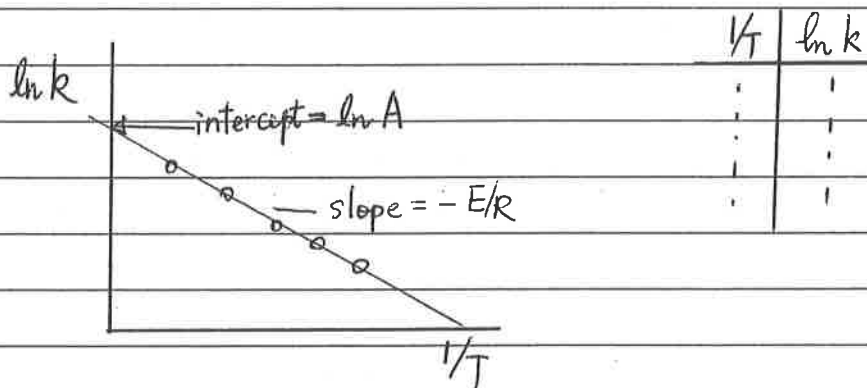


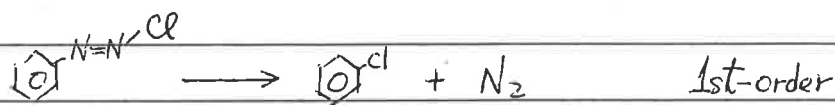
$e^{-E/RT}$: fraction of successful collisions ≤ 1

$k_A \uparrow$ as $T \uparrow$ and $k_A = A$ as $T \rightarrow \infty$

Arrhenius eq. $\Rightarrow \ln k_A = \ln A - \frac{E}{R} \frac{1}{T}$
 \uparrow 8.314 J/mol·K or 1.987 cal/mol·K



Ex 3-1



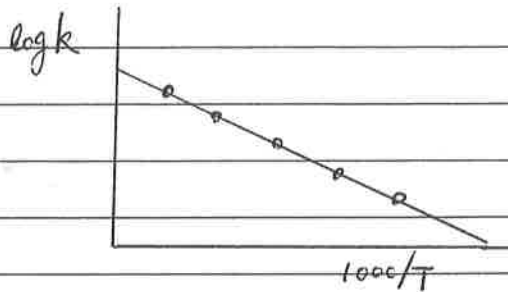
$k(s^{-1})$	- 0.0018 - -	0.00717
$T(K)$	- 323 - - -	333

find activation energy

Sol.

Arrhenius

$$\log k = \log A - \frac{E}{2.3R} \left(\frac{1}{T} \right)$$



slope = ? \rightarrow decade method

$$\begin{aligned} \log k_1 &= \log A - \frac{E}{2.3R} \left(\frac{1}{T_1} \right) \\ \log k_2 &= \log A - \frac{E}{2.3R} \left(\frac{1}{T_2} \right) \end{aligned} \Rightarrow \log \frac{k_2}{k_1} = \frac{-E}{2.3R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

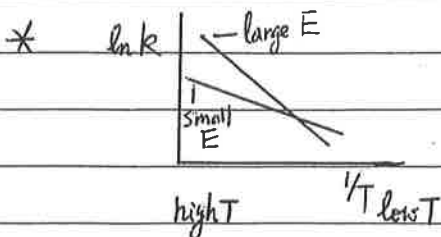
$$E = - \frac{(2.3R) \log(k_2/k_1)}{1/T_2 - 1/T_1}$$

refer to the text book
for Excel Analysis
and find the value
of A

from fig. $k_1 = 0.005$ $1/T_1 = 0.00303$
 $k_2 = 0.0005$ $1/T_2 = 0.00319$

$$\Rightarrow \log \left(\frac{k_1}{k_2} \right) = 1$$

$$\Rightarrow E = 120 \text{ kJ/mol}$$



larger E means more temperature-sensitive

* other expression

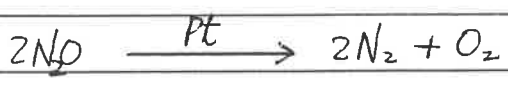
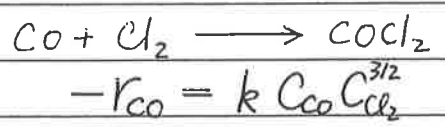
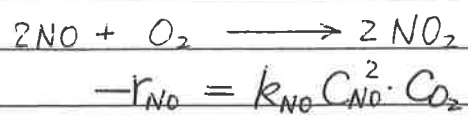
$$k(T) = A' T^n e^{-E/RT}, \quad 0 \leq n \leq 1$$

