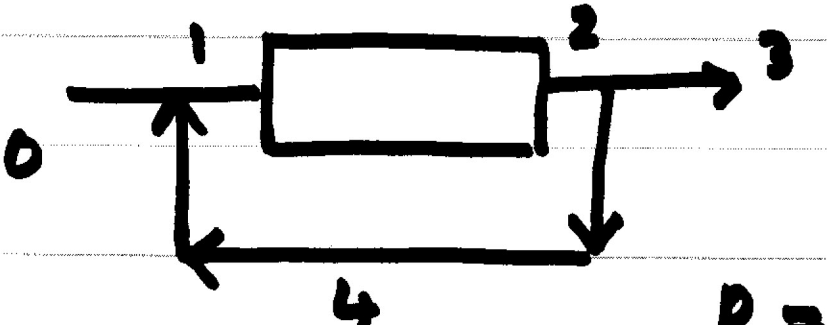
Prof. H. Shankar Lec. 6 I
(1/11/12

Advanced Reaction Engineering

Plug flow Recycle Reactors

Illustrative Examples

Plug Flow recycle Reactor



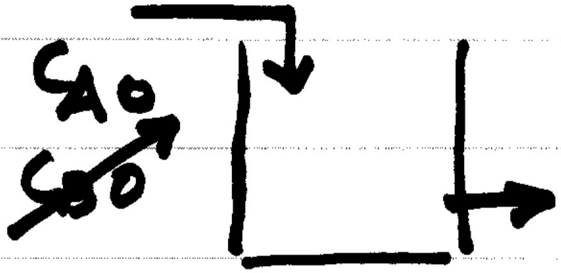
$$R = \frac{F_{A4}}{F_{A3}}$$

Autocatalytic Reactions in Mixed flow (CSTR)

Design Eqn for CSTR

$$r_A = -k C_A C_B$$

$$\frac{V}{F_{A0}} = \frac{X}{k C_A C_B} = \frac{X}{k(C_{A0} - C_{A0}X)(C_{B0} + C_{A0}X)}$$



$$A + \rightarrow B$$

Note that even if $C_{B0} = 0$ the design states that Reactor produces B. This feature seems inconsistent with our expectations

Auto Cat Rxn in CSTR

$$F_{A0} - F_A - k C_A C_B V = \frac{dN_A}{dt}$$

$$\rightarrow C_{A0} - C_A - \underbrace{k C_A C_B \tau} = \tau \frac{dC_A}{dt}$$

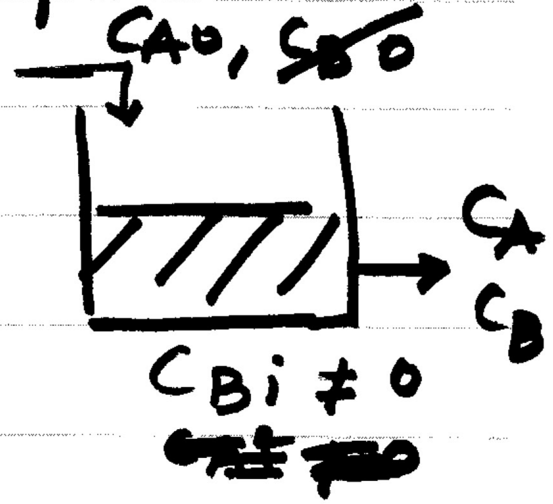
$$C_{A0} - C_A - k\tau C_A \underline{\underline{C_B}} = \tau \frac{dC_A}{dt}$$

Similarly

$$\rightarrow \cancel{C_{B0}} - C_B + \underbrace{k\tau C_A C_B} = \tau \frac{dC_B}{dt}$$

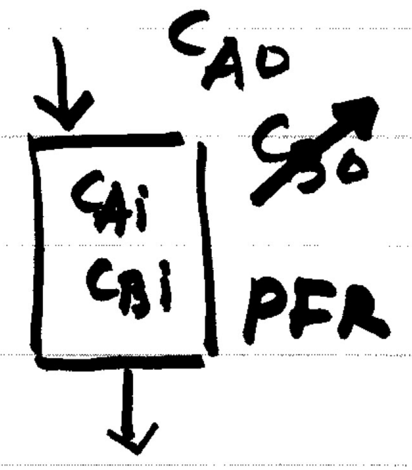
$t = 0 \quad C_A = \cancel{C_{Ai}}\;;\; [C_B = C_{Bi}]$

So even if $C_{B0} = 0$ as long as $C_{Bi} \neq 0$ the reaction proceeds.



