Following the course of a 'R' reaction system

Independent

Rank of $\underline{\underline{N}} = R$ No. of ind. columns $= R =$ no. of indpdt species $\rightarrow$ First R columns

LI $\longrightarrow$ $n_j = n_{j0} + \sum_{i=1}^{R} \nu_{ij} \epsilon_i$; $j = 1(1)R$

$n_k = n_{k0} + \sum_{i=1}^{R} \nu_{ik} \epsilon_i$; $j = R+1, R+2, \ldots S$

$S > R$

$\underline{\underline{N}}^T \underline{\epsilon} = \underline{n} - \underline{n}_0$

Cal $\epsilon_1 \cdots \epsilon_R$

Ex:

$$\begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ A_4 \\ A_5 \end{bmatrix} = \begin{bmatrix} C_2H_4 \\ O_2 \\ C_2H_4O \\ CO_2 \\ H_2O \end{bmatrix}$$

$$\underline{\underline{N}} = \begin{bmatrix} -1 & -\frac{1}{2} & 1 & 0 & 0 \\ -1 & -3 & 0 & 2 & 2 \end{bmatrix}$$

$C_2H_4 + \frac{1}{2}O_2 \longrightarrow C_2H_4O$

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$

t	n_1	n_3
⋮	⋮	⋮

$n_1 - n_{10} = -\epsilon_1 - \epsilon_2$ ✓

$\longrightarrow n_2 - n_{20} = -\frac{1}{2}\epsilon_1 - 3\epsilon_2$

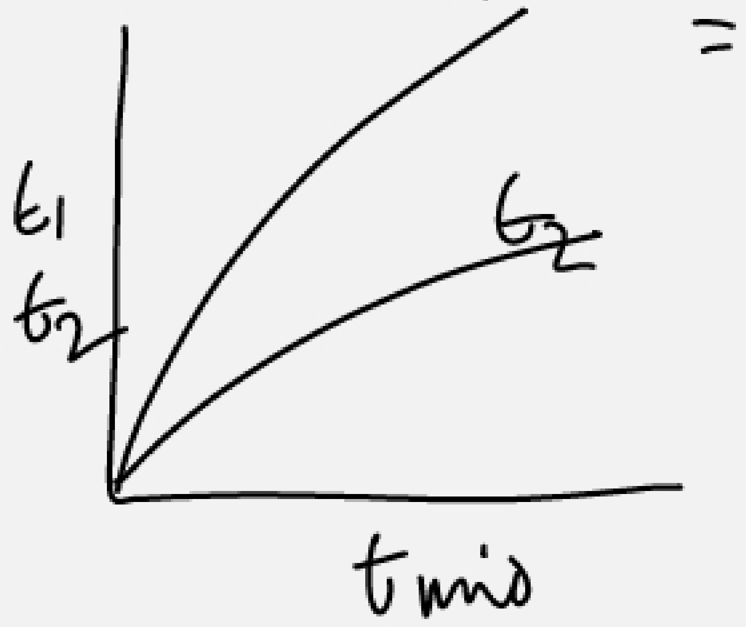
$n_3 - n_{30} = \epsilon_1$ ✓

$\longrightarrow n_4 - n_{40} = 2\epsilon_2$

$\longrightarrow n_5 - n_{50} = 2\epsilon_2$

$\epsilon_1 = n_3 - n_{30}$ ✓

$$\begin{aligned} \epsilon_2 &= -\epsilon_1 - n_1 + n_{10} \\ &= n_{30} - n_3 - n_1 + n_{10} \\ &= (n_{10} + n_{30}) - (n_1 + n_3) \end{aligned}$$ ✓



Suppose

ϵ_1' $C_2H_4 + \frac{1}{2}O_2 \Rightarrow C_2H_4O$

ϵ_2' $C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$

X ϵ_3' $C_2H_4O + \frac{5}{2}O_2 = 2CO_2 + 2H_2O$

$$\begin{bmatrix} -1 & -\frac{1}{2} & 1 & 0 & 0 \\ -1 & -3 & 0 & 2 & 2 \\ 0 & -\frac{5}{2} & -1 & 2 & 2 \end{bmatrix}$$
$\uparrow$ $\uparrow$

Rank = 2

Reac 3 = Reac 2 − Reac 1

Degrees of freedom = R ← Use n_1 & n_3

In the 2-Rxn set (R1 & R2)

$\epsilon_1 = \epsilon_1' - \epsilon_3'$

$\epsilon_2 = \epsilon_2' + \epsilon_3'$

Calcn of n_2, n_4, n_5

INVARIANTS

$$\left.\begin{aligned} -3n_1 + n_2 - \frac{5}{2}n_3 &= -3n_{10} + n_{20} - \frac{5}{2}n_{30} \\ 2n_1 + 2n_3 + n_4 &= 2n_{10} + 2n_{30} + n_{40} \\ 2n_1 + 2n_3 + n_5 &= 2n_{10} + 2n_{30} + n_{50} \end{aligned}\right\}$$

s Species

R independent Rxns

DOF = R

no. of invariants = $s - R$ $\longrightarrow$ $\sum \alpha_{kj} (n_j - n_{jo}) = 0$ $\quad k = 1, 2, \ldots s-R$

$n_1, \ldots n_5$

Reaction Kinetics:

$$2H_2 + O_2 = 2H_2O$$

ϵ

- 'Intensive' Rate of reaction: moles of Rxn per unit time per unit vol