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

Q NO. II.

I (a) Gibb's Duhem equation

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

On differentiating eqⁿ (1) we get

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

$$\cdots \partial n_i.\mu_i + \partial\mu_i n_i \rightarrow (2)$$

Seperating the terms

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

4

$$\because \partial\mu_1 n_1 + \partial\mu_2 n_2 \cdots \partial\mu_i n_i = G$$

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

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

On integrating eqⁿ (3)

we get $= n_1\mu_1 + n_2\mu_2 \cdots + n_i\mu_i = 0$

for two Component System.

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

$\Delta G mix = RT \ln n_i . x_i$

$\Delta H mix = 0$

$\Delta V mix = 0$

$\Delta S mix = -RT \ln n_i . x_i$

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

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

x = Any molarfraction.

n = no. of Component

T = Temperature

R = Gas Constant.

2

4. Two application of nanoparticle in medical feild.

= x-RD - xray defraction - To know the Cracks in the Human bones. & even other defect in body.

1

= Cancer treatment.

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

________________ Semester 202____

Name : Pruthvik. B. Pujari

Roll No. : __________ R.C.U. Exam Seat No. S0003

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)

2 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 reaction are the reactions in which the reactant react to form

2 product in a continously written to the explain the overall reaction.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

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

$$A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$$

Q4. Rice Herzfeld Mechanism with Example CH_3CHO
Rice Herzfeld mechanism explain the 3 halves of 3/2 order kinetics
Here initiation is 1^{st} order reaction and Propogation is 2^{nd} 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.

$$CH_3CHO \longrightarrow CH_4 + CO \quad \text{(Main Rxn)}$$

The elementary steps of the reaction are

1) $CH_3CHO \xrightarrow{k_1} CH_3 + CHO$ } Initiation
2) $CH_3 + CH_3CHO \xrightarrow{k_2} CH_4 + CH_3CO$ } Propogation
3) $CH_3CO \xrightarrow{k_3} CH_3 + CO$
4) $2CH_3 \; (\dot{C}H_3 + \dot{C}H_3) \xrightarrow{k_4} C_2H_6$ or $2CH_3$ } Termination

According to steady state approximation for methyl radical

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CHO] - k_4[CH_3]^2 = 0 \quad \text{--- (1)}$$

And for CH_3CO radical,

$$k_2[CH_3][CH_3CHO] - k_3[CH_3CO] = 0 \quad \text{--- (2)}$$

on adding (1) and (2)

$$\frac{d[CH_3]}{dt} = k_1[CH_3CHO] - k_2[CH_3][CH_3CHO] + k_3[CH_3CO] - k_4[CH_3]^2 = 0$$

$$= \underline{k_2[\cancel{CH_3CHO}][CH_3] - k_3[CH_3CO] = 0}$$

$$k_1[CH_3CHO] - k_4[CH_3]^2 = 0$$

$$= k_1[CH_3CHO] = k_4[CH_3]^2$$

$$[CH_3]^2 = \frac{k_1}{k_4}[CH_3CHO]$$

$$[CH_3] = \left(\frac{k_1}{k_4}\right)^{1/2}[CH_3CHO]^{1/2} \quad \text{---- (3)}$$

similarly the rate of formation of methane is given by

$$\frac{d[CH_4]}{dt} = K_2 [CH_3][CH_3CHO]$$

Substitute the $[CH_3]$ in Eqn ③

$$\frac{d[CH_4]}{dt} = K_2 \left(\frac{K_1}{K_4}\right)^{1/2} [CH_3CHO]^{1/2} (CH_3CHO)$$

$$= K_2 \left(\frac{K_1}{K_2}\right)^{1/2} [CH_3CHO]^{3/2} \quad \text{---} \rightarrow ④$$

4p

Thus the mechanism Explains correctly the 3/2 order kinetics.

05. Kinetics of free radical mechanism

1) $n \longrightarrow R_1$ } Initiation

2) $R_1 + M \longrightarrow R_2$

3) $R_2 + M \longrightarrow R_3$ Propogation

⋮

4) $R_{n-1} + M \longrightarrow R_n$

5) $R_n + R_m \longrightarrow M_{n+m}$ } Termination

'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 I and the rate constant for propogation 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