It is clear that if $C_{Bi} \neq 0$ then reaction proceeds. If $C_{Bi} = 0$ then reaction does not go.

Autocatalytic Reaction in a PFR



$$-\frac{\partial F_A}{\partial V} + r_A = \frac{\partial c_A}{\partial t} \quad ; \quad c_A(V,t)$$

$$-\frac{\partial F_B}{\partial V} + r_B = \frac{\partial c_B}{\partial t} \quad \quad c_B(V,t)$$

$$r_A = -k c_A c_B \; ; \; r_B = k c_A c_B$$

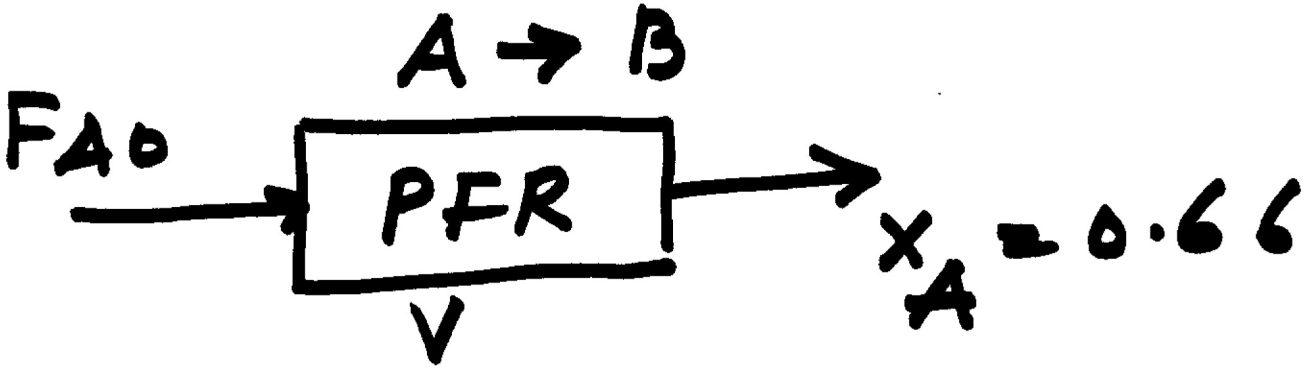
$c_A(0,t) = c_{A0}$; $c_B(0,t) = c_{B0}$ at inlet

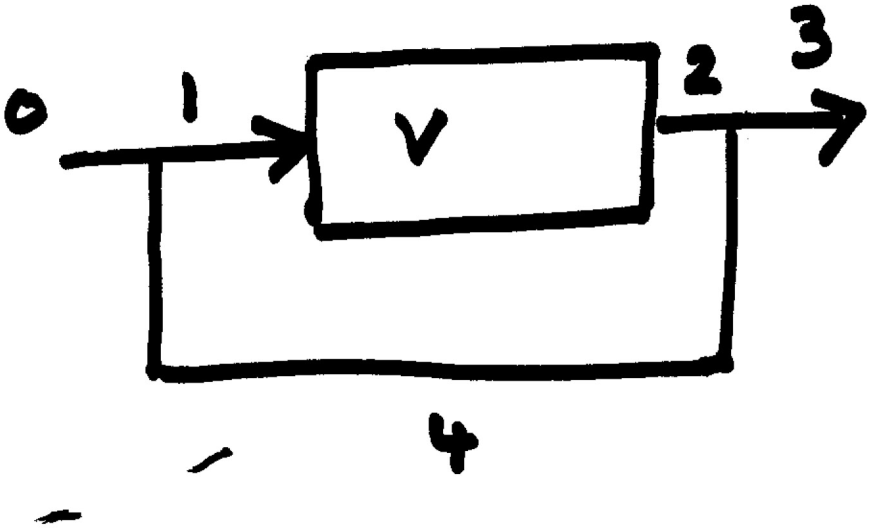
$c_A(V,0) = c_{Ai}$; $c_B(V,0) = c_{Bi}$ at $t=0$

Solution of the transient problem for PFR shows that if $c_{B0} = 0$ rxn does not move.

