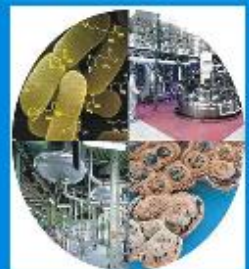
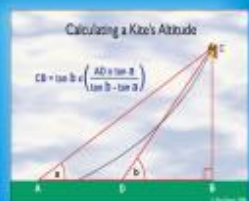
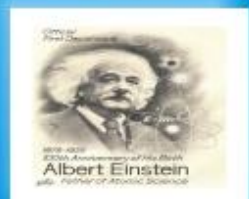


# CSIR UGC NET CHEMICAL SCIENCE SAMPLE THEORY

- \* THERMODYNAMICS
- \* QUANTUM CHEMISTRY





## CSIR NET - CHEMICAL SCIENCE

### SAMPLE THEORY

- THERMODYNAMICS (SECOND LAW: ENTROPY)
- QUANTUM CHEMISTRY (THE SCHRÖDINGER EQUATION)

# VPM CLASSES

FOR IIT-JAM, JNU, GATE, NET, NIMCET AND OTHER ENTRANCE EXAMS

Web Site [www.vpmclasses.com](http://www.vpmclasses.com) E-mail [vpmclasses@yahoo.com](mailto:vpmclasses@yahoo.com)

## THERMODYNAMICS

### Second Law of Thermodynamics

#### Entropy

The entropy is a state function and depends only on the initial and final states of the system.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

When  $S_{\text{final}} > S_{\text{initial}}$ ,  $\Delta S$  is positive.

For a chemical reaction,

$$\Delta S = S_{(\text{products})} - S_{(\text{reactants})}$$

#### Entropy change in reversible process

In an isothermal reversible process, let the system absorb  $q$  amount of heat from surroundings at temperature  $T$ . The increase in the entropy of the system will be

$$\Delta S_{\text{system}} = + \frac{q}{T}$$

Surroundings also lose the same amount of heat at the same temperature. The decrease in the entropy of the surroundings will be

$$\Delta S_{\text{surroundings}} = - \frac{q}{T}$$

Total change in entropy of the process = Entropy change in system + Entropy change in surroundings

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = \frac{q}{T} - \frac{q}{T} = 0$$

When the reversible process is adiabatic, there will be no heat exchange between system and surroundings, i.e.

$$q = 0$$

$$\therefore \Delta S_{\text{system}} = 0, \quad \Delta S_{\text{surroundings}} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = 0$$

## Entropy change in irreversible processes

Let us consider a system at higher temperature  $T_1$  and its surroundings at lower temperature  $T_2$ . 'q' amount of heat goes irreversibly from system to surroundings.

$$\therefore \Delta S_{\text{system}} = -\frac{q}{T_1}$$

$$\Delta S_{\text{surroundings}} = +\frac{q}{T_2}$$

$$\Delta S_{\text{process}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} = -\frac{q}{T_1} + \frac{q}{T_2} = q \left[ \frac{T_1 - T_2}{T_1 T_2} \right]$$

But  $T_1 > T_2$ ,  $\therefore T_1 - T_2 = +ve$  or  $\Delta S_{\text{process}} > 0$

Hence, entropy increases in an irreversible process.

## Entropy change for ideal gases

Change in entropy for an ideal gas under different conditions may be calculated as:

- (i) When changes from initial state (1) to final state (2):

$$\Delta S = 2.303nC_v \log_{10} \left( \frac{T_2}{T_1} \right) + 2.303nR \log_{10} \left( \frac{V_2}{V_1} \right)$$

(when T and V are variables)

$$\Delta S = 2.303nC_p \log_{10} \left( \frac{T_2}{T_1} \right) + 2.303nR \log_{10} \left( \frac{P_1}{P_2} \right)$$

(when T and P are variables)

- (ii) Entropy change for isothermal process:

$$\Delta S = 2.303nR \log_{10} \left( \frac{V_2}{V_1} \right) = 2.303nR \log_{10} \left( \frac{P_1}{P_2} \right)$$

- (iii) Entropy change for isobaric process (at constant pressure):

$$\Delta S = 2.303nC_p \log_{10} \left( \frac{T_2}{T_1} \right) = 2.303nC_p \log_{10} \left( \frac{V_2}{V_1} \right)$$

- (iv) Entropy change for isochoric process (at constant volume):



$$\Delta S = 2.303nC_v \log_{10} \left( \frac{T_2}{T_1} \right) = 2.303nC_v \log_{10} \left( \frac{P_2}{P_1} \right)$$

- (v) Entropy change in mixing of ideal gases: Let  $n_1$  mole of gas A and  $n_2$  mole of gas B are mixed; then total entropy change can be calculated as:

$$\Delta S = -2.303R [n_1 \log_{10} x_1 + n_2 \log_{10} x_2]$$

$x_1, x_2$  are mole fractions of gases A and B,

$$\text{i.e., } x_1 = \frac{n_1}{n_1 + n_2} ; x_2 = \frac{n_2}{n_1 + n_2}$$

$$\Delta S/\text{mol} = -2.303R \left[ \frac{n_1}{n_1 + n_2} \log_{10} x_1 + \frac{n_2}{n_1 + n_2} \log_{10} x_2 \right]$$

Entropy change in adiabatic expansion will be zero,  $\Delta S = 0$

## Entropy Change During Phase Transitions

The change of a substance from one form to another is known as phase transformation. Such changes occur at definite temperatures and are accompanied by entropy change. During these transformations either heat is absorbed or evolved, i.e., the entropy either increases or decreases accordingly.