3.1.2 Reaction order

$$-r_A = k C_A^\alpha C_B^\beta \quad \text{was found from exp.}$$

\Rightarrow α order with respect to A
 β order w.r.t. B
 overall order = $n = \alpha + \beta$

Ex



$$-r_{N_2O} = \frac{k_{N_2O} C_{N_2O}}{1 + k' C_{O_2}}$$

different expressions for different conditions

e.g. at low C_{O_2} ($1 \gg k' C_{O_2}$)

$$-r_{N_2O} \propto C_{N_2O} \quad \because \text{"apparent" 1st order w.r.t. } N_2O$$

表觀

at high C_{O_2} ($k' C_{O_2} \gg 1$)

$$-r_{N_2O} \propto C_{N_2O} C_{O_2}^{-1} \quad \because \text{apparent rxn order: } -1 \text{ w.r.t. } O_2$$

1 w.r.t. N_2O

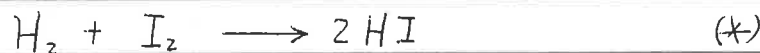
units of rate constant

$$-r_A = k_A C_A^n$$

$$\left[\frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \right] = k_A \cdot \left[\frac{\text{mol}}{\text{dm}^3} \right]^n$$

$$\Rightarrow k_A \equiv \left[\left(\frac{\text{dm}^3}{\text{mol}} \right)^{n-1} \cdot \text{s}^{-1} \right] \quad \therefore \begin{array}{ll} \text{Zero-order} & \frac{\text{mol}}{\text{dm}^3 \cdot \text{s}} \\ \text{1st-order} & \text{s}^{-1} \\ \text{2nd-order} & \frac{\text{dm}^3}{\text{mol} \cdot \text{s}} \\ \text{3rd-order} & \left(\frac{\text{dm}^3}{\text{mol}} \right)^2 \cdot \text{s}^{-1} \end{array}$$

3.1.3 Elementary Rate Laws and Molecularity



$$-r_{\text{H}_2} = k C_{\text{H}_2} C_{\text{I}_2}$$

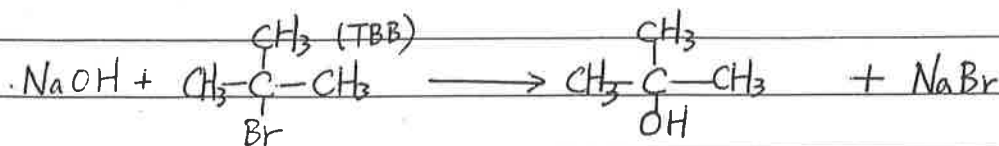
this rxn (*) has an elementary rate law \therefore rxn order \equiv stoich. coeff. and rxn (*) is an elementary rxn.

molecularity : no. of molecules involved in rate-limiting step.
(Colliding)

Ex. (3-2) old



$$-r_{\text{MB}} = k C_{\text{NaOH}} C_{\text{CH}_3\text{Br}} \quad \text{2nd order}$$



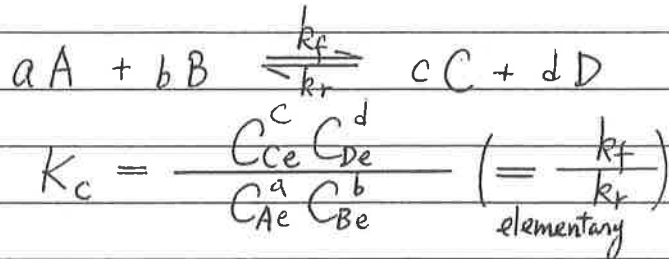
rxn order = ?

$$\text{Ans} : -r_{\text{TBB}} = k C_{\text{TBB}} \quad \text{from exp.}$$

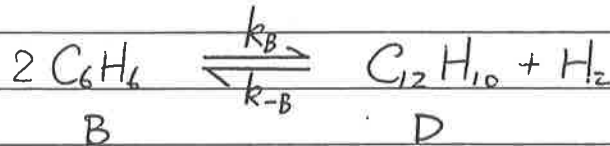
3.1.4 Reversible Rxns

All rate laws for rev. rxns must reduce to thermodynamic relationship at equilibrium.

i.e.



