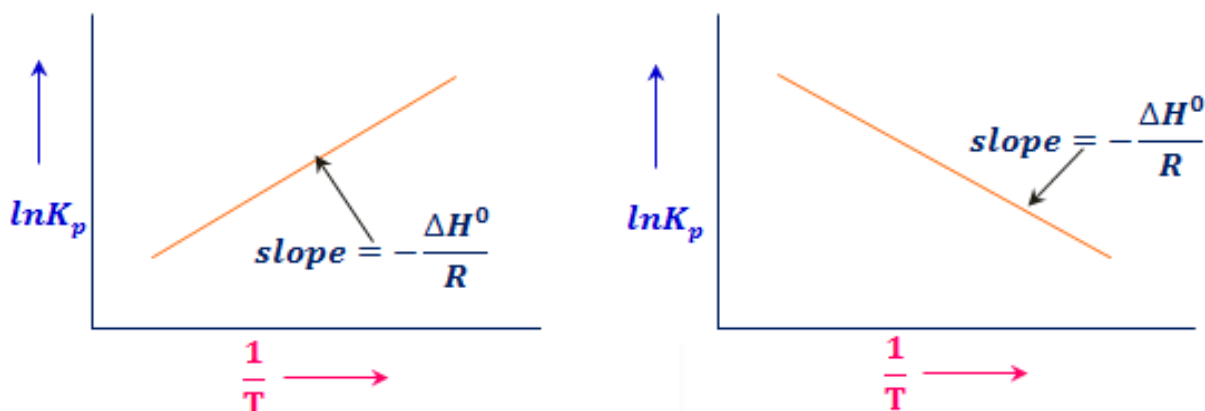**van't Hoff equations-**

$$G = G^0 + RTlnP\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.15$$

So, for a reversible reaction $aA + bB \rightleftharpoons cC + dD$

$$\Delta G = \Delta G^0 + RTlnQ_p\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.16$$

At equllibrium, ΔG is zero.

$$\Delta G^0 = -RTlnK_{eq}\ (\textbf{van't Hoff isotherm})\dots\dots\dots\dots\dots..\dots.17$$

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$$\ln K_{eq} = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \ldots (\textbf{van't Hoff isochore})\ldots\ldots\ldots\ldots\ldots\ldots 18$$

Exothermic reaction *vs* **endothermic reaction (Plot).**

$$\ln\frac{K_{p1}}{K_{p2}} = \frac{\Delta H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 19$$

van't Hoff equation correlates the equilibrium constant of a reaction to the change in temperature (enthalpy and entropy change in that temperature change is assumed to be constant).

Review Question-

1 For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, K_p is 4.34×10⁻³ at 300K. Estimate K_p at 600K.

2 Derive van't Hoff equation.

3 What will be the nature of lnK vs. 1/T plot. Give the reasoning.

4 For the reaction $C(s) + H_2O\ (g) = CO\ (g) + H_2(g)$; equilibrium constant is 9.36×10⁻¹⁷ at 25 °C. What will be the eqillibrium constant at 700 °C, given ΔH is 131 kJ/mol.

Lecture-5: Derivation and applications of Clapeyron-Clausius equation

Clapeyron-Clausius equation is Pressure and Temperature relation for equilibrium condition between two phases;

   I.   Single component system

   II.   Two phase are in equilibrium such as

      $H_2O(l) \rightleftharpoons H_2O(g)$ Vaporization $H_2O(s) \rightleftharpoons H_2O(g)$ Sublimation

$$ln\frac{P_2}{P_1} = \frac{\Delta H}{R}\left[\frac{T_2-T_1}{T_1T_2}\right]\dots\dots\dots\dots\dots\dots\dots\dots.20$$

ΔH_{vap} (liq$\rightleftharpoons$gas) and ΔH_{sub} (solid$\rightleftharpoons$Vap)

Review Question-

1. Benzene boiling point at atmospheric pressure is 80.1 °C. At what temperature it will evaporate if the pressure drops to 260 mmHg. Ginen ΔH_{vap}=30.72 kJ/mol.

2. Derive Clapeyron-Clausius equation for water vapour in equilibrium with liquid water.

3. The vapor pressure of water is 1.0 atm at 100 °C and the enthalpy of vaporization is 40.7 kJ mol⁻¹. If the pressure inside a pressure cooker can reach up to 2 atm, proof the food will cook faster.

Lecture-6: Partial molar properties, concept of chemical potential, Gibb's -Duhem equation & application

<u>Partial molar properties; Chemical potential</u>

The partial molar free energy is equal to the chemical potential. In words, the partial molar free energy is the change in total free energy that occurs per mole of component i added, with all other components constant (at constant T, P and other component amounts).

$$\mu_i = (\frac{\partial G_i}{\partial n_i})_{T,P,1,2,3\dots\dots\dots\dots\dots\dots i-1}\dots\dots\dots\dots\dots\dots\dots..20$$

$$\mu_i = \mu_i^0 + RTlnx_i$$

μ_i^0 is chemical potential of pure substance and $RTlnx_i$ is entropy of mixing.

$$G=f(T, P, n_1, n_2\dots\dots.n_i)\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots.21$$

$$dG = \sum \mu_i dn_i\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots..22$$

$$n_i d\mu_i = 0\dots\dots\text{(\textbf{Gibb's Duhem equation})}\dots\dots\dots\dots\dots..23$$

Review Question-

1. Prove that chemical potentials of both the component are interdependent in a binary component system.

2. What will be the change in chemical potential of water at 25 °C if NaCl is added in such an amount that the mole fraction of NaCl is 0.1?

3. Prove that the $(\Delta G)_{mix}$ is negative (from Equation 22).