

BLDE Association's

**S. B. Arts & K.C.P. Science College,
Vijayapur - 586 103**

(Accredited at the B++ Grade with 2.99 CGPA in 4th cycle by NAAC)



_____ Programme

Internl Assessment Test Booklet

IV Semester 2023-24

Name : Divya. R. Sidaraddi

Roll No. : _____ R.C.U. Exam Seat No. PISKM21S0002

Subject Code : _____

Subject : Physical chemistry

1 (a) Gibb's Duhem equation.

$$G = n_1 \mu_1 + n_2 \mu_2 + \dots + n_i \mu_i \rightarrow (1)$$

On differentiating eqⁿ (1) we get

$$\frac{\partial G}{\partial t} = \cancel{\partial n_1 \mu_1} + \cancel{\partial \mu_1 n_1} + \partial n_2 \mu_2 + \partial \mu_2 n_2 + \dots$$

$$\dots \partial n_i \mu_i + \partial \mu_i n_i \rightarrow (2)$$

Separating the terms

$$\frac{\partial G}{\partial t} = (\partial n_1 \mu_1 + \partial n_2 \mu_2 + \dots \partial n_i \mu_i) + (\partial \mu_1 n_1 + \partial \mu_2 n_2 + \dots \partial \mu_i n_i)$$

$$\forall \partial \mu_1 n_1 + \partial \mu_2 n_2 + \dots \partial \mu_i n_i = 0$$

$$\cancel{\frac{\partial G}{\partial t}} = \cancel{\frac{\partial G}{\partial t}} + (\partial n_1 \mu_1 + \partial n_2 \mu_2 + \partial n_3 \mu_3 + \dots \partial n_i \mu_i)$$

$$\partial n_1 \mu_1 + \partial n_2 \mu_2 + \partial n_3 \mu_3 + \dots \partial n_i \mu_i = 0 \rightarrow (3)$$

On integrating eqⁿ (3)

$$\text{we get } = n_1 \mu_1 + n_2 \mu_2 + \dots + n_i \mu_i = 0$$

For two component system.

$$(n_1 \mu_1) + (n_2 \mu_2) = 0.$$

$$\Delta G_{mix} = RT \ln n_i \cdot x_i$$

$$\Delta H_{mix} = 0$$

$$\Delta V_{mix} = 0$$

$$\Delta S_{mix} = -RT \ln n_i \cdot x_i$$

$$\Delta A = 2RT n_i \ln x_i$$

③. Expression for Entropy of ideal gas mixing is $\Delta S = -RT \ln x_i$

x_i = Any molar fraction.

n = no. of Component

T = Temperature

R = Gas Constant.

④. Two application of nanoparticle in medical field.

= XRD - X-ray diffraction. - To know

the cracks in the

Human bones. & even

other defect in body.

= Cancer treatment.

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_____ Programme

Internl Assessment Test Booklet

_____ Semester 202_____

Name : Pruthvik B. Pujari

Roll No. : _____ R.C.U. Exam Seat No. 50003

Subject Code : _____

Subject : Physical chemistry

PART-2

01. Opposing Reactions :

Opposing reactions are the reactions in which the reactants react to form the products and at the same time the product gives or react to form the reactants.

(or)

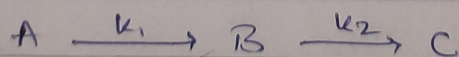
Opposing reactions are the reactions in which the product obtained also react to give the reactants.

02. Simultaneous Reactions :

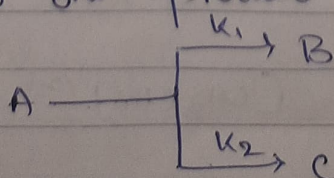
Simultaneous reactions are the reactions in which the reaction takes place simultaneously.

Types

1) Consecutive Reaction :- Consecutive reactions are the reactions in which the reactant react to form product in a continuously written to the overall reaction. Explain the overall reaction.



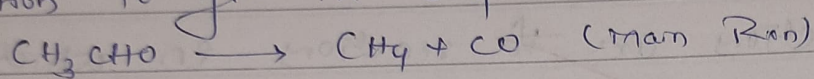
2) Parallel Reaction :- Parallel reactions are the reactions in which the reactant react each and give the more than one product simultaneously.