So in PFR autocat rxn needs c_B in feed

R1





R = 4

Find X

PFR

$$k\tau_p = -\ln(1-X_3)$$ ✓

$$k\tau_p = -\ln(1-0.66)$$

$$= -\ln(0.34)$$

$$= 1.07$$

✓ $$k\tau_R = \ln\left[\frac{1-\frac{R}{R+1}X_3}{1-X_3}\right](R+1)$$

Since Same reactor is used and flow is the same V/v_0 = Same for both data

$$k\tau_p = 1.07 = k\tau_R$$

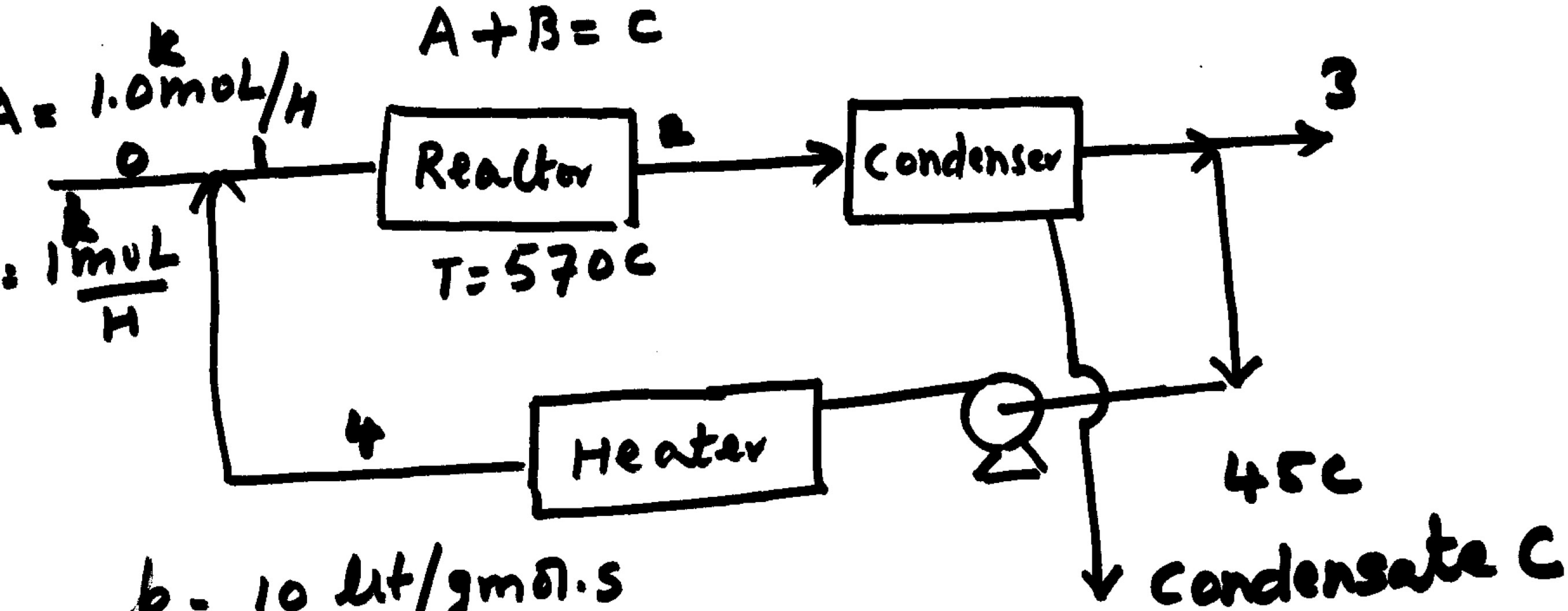
$$1.07 = (5)\ln\left[\frac{1-0.8X_3}{1-X_3}\right]$$