An elementary and reversible rxn



$$-r_{B, \text{forward}} = k_B C_B^2$$

$$r_{B, \text{reverse}} = k_{-B} C_D C_{H_2}$$

$$r_B = r_{B, \text{net}} = -k_B C_B^2 + k_{-B} C_D C_{H_2}$$

$$\Rightarrow -r_B = k_B C_B^2 - k_{-B} C_D C_{H_2} = k_B \left[C_B^2 - \frac{k_{-B}}{k_B} C_D C_{H_2} \right]$$

$$= k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_c} \right)$$

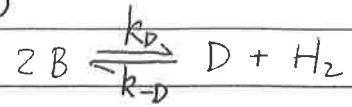
equili. const. = $\frac{k_f}{k_r} = \frac{k_B}{k_{-B}}$

check if thermodynamically consistent at equili

$$\underset{\text{at equili}}{-r_B} \equiv 0 = k_B \left[C_{Be}^2 - \frac{C_{De} C_{He}}{K_c} \right]$$

$$\Rightarrow K_c = \frac{C_{De} C_{He}}{C_{Be}^2} \quad \text{o.k.}$$

Similarly for the formation of diphenyl (D)



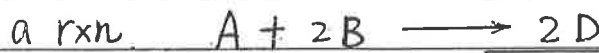
$$r_D = k_D \left[C_B^2 - \frac{C_D C_{H_2}}{K_C} \right]$$

$$\therefore \frac{r_D}{1} = \frac{r_B}{-2} = \frac{k_B}{2} \left[C_B^2 - \frac{C_D C_{H_2}}{K_C} \right]$$

$$\therefore k_D = \frac{k_B}{2}$$

∴ k 值須視所選取的 species 而定。

Ex(3-3) old



irrev. at low temp. $-r_A = k_A C_A^{1/2} C_B$ (*) rate law from exp.

at high temp, the rxn found to be rev. $A + 2B \rightleftharpoons 2D$

suggest a rate law at high temp.

Sol.

two requirements : a. thermodynamic relationship for the rate law b. reduce to the irrev. rate law when product conc. = 0

$$\therefore K_C = \frac{C_{De}^2}{C_{Ae} C_{Be}^2} \quad \left[\frac{dm^3}{mol} \right] \quad \text{須成立}$$

$$\Rightarrow C_{Ae} C_{Be}^2 - \frac{C_{De}^2}{K_C} = 0 \quad \text{suggest} \quad -r_A = k_A \left[C_A C_B^2 - \frac{C_D^2}{K_C} \right]$$

at $C_D = 0 \Rightarrow -r_{A0} = k_A C_{A0} C_{B0}^2$, 與 (*) 不合。

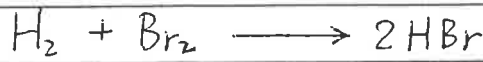
另試 $\sqrt{K_C} = \frac{C_{De}}{C_{Ae}^{1/2} C_{Be}} = K_{C2} \quad \left[\left(\frac{dm^3}{mol} \right)^{1/2} \right]$

$$\Rightarrow C_{Ae}^{1/2} C_{Be} - \frac{C_{De}}{K_{C2}} = 0$$

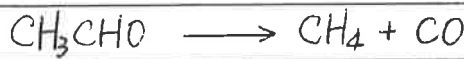
$$\Rightarrow -r_A = k_A \left[C_A^{1/2} C_B - \frac{C_D}{K_{C2}} \right] \quad \text{能符合 (*) at } C_D = 0$$

3.1.5 Nonelementary Rate Laws and Reactions

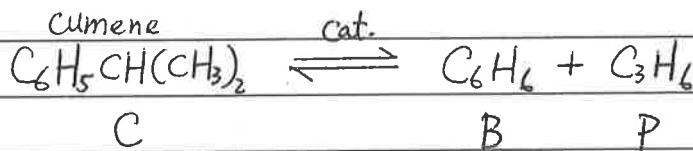
non-elementary rxns



$$r_{\text{HBr}} = \frac{k_1 C_{\text{H}_2} C_{\text{Br}_2}^{1/2}}{k_2 + C_{\text{HBr}}/C_{\text{Br}_2}}$$



