

Chemical Kinetics:

- 1) Show that in case of a first order reaction, the time taken for completion of 99.9% reaction is ten times the time required for half change of the reaction.
- 2) (a) The rate of a particular reaction doubles when the temperature changes from 300 K to 310 K. calculate the energy of activation of the reaction [given $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$]
(b) Show that the half-life period of a first order reaction is independent of initial concentration of reacting species.
- 3) The time required for 10% completion of first order reaction at 298 K is equal to that required for its 25% completion at 308 K. If the preexponential factor for the reaction is $3.56 \times 10^9 \text{ s}^{-1}$, calculate the energy of activation.
- 4) At 380 °C, the half-life period for the first order decomposition of H_2O_2 is 360 min. the energy of activation of the reaction is 200 kJ mol^{-1} , Calculate the time required for 75% decomposition at 450 °C.
- 5) For a reaction, the energy of activation is zero. What is the value of rate constant at 300 K if $k = 1.6 \times 10^6 \text{ s}^{-1}$ at 280 K? ($R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$).

Colligative Properties

1. Explain along with diagram, why some of the non- ideal solution show positive deviation while some other show negative deviation from ideal solution.
2. Explain the relevance of elevation of boiling point in determining the molecular weight of non- volatile solute.
3. Explain molal depression constant. Derive the relation between the depression in freezing point and the molecular weight of non- volatile solute in the solution.
4. What is van't hoff factor? What possible value can it have if the solute molecules undergo:- i) association ii) dissociation in solution.
5. Define osmosis and osmotic pressure. How is it dependent on temperature and atmospheric pressure and explain how the molecular mass of a non- volatile solute can be determined from it.

Chemical Bonding

- Q1. Using the concept of hybridization, explain the possible shape and geometry of IOCl_3 , ICl_5 and XeOF_4 . With suitable arguments, predict which of the shapes are most stable.
- Q2. Establish the relation between enthalpy of formation and lattice energy of CaCl_2 using Born Haber's cycle.
- Q3. Draw the molecular orbital energy diagram for NO and NO^+ . Calculate the bond order and explain their magnetic properties.

Electrochemistry-Corrosion-Coordination

- ① Draw crystal field splitting energy diagram for d-orbitals in a square planar environment. Give suitable examples.
- ② What is spectrochemical series?
- ③ What is standard electrode potential? Mention the value of standard hydrogen electrode potential?
Draw the electrode diagram, electrode representation and chemical reaction involving in standard hydrogen electrode.
- ④ What is calomel electrode? Calculate its potential for
 - (a) Decinormal KCl solution
 - (b) Normal KCl solution
 - (c) Saturated KCl solution
- ⑤ What is corrosion? Which corrosion protection technique used for the underground pipe lines and explain it with neat diagram.

Thermodynamics

THERMODYNAMICS

ASSIGNMENT → B.Tech. - Sem II (CH1201)

- ① Show that pressure is a state-function for a gas obeying

$$\left(P + \frac{a}{V^2}\right)V = RT$$

- ② Show that for fixed amount of an ideal gas (for which $\left(\frac{\partial U}{\partial V}\right)_T = 0$)

(i) $\left(\frac{\partial H}{\partial P}\right)_T = 0$ (ii) $\left(\frac{\partial U}{\partial V}\right)_P = C_V \frac{P}{nR} = C_P \left(\frac{\partial T}{\partial V}\right)_P - P$

(iii) $\left(\frac{\partial U}{\partial P}\right)_V = C_V \left(\frac{\partial T}{\partial P}\right)_V = \left(\frac{\beta}{\alpha}\right) C_V$

(iv) $\left(\frac{\partial H}{\partial V}\right)_T = 0$

(v) $\left(\frac{\partial U}{\partial T}\right)_P = C_P - P \left(\frac{\partial V}{\partial T}\right)_P$

- ③ For Van der Waals gas $\left(P + \frac{a}{V^2}\right)(V-b) = RT$ under high temp and low pressure

$$C_P - C_V \approx R \left(1 + \frac{2ap}{R^2 T^2 V}\right)$$

- ④ The virial equation for a van der Waals gas retained upto second virial coefficient is

$$PV = RT \left(1 + \frac{B}{V} \right) \quad \text{where} \quad B = b - \left(\frac{a}{RT} \right)$$

Show that the expression for Joule-Thomson coefficient for this gas is given by

$$\text{(i)} \quad \mu_{JT} = \frac{1}{C_p} \left[\frac{-B + T \left(\frac{\partial B}{\partial T} \right)_p}{1 + 2B/V} \right]$$

- ⑵ At inversion temperature $\mu_{JT} = 0$. Hence

$B - T \left(\frac{\partial B}{\partial T} \right)_p = 0$. Show that it leads to the expression $T_i = \frac{2a}{Rb}$. Calculate the inversion temperature of nitrogen for which $a = 141 \text{ kPa dm}^6 \text{ mol}^{-2}$ and $b = 0.0392 \text{ dm}^3 \text{ mol}^{-1}$

- ⑤ One mole of an ideal monatomic gas ($C_v = 1.5R$) is subjected to the following sequence of steps (i) The gas heated reversibly at constant pressure at 101.325 kPa from 298 K to 373 K (ii) Next, the gas is expanded reversibly and isothermally to double its volume. (iii) Finally, the gas is cooled reversibly and adiabatically to 308 K . Calculate $q, w, \Delta U$ and ΔH for the overall process.