$$1.23 = \frac{1-0.8X_3}{1-X_3}$$

$$1.23 - 1.23X_3 = 1-0.8X_3$$

$$0.23 = 043X_3 \Rightarrow X_3 = 0.53$$

2



$k = 10$ lit/gmol.s

$r_A = -k C_A C_B$

vapor pressure C at 45 C = 0.2 atm

$F_{A0} = F_{B0} = 1$ kmoL/hr

Reactor at 1 atm , R=4

g A $(R+1)F_{A0}(1-X)$

g B $(R+1)F_{A0}(1-X)$

(g) C $\dfrac{(R+1)F_{A0}(X)}{F_t = 2(R+1)F_{A0}(1-X) + (R+1)F_{A0}X}$ — Condensible

At incipient condensation

$$0.2 = \frac{(R+1)F_{A0}X_s}{2(R+1)F_{A0}(1-X_s)+(R+1)F_{A0}X_s} = \frac{X_s}{2(1-X_s)+X_s}$$

$$0.2 = \frac{X_s}{2-X_s} \Rightarrow X_s = 0.33$$

Before Condensation

A	$(R+1)\,F_{A0}\,(1-X)$	(g)
B	$(R+1)\,F_{A0}\,(1-X)$	(g)
C	$(R+1)\,F_{A0}\,X$	(g)

After Condensation

A	$(R+1)\,F_{A0}(1-X)$	(g)
B	$(R+1)\,F_{A0}\,(1-X)$	(g)
C	$(R+1)\,F_{A0}\,X_s$	(g)

$\rightarrow F_t = (R+1)\,F_{A0}\,(2-2X+X_s)$ for $X > X_s$

After $X_3 > X_S$

$$\frac{v}{v_0} = \frac{F_t}{F_{t0}} = \frac{2-2x+X_S}{2}$$

$$C_A = \frac{F_A}{v} = \frac{(R+1)\,F_{A0}\,(1-x)\,2}{v_0\,(2-2x+X_3)} = \frac{2\,(R+1)\,C_{A0}\,(1-x)}{(2-2x+X_S)}$$

$$F_{A1} = (R+1)\,F_{A0}\,(1-X_1)$$

$$= R\,F_{A0}\,(1-X_3) + F_{A0}$$

$$(R+1)(1-X_1) = R\,(1-X_3)+1$$

$$X_1 = \frac{R}{R+1}X_3$$

$$\frac{dF_A}{dV} = r_A = -k\, C_A C_B = -k\, C_A^2 \quad (\because C_A = C_B)$$

$$-(R+1)\, F_{A0} \frac{dX}{dV} = -k\, C_{A0}^2 \frac{\left[2(R+1)(1-X)\right]^2}{(2-2X+X_3)^2}$$

$$\tau = \frac{(R+1)}{k\, C_{A0}} \int_{X_1}^{X_3 = 0.5} \frac{(2-2X+X_3)^2}{(2(R+1)(1-X))^2}\, dX$$

$$v_0 = \frac{F_{t0}}{P} RT = \frac{(2)(0.082)843}{1.0} = 138\ m^3/hr$$

$$C_{A0} = \frac{(P_0)\,0.5}{RT} = \frac{(1)(0.5)}{(0.082)\,843} = (3.6)\,10^{-3}\ \frac{mol}{L}$$

$$kC_{A0} = \frac{(10)}{s}(3.6)\,10^{-3}\ \frac{mol}{L} = (3.6)\,10^{-2}\ \frac{mol}{L\cdot s}$$

$$\therefore \quad \tau = \frac{(R+1)}{kC_{A0}} \int_{X_1}^{X_2} \frac{(2-2X+X_s)}{\left[2\,(R+1)(1-X)\right]^2}\,dX \quad \therefore$$

Putting numbers and integrating numerically

$\tau = 1.$ second.

$$V_R = (v_0\,\tau) = \frac{(138)\,10^{3}}{3600} \times 1 = 38 \text{ Lit}$$

These numbers may correlate well with

$$SO_2 + \frac{1}{2} O_2 = SO_3$$

Here $\underline{38}$ lit catalyst gives $\underline{64}$ kg/hr SO_2 processed.