$$-r_{\text{CH}_3\text{CHO}} = k C_{\text{CH}_3\text{CHO}}^{3/2}$$



gas-solid rxn, partial pressure sometimes used
equili. const. [atm] or [kPa]

$$-r'_C = \frac{k(P_C - P_B P_P / K_P)}{1 + K_C P_C + K_B P_B}$$

adsorption const. [atm⁻¹]

checking thermodynamical consistency

$$-r'_C = 0 = k \frac{P_C - P_B P_P / K_P}{1 + K_C P_C + K_B P_B}$$

$$\Rightarrow K_P = \frac{P_B P_P}{P_C} \quad \text{O.K.}$$

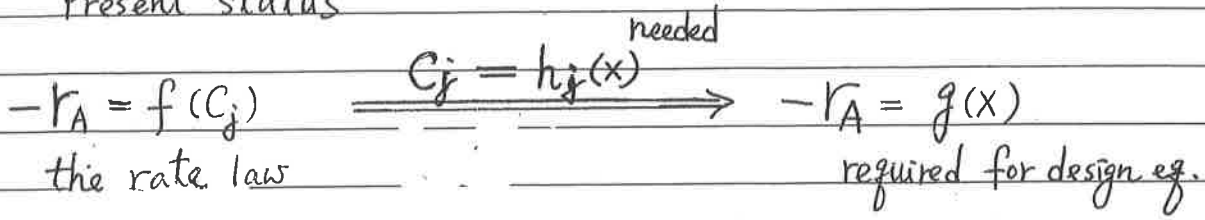
units $P_C = C_C R T$

bulk density of cat.

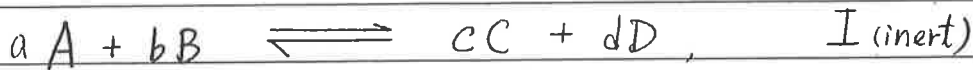
$$-r_A = \rho_b (-r'_A)$$

[mol / time · vol] [mass / vol] [mol / time · mass]

3.2 Present status



3.3. Stoichiometric Table



3.3.1 Batch systems

	aA	$+ bB$	\longrightarrow	cC	$+ dD$	$(+ I)$	Total
time = 0	N_{A0}	N_{B0}		N_{C0}	N_{D0}	N_{I0}	N_{T0}
time t	$\frac{N_{A0} - N_{A0}x}{N_A}$	$\frac{N_{B0} - \frac{b}{a}N_{A0}x}{N_B}$		$\frac{N_{C0} + \frac{c}{a}N_{A0}x}{N_C}$	$\frac{N_{D0} + \frac{d}{a}N_{A0}x}{N_D}$	$\frac{N_{I0}}{N_I}$	N_T


time = 0, $N_{T0} = N_{A0} + N_{B0} + N_{C0} + N_{D0} + N_{I0}$

time t, $N_T = N_{A0} + N_{B0} + N_{C0} + N_{D0} + N_{I0} + N_{A0}x \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right)$

$$N_T = N_{T0} + \delta N_{A0}x, \quad \text{where } \delta = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right)$$

Conc. at time t	$\frac{N_{A0}(1-x)}{V}$	$\frac{N_{B0} - \frac{b}{a}N_{A0}x}{V}$	$\frac{N_{C0} + \frac{c}{a}N_{A0}x}{V}$	$\frac{N_{D0} + \frac{d}{a}N_{A0}x}{V}$	let $\theta_i = \frac{N_{i0}}{N_{A0}}$
	C_A	C_B	C_C	C_D	
	\parallel	\parallel	\parallel	\parallel	
	$\frac{N_{A0}[1-x]}{V}$	$\frac{N_{A0}[\theta_B - \frac{b}{a}x]}{V}$	$\frac{N_{A0}[\theta_C + \frac{c}{a}x]}{V}$	$\frac{N_{A0}[\theta_D + \frac{d}{a}x]}{V}$	

3.3.2 Constant-Volume Reaction Systems (constant-density)

gas phase: * bomb reactor 

* eg. $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ isothermal const. mole

liquid phase: all

$$V = V_0$$

$$C_A = \frac{N_{A0}(1-X)}{V_0} = C_{A0}(1-X)$$

$$C_B = C_{A0} \left[\theta_B - \frac{b}{a} X \right]$$

$$C_C = C_{A0} \left[\theta_C + \frac{c}{a} X \right]$$

$$C_D = C_{A0} \left[\theta_D + \frac{d}{a} X \right]$$

Ex 3-2 Expressing $C_j = h_j(X)$



Let $X = \text{conv. of NaOH}_A$

find $C_j = h_j(X)$

Sol.