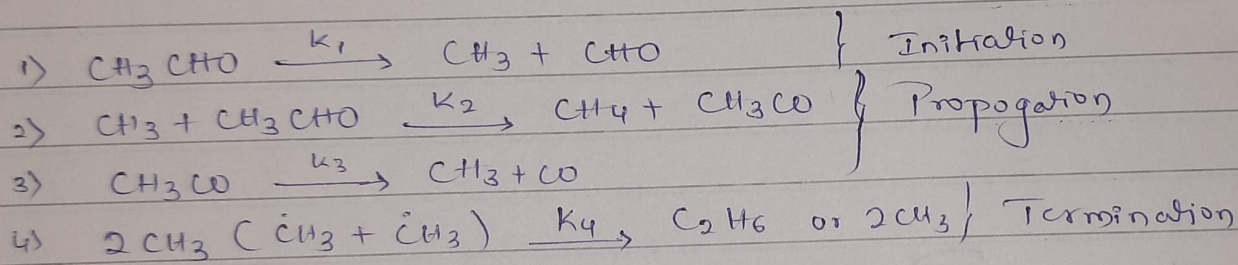
04. Rice Herzfeld Mechanism with example CH_3CHO
 Rice Herzfeld mechanism explains the 3 halves of $3/2$ order kinetics.

Here initiation is 1st order reaction and Propagation is 2nd order this can be explained with the example of thermal decomposition of CH_3CHO .

The reaction of the Acetaldehyde in the thermal condition to give the CH_4 and CO .



The elementary steps of the reaction are



According to steady state approximation for methyl radical

$$\frac{d[\text{CH}_3]}{dt} = k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}] + k_3 [\text{CH}_3\text{CO}] - k_4 [\text{CH}_3]^2 = 0 \quad \text{--- (1)}$$

And for CH_3CO radical,

$$k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}] - k_3 [\text{CH}_3\text{CO}] = 0 \quad \text{--- (2)}$$

on adding (1) and (2)

$$\frac{d[\text{CH}_3]}{dt} = k_1 [\text{CH}_3\text{CHO}] - k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}] + k_3 [\text{CH}_3\text{CO}] - k_4 [\text{CH}_3]^2 = 0$$

$$= \frac{k_2 [\text{CH}_3\text{CHO}] [\text{CH}_3] - k_3 [\text{CH}_3\text{CO}]}{k_1 [\text{CH}_3\text{CHO}] - k_4 [\text{CH}_3]^2} = 0$$

$$= k_1 [\text{CH}_3\text{CHO}] = k_4 [\text{CH}_3]^2$$

$$[\text{CH}_3]^2 = \frac{k_1 [\text{CH}_3\text{CHO}]}{k_4}$$

$$[\text{CH}_3] = \left(\frac{k_1}{k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} \quad \text{--- (3)}$$

similarly the rate of formation of methane is given by

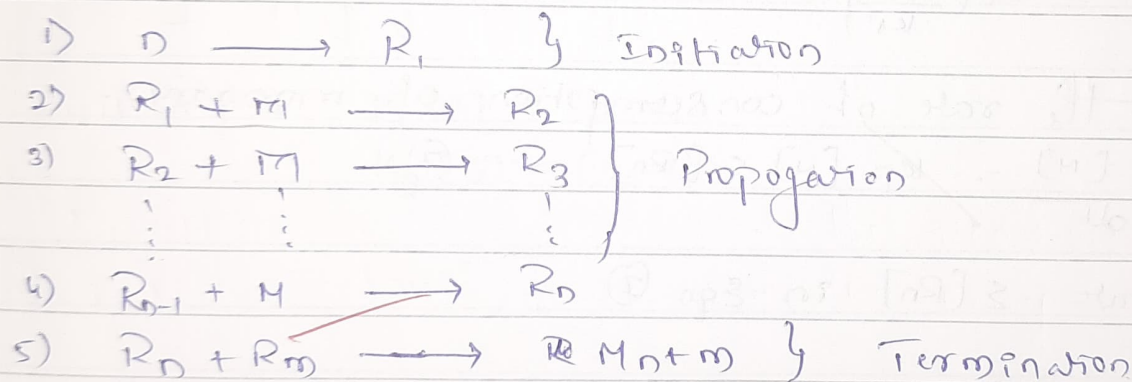
$$\frac{d[\text{CH}_4]}{dt} = k_2 [\text{CH}_3] [\text{CH}_3\text{CHO}]$$

Substitute the $[\text{CH}_3]$ in eqn (3)

$$\begin{aligned} \frac{d[\text{CH}_4]}{dt} &= k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{1/2} [\text{CH}_3\text{CHO}] \\ &= k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2} \quad \text{--- (4)} \end{aligned}$$

Thus the mechanism explains correctly the $3/2$ order kinetics.

05. Kinetics of free radical mechanism



'M' is monomer and R is the radical produced in initiation. R_n is radical produced or consisting of R_1 as the chain of (n-1) monomer molecule.

* The net rate of initiation or initial formation of carbon $\cancel{2}$ and the rate constant for propagation step is k_p and the rate constant for termination is k_t .

Now applying steady state approximation to the R_1 is given by