Accor $\underline{70\ m^3}$ of catalyst will process

$$\left(\frac{64}{38}\right) 70 \ \text{ton/hr} = 117 \ \text{ton/hr}$$

$$= \underline{\underline{2900}} \ \frac{\text{ton}}{\text{d}}.$$

Prof Shankar
LC9·17
2/11/12

Advanced Reaction Engineering

Multiple Reactions

Thursday 1/Nov 12 (1400-1530).
Friday 2/Nov/12
↗ 1515-1805

Multiple Reactions

$$aA + bB = cC + dD \qquad -(1)$$

$$gA + fC = eE \qquad (2)$$

$$A + \frac{b}{a}B = \frac{c}{a}C + \frac{d}{a}D$$

$$A + \frac{f}{g}C = \frac{e}{g}E$$

$$\delta_{A1} = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$\delta_{A2} = \frac{e}{g} - \frac{f}{g} - 1$$

Stoichiometric Table

A	F_{A0}	$F_A = F_{A0}(1 - X_1 - X_2)$
B	F_{B0}	$F_B = F_{B0} - \frac{b}{a} F_{A0} X_1$
C	F_{C0}	$F_C = F_{C0} + \frac{c}{a} F_{A0} X_1 - \frac{d}{a} F_{A0} X_2$
D	F_{D0}	$F_D = F_{D0} + d/a\, F_{A0} X_1$
E	F_{E0}	$F_E = F_{E0} + e/g\, F_{A0} X_2$
I	$\frac{F_{I0}}{F_{t0}}$	$\frac{F_{I0}}{F_{t0}} = \underline{F_{I0}}$

$$F_t = \left(F_{t0}\right) + \underline{F_{A0} X_1} \downarrow \delta_{A_1} + \underline{F_{A0} X_2} \downarrow \delta_{A2}$$

gas phase reaction

$C_A = F_A / v$

$$\frac{v}{v_0} = \frac{F_t}{F_{t0}} \frac{T}{T_0} \frac{Z}{Z_0} \frac{P_0}{P} \quad \text{(gas Law)}$$

$$C_{\underline{A}} = \frac{F_{A0}(1 - \underline{X_1} - \underline{X_2})}{v_0 (1 + y_{A0} x_{A1} \delta_{A1} + y_{A0} x_{A2} \delta_{A2}) \frac{T}{T_0} \frac{Z}{Z_0} \frac{P_0}{P}}$$

Similarly C_B, C_C, C_D, C_I

Liquid phase reaction

$$C_A = F_A / v = \frac{F_{A0}}{v_0}(1 - X_1 - X_2) = C_{A0}(1 - X_1 - X_2)$$

$$A \underset{2}{\overset{1}{\rightleftarrows}} B \quad ; \quad A \xrightarrow{1} B \ + \ B \xrightarrow{2} A$$

<u>PFR</u> Equation

Intensive Rates.

$$\frac{dF_A}{dV} = \left(r_{\underline{\underline{A}}}\right) = r_1(-1) + r_2(+1)$$

$$\frac{dF_A}{dV} = r_2 - r_1$$

Note r_1 is intensive rate of step $A \rightarrow B$

and r_2 is intensive rate of step $B \rightarrow A$

So rate of formation of say A

$$r_A = r_1(-1) + r_2(+1) = -r_1 + r_2$$

$$-F_{A0}\frac{dX_1}{dV} = -r_1 + r_2$$

$$F_{A0}\frac{dX_1}{dV} = r_1 - r_2$$

How will you find r_1 and r_2.