The entropy change for these transformations is given by

$$\Delta S_{\text{trans}} = \frac{q_{\text{rev}}}{T}$$

where  $q_{\text{rev}}$  is the heat absorbed or evolved and  $T$  is the temperature of transition.  $q_{\text{rev}}$  is actually the molar enthalpy change of the substance.

- (i) **Entropy of fusion:** The entropy of fusion is defined as the change in entropy when one mole of a solid substance changes into liquid form at the melting temperature. The heat absorbed is equal to the latent heat of fusion

$$\Delta S_{\text{fusion}} = S_{\text{liquid}} - S_{\text{solid}} = \frac{\Delta H_{\text{fusion}}}{T_f}$$

- (ii) **Entropy of vaporization:** It is defined as the change in entropy when one mole of the liquid substance changes into vapor gas at its boiling point.

$$\Delta S_{\text{vapour}} = S_{\text{vapour}} - S_{\text{liquid}} = \frac{\Delta H_{\text{vapour}}}{T_b}$$

where  $\Delta H_{\text{vapour}}$  is the latent heat of vaporization and  $T_b$  is the boiling point.

- (iii) **Entropy of sublimation:** Sublimation involves the direct conversion of a solid into its vapour. The entropy of sublimation is defined as the change in entropy when one mole of a solid changes into vapour at a particular temperature.

$$\Delta S_{\text{sub}} = S_{\text{vapour}} - S_{\text{solid}} = \frac{\Delta H_{\text{sub}}}{T}$$

where  $\Delta H_{\text{sub}}$  = Heat of sublimation at temperature T.

## STANDARD FREE ENERGY CHANGE

The absolute value of Gibb's free energy cannot be determined. The standard free energy change can be determined and it is defined as the free energy change for a process at 298 K and 1 atm pressure in which the reactants in their standard state are converted into products in their standard state. It is denoted as  $\Delta G^\circ$ . It can be related to standard enthalpy and entropy change in the following manner:

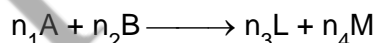
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Like  $\Delta H^\circ$ ,  $\Delta G^\circ$  can be calculated from the standard free energies of formation of the products and the reactants.

$$\Delta G^\circ = \sum G_f^\circ (\text{products}) - \sum G_f^\circ (\text{reactants})$$

$$\text{OR } \Delta G^\circ = \left[ \begin{array}{l} \text{Sum of standard free} \\ \text{energies of formation} \\ \text{of products} \end{array} \right] - \left[ \begin{array}{l} \text{Sum of standard free} \\ \text{energies of formation} \\ \text{of reactants} \end{array} \right]$$

Let us consider a general reaction:



$$\Delta G^\circ = \sum G_f^\circ (\text{products}) - \sum G_f^\circ (\text{reactants})$$

$$= [n_3 G_f^\circ (L) + n_4 G_f^\circ (M)] - [n_1 G_f^\circ (A) + n_2 G_f^\circ (B)]$$

Thus the standard free energy of formation ( $\Delta G^\circ$ ) may be defined as the free energy change when 1 mole of a compound is formed from its constituent elements in their standard state. The standard free energy of formation of an element in its standard state is assumed to be zero.

## QUANTUM CHEMISTRY

### The Schrödinger Equation

The **time-independent Schrödinger equation** for a particle of mass  $m$  moving in one dimension with energy  $E$  is

$$\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \quad \dots (1)$$

The factor  $V(x)$  is the potential energy of the particle at the point  $x$ ;  $\hbar$  (which is read h-cross or h-bar) is convenient modification of Planck's constant:

$$\hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-34} \text{ Js}$$

**Table 1 The Schrödinger equation**

For one-dimensional systems:

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V(x)\psi = E\psi$$

Where  $V(x)$  is the potential energy of the particle and  $E$  is its total energy.

For three-dimensional system

$$-\frac{\hbar^2}{2m} \nabla^2\psi + V\psi = E\psi$$

where  $V$  may depend on position and  $\nabla^2$  ('del squared') is

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

In systems with spherical symmetry:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{2}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \Lambda^2$$

where

$$\Lambda^2 = \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \phi^2} + \frac{1}{\sin\theta} \frac{\partial}{\partial \theta} \sin\theta \frac{\partial}{\partial \theta}$$

In the general case the Schrödinger equation is written

$$H\psi = E\psi$$

Where  $H$  is the Hamiltonian operator for the system:

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V$$

For the evolution of a system with time, it is necessary to solve the time-dependent

Schrödinger

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

$$\frac{d^2\psi}{dx^2} = -\frac{2m}{\hbar^2} (E - V)\psi$$

A solution of this equation is



$$\psi = e^{ikx} = \cos kx + i \sin kx \quad k = \left\{ \frac{2m(E - V)}{\hbar^2} \right\}^{1/2}$$

Now we recognize that  $\cos kx$  (or  $\sin kx$ ) is a wave of wavelength  $\lambda = 2\pi/k$  (by comparing  $\cos kx$  with the standard form of a harmonic wave,  $\cos (2\pi x/\lambda)$ ). The quantity  $E - V$  is equal to the kinetic energy of the particle,  $E_K$ , so  $k = (2mE_K / \hbar^2)^{1/2}$ , which implies that  $E_K = k^2 \hbar^2 / 2m$ . Because  $E_K = p^2 / 2m$ , it follows that  $p = k\hbar$

Therefore, the linear momentum is related to the wavelength of the wave function by

$$p = \frac{2\pi}{\lambda} \times \frac{h}{2\pi} = \frac{h}{\lambda} \quad (\text{De Broglie relation})$$