	A	+ $\frac{1}{3}$ B	→	C	+ $\frac{1}{3}$ D	water (I)
t=0	N_{A0}	N_{B0}		N_{C0}	N_{D0}	N_{I0}
time t	$N_{A0} - N_{A0}X$	$N_{B0} - \frac{1}{3}N_{A0}X$		$N_{C0} + N_{A0}X$	$N_{D0} + \frac{1}{3}N_{A0}X$	N_{I0}
	$N_{A0}(1-X)$	$N_{A0}(\theta_B - \frac{1}{3}X)$		$N_{A0}(\theta_C + X)$	$N_{A0}(\theta_D + \frac{1}{3}X)$	$N_{A0}(\theta_I)$
conc.	$C_{A0}(1-X)$	$C_{A0}(\theta_B - \frac{1}{3}X)$		$C_{A0}(\theta_C + X)$	$C_{A0}(\theta_D + \frac{1}{3}X)$	C_{I0}

Ex 3-3 limiting reactant

in Ex 3-4, initial conc.: A 10 mol/dm³ no C, D
B 2 mol/dm³conc. of D = ? (a) at 20% NaOH conv.
(b) at 90% "

sol.

(a) 20%

$$C_D = C_{A0}(\theta_D + \frac{1}{3}X)$$
$$= 10(0 + \frac{1}{3} \times 0.2) = 0.67 \text{ mol/dm}^3$$

$$C_B = C_{A0}(\theta_B - \frac{1}{3}X)$$
$$= 10(\frac{2}{10} - \frac{0.2}{3}) = 1.33 \text{ mol/dm}^3$$

(b) 90%

$$C_D = C_{A0}(\theta_D + \frac{1}{3}X)$$
$$= 10(0 + \frac{0.9}{3}) = 3 \text{ mol/dm}^3$$

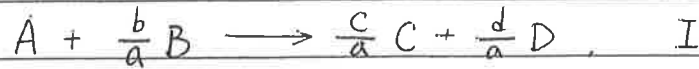
$$C_B = 10(\frac{2}{10} - \frac{0.9}{3}) = -1 \text{ mol/dm}^3$$

impossible

∴ B is the limiting reactant
達 X=90% 前, B 已消耗完∴ 應選擇 glyceryl stearate (B)
來算 conv. 否則產生錯誤。

(尤其以電腦運算)

3.3.3 Flow Systems



$$C_A = \frac{F_A}{v}, \quad \theta_B = \frac{F_{B0}}{F_{A0}}$$

$$\theta_C \quad \vdots$$

$$\theta_D \quad \vdots$$

Stoichiometric table 每 batch system 極相似，
僅 N_{j0}, N_j 被 F_{j0}, F_j 取代。

for ex: $v = v_0$

$$C_A = \frac{F_{A0}}{v} (1 - X) = C_{A0} (1 - X)$$

$$C_B = C_{A0} (\theta_B - \frac{b}{a} X)$$

Const vol. : * liquid-phase

* const-mol gas-phase

3.3.4 Volume Change with Reaction

Volume change 基本上由 mol. no. change 造成

- pressure "

- temp. "

Compressibility "
(Z)

Z = 1 ideal gas
↑
func. of P, T

Eg. of state :

batch

$$PV = Z N_T R T$$

flow

$$Pv = Z F_T R T$$

$$t=0 \quad P_0 V_0 = Z_0 N_{T0} R T_0$$

$$P_0 v_0 = Z_0 F_{T0} R T_0 \quad \text{input}$$

$$\therefore V = V_0 \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right) \underbrace{\left(\frac{Z}{Z_0}\right)}_1 \underbrace{\left(\frac{N_T}{N_{T0}}\right)}$$