1) Postulate a model for $r_1 - r_2$. Carry out measurement of $(r_1 - r_2) = r_B$. Fit data to model. Find parameters by fitting: say

$$-r_A = r_1 - r_2 = k_1 C_A^{\alpha} C_B^{\beta} - k_2 C_A^{\gamma} C_B^{\delta}$$

We know from experience that one measurement is sufficient to specify the system from a known stat. This means that there is only one degree of freedom.

$$\begin{array}{lll} A \rightarrow B \; ; & B - A = 0 \; ; & \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \\ B \rightarrow A \; ; & A - B = 0 \; ; & \end{array}$$

Determinant of Coefficient matrix is ~~a~~. zero showing that rank is 1 and so there is only one independent reaction. So one measurement is adequate to specify system composition.

General Case

$$\alpha_{11} A_1 + \alpha_{12} A_2 + \cdots \alpha_{1n} A_n = 0$$

$$\alpha_{21} A_1 + \alpha_{22} A_2 + \cdots \alpha_{2n} A_n = 0$$

$$\alpha_{p1} A_1 + \alpha_{p2} A_2 + \cdots \alpha_{pn} A_n = 0$$

$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{1n} \\ \alpha_{21} & \alpha_{22} & \alpha_{2n} \\ \alpha_{p1} & \alpha_{p2} & \alpha_{pn} \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_n \end{bmatrix} = 0$$

Rate process — p

First subscript - rxn

second subscript - species

Rank = r,

p rows; n Columns

$$A_j - A_{j0} = \Delta_{1j} + \Delta_{2j} + \cdots \Delta_{rj}$$

where there are 'r' independent reactions

$$\frac{\Delta_{1j}}{\alpha_{1j}} = \frac{\Delta_{11}}{\alpha_{11}} = \frac{\Delta_{1k}}{\alpha_{1k}} = \frac{\Delta_{1n}}{\alpha_{1n}} = \beta_1$$

$$\frac{\Delta_{2j}}{\alpha_{2j}} = \frac{\Delta_{21}}{\alpha_{21}} = \frac{\Delta_{2k}}{\alpha_{2k}} = \frac{\Delta_{2n}}{\alpha_{2n}} = \beta_2$$

$$\frac{\Delta_{rj}}{\alpha_{rj}} = \frac{\Delta_{r1}}{\alpha_{r1}} = \frac{\Delta_{rk}}{\alpha_{rk}} = \frac{\Delta_{rn}}{\alpha_{rn}} = \beta_r$$

$$A_j - A_{j0} = \beta_1 \alpha_{1j} + \beta_2 \alpha_{2j} + \cdots \beta_r \alpha_{rj}$$

If reference species is A_{10} we have

$$\frac{(A_j - A_{j0})}{\underline{\underline{A_{10}}}} = \left(\frac{\beta_1}{A_{10}}\right)\alpha_{1j} + \frac{\beta_2}{A_{10}}\alpha_{2j} + \cdots \frac{\beta_r}{A_{10}}\alpha_{rj}$$

$$= x_1 \alpha_{1j} + x_2 \alpha_{2j} + \cdots x_r \alpha_{rj}$$

This shows that in a network we choose a set of rank r and set up stoichiometric table. And r such eqns are sufficient to specify the system.

Example

$$\underset{2}{B} + \underset{1}{C} = \underset{3}{MB} + \underset{6}{HCl} \quad \text{RXN1}$$

$$\underset{3}{MB} + \underset{1}{C} = \underset{4}{DB} + \underset{6}{HCl} \quad \text{RXN2}$$

$$\underset{4}{DB} + \underset{1}{C} = \underset{5}{TB} + \underset{6}{HCl} \quad \text{RXN3}$$

$$\frac{A_j - A_{j0}}{A_{10}} = x_1 \alpha_{1j} + x_2 \alpha_{2j} + \cdots x_r \alpha_{rj}$$