討論之重點, 可由 stoichiometric table 獲得

$$\therefore N_T = N_{T0} + \delta N_{A0} \chi \Rightarrow \frac{N_T}{N_{T0}} = 1 + \delta \frac{N_{A0}}{N_{T0}} \chi$$

$$= 1 + \delta y_{A0} \chi, \quad \text{let } \epsilon = \delta y_{A0}$$

$$\Rightarrow \boxed{\frac{N_T}{N_{T0}} = 1 + \epsilon \chi}$$

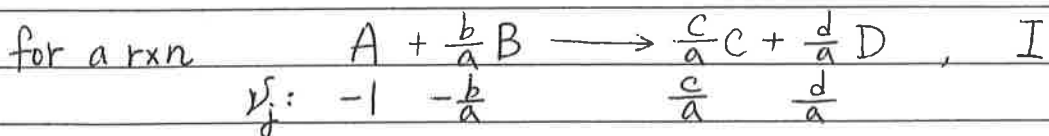
$$\epsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1\right) \frac{N_{A0}}{N_{T0}} = \frac{\text{change in total mol. no. for complete conv.}}{\text{total mol. no. fed}}$$

$$\therefore \boxed{V = V_0 \cdot \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right) (1 + \epsilon \chi)}$$

Similarly for flow systems

$$v = v_0 \left(\frac{F_T}{F_{T0}}\right) \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right), \quad F_T = F_{T0} + F_{A0} \delta \chi$$

$$\Rightarrow \boxed{v = v_0 (1 + \epsilon \chi) \left(\frac{P_0}{P}\right) \left(\frac{T}{T_0}\right)}$$



$$v_j: \quad -1 \quad -\frac{b}{a} \quad \quad \frac{c}{a} \quad \frac{d}{a}$$

$$\Rightarrow N_j = N_{A0} (\theta_j + v_j \chi)$$

or

$$F_j = F_{A0} (\theta_j + v_j \chi)$$

$$\therefore C_j = \frac{F_j}{v} = \frac{F_{A0} (\theta_j + \nu_j x)}{v_0 (1 + \epsilon x) \left(\frac{P}{P_0}\right) \left(\frac{T}{T_0}\right)}$$

$$\Rightarrow C_j = \frac{C_{A0} (\theta_j + \nu_j x)}{(1 + \epsilon x)} \cdot \left(\frac{P}{P_0}\right) \left(\frac{T_0}{T}\right) \quad \leftarrow \text{Ex 3-4}$$

also $C_j = \frac{F_j}{v} = \frac{P_j}{RT} = \frac{F_j}{F_T} \frac{P}{RT}$

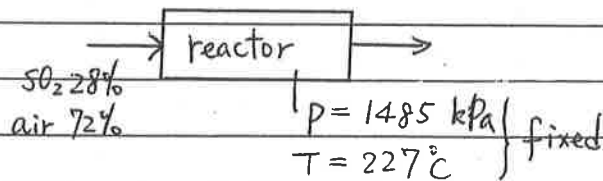
$$C_{T0} = \frac{F_{T0}}{v_0} = \frac{P_0}{RT_0}$$

$$C_T = \frac{P}{RT} \Rightarrow C_T = C_{T0} \left(\frac{P}{P_0}\right) \left(\frac{T_0}{T}\right)$$

$$\Rightarrow C_j = C_{T0} \left(\frac{F_j}{F_T}\right) \left(\frac{P}{P_0}\right) \left(\frac{T_0}{T}\right)$$

$$\therefore C_j = \frac{F_j}{F_T} \cdot C_T = C_{T0} \left(\frac{F_j}{F_T}\right) \left(\frac{P}{P_0}\right) \left(\frac{T_0}{T}\right)$$

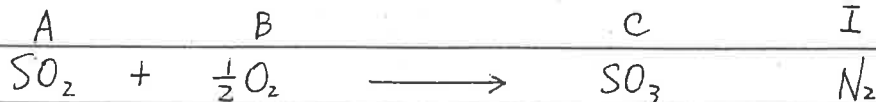
Ex 3-5 $C_j = h_j(x)$ for a gas-phase rxn



set up a stoichiometric table, and find C_j at different conv.