Here there are 3 independent reactions

$$(A_2 - A_{20})/A_{10} = x_1 \alpha_{12} + x_2 \alpha_{22} + x_3 \alpha_{32} = -x_1$$

$$(A_5 - A_{50})/A_{10} = x_1 \alpha_{15} + x_2 \alpha_{25} + x_3 \alpha_{35} = x_3$$

$$(A_3 - A_{30})/A_{10} = x_1 \alpha_{13} + x_2 \alpha_{23} + x_3 \alpha_{33} = x_1 - x_2$$

suppose we take Benzene as reference

$$(A_2 - A_{20})/A_{20} = x_1 \alpha_{12} + x_2 \alpha_{22} + x_3 \alpha_{32} = -x_1$$

$$(A_5 - A_{50})/A_{20} = x_1 \alpha_{15} + x_2 \alpha_{25} + x_3 \alpha_{35} = x_2$$

$$(A_3 - A_{30})/A_{10} = x_1 \alpha_{13} + x_2 \alpha_{23} + x_3 \alpha_{33} = x_1 - x_2$$

Q2.

$4NH_3 + 5O_2 = 4NO + 6H_2O$

$4NH_3 + 3O_2 = 2N_2 + 6H_2O \Leftarrow$

$2NO + O_2 = 2NO_2$

$4NH_3 + 6NO = 5N_2 + 6H_2O$

$2NO = N_2 + O_2$

$N_2 + 2O_2 = 2NO_2 \Leftarrow 2$

	①	②	③	④	⑤	⑥
RXN	NH_3	O_2	NO	H_2O	NO_2	N_2
1	−4	−5	4	6	0	0
2	−4	−3	0	6	0	2
3	0	−1	−2	0	2	0
4	−4	0	−6	6	0	5
5	0	1	−2	0	0	1
6	0	−2	0	0	2	−1

It can be shown that rank 3

And RXN 1, 2, 3 are an independent set

First subscript rxn

Second subscript species.

$$\frac{A_1 - A_{10}}{A_{10}} = x_1 \alpha_{11} + x_2 \alpha_{21} + x_3 \alpha_{31} = -4x_1 - 4x_2 \quad -(1)$$

$$\frac{A_5 - A_{50}}{A_{10}} = x_1 \alpha_{15} + x_2 \alpha_{25} + x_3 \alpha_{35} = 2x_3 \quad -(2)$$

$$\frac{A_6 - A_{60}}{A_{10}} = x_1 \alpha_{16} + x_2 \alpha_{26} + x_3 \alpha_{36} = 2x_2 \quad -(3)$$

$$\frac{dA_1}{dV} = -4r_1 - 4r_2 - 4r_4 \qquad (4)$$

$$\frac{dA_5}{dV} = 2r_3 + 2r_6 \qquad (5)$$

$$\frac{dA_6}{dV} = 2r_2 - r_6 + r_5 + 5r_4 \qquad (6)$$

$$A_{10} \frac{dx_1}{dV} = r_1 + r_4 - \frac{5}{2} r_4 + \cancel{r/2} - \cancel{r/2} + \frac{r_6}{2} - \frac{r_5}{2}$$

$$A_{10} \frac{dx_1}{dV} = r_1 - \frac{3}{2} r_4 - \frac{r_5}{2} + \frac{r_6}{2} = f_1(x_1 x_2 x_3 T)$$

$$A_{10} \frac{dx_2}{dV} = \frac{2 r_2 - r_6 + r_5 + 5 r_4}{2} = f_2(x_1 x_2 x_3 T)$$

$$A_{10} \frac{dx_3}{dV} = r_3 + r_6 = f_3(x_1 x_2 x_3 T)$$

$x_1(V)$ $x_2(V)$ $x_3(V)$

$$2A_{10}\frac{dX_3}{dV} = 2r_3 + 2r_6$$ (7) From (2) + (5)

$$2A_{10}\frac{dX_2}{dV} = 2r_2 - r_6 + r_5 + 5r_4$$ (8) From (3 + 6)

$$-4A_{10}\left[\frac{dX_1}{dV} + \frac{dX_2}{dV}\right] = -4r_1 - 4r_2 - 4r_4$$ (From 1 + 4)

(9)

$$A_{10}\left[\frac{dX_1}{dV} + \frac{dX_2}{dV}\right] = r_1 + r_2 + r_4$$

$$A_{10}\frac{dX_1}{dV} = (r_1 + r_2 + r_4) - \left(\frac{2r_2 - r_6 + r_5 + 5r_4}{2}\right)$$