Sol.

taking SO_2 as the basis



input	F_{A0}	F_{B0}	0	F_{I0}
at conv. x	$F_{A0} - F_{A0}x$	$F_{B0} - \frac{1}{2}F_{A0}x$	$F_{A0}x$	F_{I0}
	$F_{A0}(1-x)$	$F_{A0}(\theta_B - \frac{1}{2}x)$	$F_{A0}x$	$\theta_I F_{A0}$

$F_T = F_{T0}(1 + \epsilon x), v = v_0(1 + \epsilon x) \quad \because T = T_0, P = P_0$					
<table style="width: 100%; border-collapse: collapse;"> <tr> <td style="text-align: right; padding-right: 10px;">Conc. at t</td> <td style="text-align: center;">$C_{A0} \frac{1-x}{1+\epsilon x}$</td> <td style="text-align: center;">$C_{A0} \frac{\theta_B - \frac{1}{2}x}{1+\epsilon x}$</td> <td style="text-align: center;">$C_{A0} \frac{x}{1+\epsilon x}$</td> <td style="text-align: center;">$C_{A0} \frac{\theta_I}{1+\epsilon x}$</td> </tr> </table>	Conc. at t	$C_{A0} \frac{1-x}{1+\epsilon x}$	$C_{A0} \frac{\theta_B - \frac{1}{2}x}{1+\epsilon x}$	$C_{A0} \frac{x}{1+\epsilon x}$	$C_{A0} \frac{\theta_I}{1+\epsilon x}$
Conc. at t	$C_{A0} \frac{1-x}{1+\epsilon x}$	$C_{A0} \frac{\theta_B - \frac{1}{2}x}{1+\epsilon x}$	$C_{A0} \frac{x}{1+\epsilon x}$	$C_{A0} \frac{\theta_I}{1+\epsilon x}$	

$$F_{A0} = (0.28)(F_{T0})$$

$$F_{B0} = (0.72)(0.21)F_{T0} = (0.151)F_{T0}$$

$$F_{C0} = 0, \quad F_{I0} = (0.72)(0.79)F_{T0} = (0.569)F_{T0}$$

$$\theta_B = F_{B0}/F_{A0} = 0.54$$

$$\theta_I = F_{I0}/F_{A0} = 2.03$$

$$C_{A0} = y_{A0} C_{T0} = y_{A0} \left(\frac{P_0}{RT_0} \right)$$

$$= (0.28) \left[\frac{1485 \text{ kPa}}{8.314 (\text{kPa} \cdot \text{dm}^3 / \text{mol} \cdot \text{K}) \times 500 \text{ K}} \right]$$

$$= 0.1 \text{ mol/dm}^3$$

$$\epsilon = y_{A0} \delta = (0.28) \left(1 - \frac{1}{2} - 1 \right) = -0.14$$

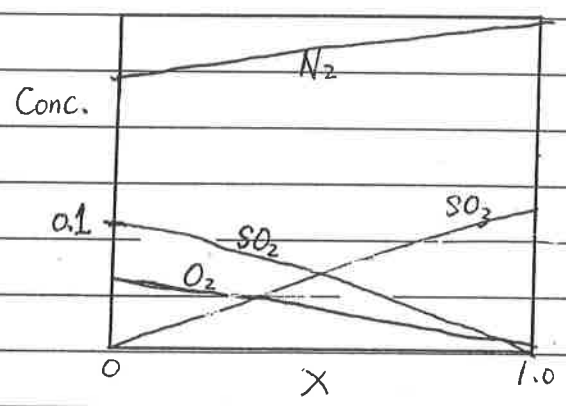
$$C_T = \frac{F_T}{V} = \frac{F_{T0}(1 + \epsilon X)}{V_0(1 + \epsilon X)} = C_{T0} = \frac{P_0}{RT_0} = 0.357 \frac{\text{mol}}{\text{dm}^3}$$

$$C_A = (0.1) \frac{1 - X}{1 - 0.14X}$$

$$C_B = (0.1) \frac{(0.54 - \frac{1}{2}X)}{(1 - 0.14X)}$$

$$C_C = (0.1) \frac{X}{(1 - 0.14X)}$$

$$C_I = (0.1) \frac{2.03}{1 - 0.14X}$$



if $\sqrt{200 \frac{\text{dm}^3}{\text{mol} \cdot \text{s}}}$

$$-r_A = k C_A C_B$$

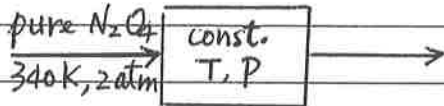
$$= k C_{A0}^2 \frac{(1 - X)(\theta_B - \frac{1}{2}X)}{(1 + \epsilon X)^2}$$

$$\frac{1}{-r_A} = \frac{0.5(1 - 0.14X)^2}{(1 - X)(0.54 - 0.5X)}$$

Ex 3-6 Equilibrium Conversion

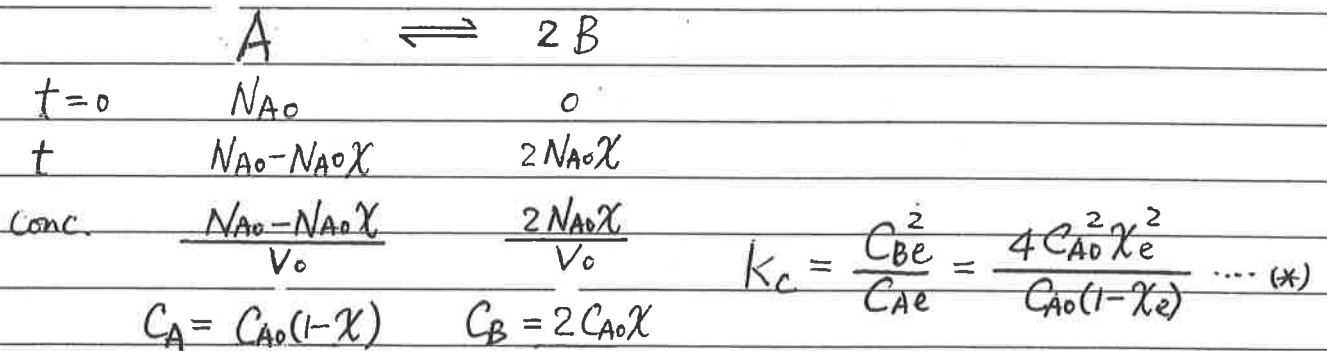
for rev. rxns, first calculate the equilibrium conv., 其餘與 irrev. 一樣

gas-phase rxn



- a) equili conv. of N_2O_4 in a const-V BR
- b) equili conv. of N_2O_4 in a flow reactor
- c) assume rxn is elementary, find $-r_A = f(x)$

a) const-V BR



need C_{A0} , $C_{A0} = \frac{y_{A0} P_0}{RT_0} = \frac{(1)(2 \text{ atm})}{(0.082 \frac{\text{atm} \cdot \text{dm}^3}{\text{mol} \cdot \text{K}})(340 \text{ K})} = 0.0717 \frac{\text{mol}}{\text{dm}^3}$

C_{A0}, K_c 代入 (*), by trial & error $\Rightarrow X_{eb} = 0.44$ *

使用 POLYMATH 亦是相同原理

b) flow system, const. T, P

$$v = v_0(1 + \varepsilon X)$$

$$\varepsilon = Y_{A0}\delta = (1)(2-1) = 1$$

$$\therefore C_A = F_A/v = \frac{F_{A0}(1-X)}{v_0(1+X)} = C_{A0} \frac{(1-X)}{(1+X)}$$

$$C_B = F_B/v = \frac{2F_{A0}X}{v_0(1+X)} = 2C_{A0} \frac{X}{1+X}$$

$$K_c = \frac{C_{Be}^2}{C_{Ae}} = \frac{4C_{A0}^2 \frac{\chi_e^2}{(1+\chi_e)^2}}{C_{A0} \frac{1-\chi_e}{1+\chi_e}} = \frac{4C_{A0}\chi_e^2}{(1-\chi_e)(1+\chi_e)}$$

將 K_c, C_{A0} 值代入 $\Rightarrow \chi_{ef} = 0.51$

$\chi_{ef} > \chi_{eb}$, 符合 Le Chatelier's principle, why?

c) Rate law $A \xrightleftharpoons[k_A]{k_A} 2B$

$$-r_A = k_A C_A - k_A C_B^2 = k_A \left[C_A - \frac{C_B^2}{K_c} \right]$$

flow system

$$-r_A = k_A \left[\frac{C_{A0}(1-X)}{1+X} - \frac{4C_{A0}^2 X^2}{K_c (1+X)^2} \right]$$

should check thermodynamic consistence

$$K_c = \frac{4C_{A0}\chi_e^2}{(1-\chi_e)(1+\chi_e)}$$

batch system

$$-r_A = k_A \left[C_{A0}(1-X) - \frac{4C_{A0}^2 X^2}{K_c} \right]$$

$\therefore -r_A = f(X)$ 會隨 reactor 不同而改變。