Can we at least reduce our work?

Species	Initial	Change per t	Final
A	N_{A0}	$-N_{A0}X_A$	$N_{A0}(1-X_A)$
B	$N_{B0}(=0)$	$C_{B0}vt - \frac{N_{A0}X_A b}{a}$	$N_{B0} + C_{B0}vt - \frac{N_{A0}X_A b}{a}$

$$\therefore \quad N_A = N_{A0}(1-X_A)$$

$$N_B = C_{B0}vt - \frac{N_{A0}X_A b}{a} \qquad (N_{B0}=0)$$

$$V = V_0 + vt$$

$$\therefore \quad C_A = \frac{N_A}{V} = \frac{N_{A0}(1-X_A)}{V_0 + vt}$$

$$C_B = \frac{C_{B0}vt - N_{A0}X_A(b/a)}{V_0 + vt}$$

$\therefore$ In the mole balance for species A:

$$\frac{dN_A}{dt} = -kC_A C_B V$$

$$\therefore \quad C_A v + (V_0 + vt)\frac{dC_A}{dt} = -kC_A C_B (V_0 + vt)$$

Let's not subst. $N_A = C_A V$ ⇒ just makes the math easier!

$$* \quad \frac{dN_A}{dt} = \frac{d}{dt}\left[N_{A0}(1-X_A)\right] = -N_{A0}\frac{dX_A}{dt}$$

$$* \quad C_A v + (V_0 + vt)\frac{d}{dt}\left[\frac{N_{A0}(1-X_A)}{V_0+vt}\right]$$

→ simplify (tedious math!) → $-N_{A0}\dfrac{dX_A}{dt}$

$$\therefore \quad \cancel{-}N_{A0}\frac{dX_A}{dt} = \cancel{-}k C_A C_B V$$

$$\therefore \quad N_{A0}\frac{dX}{dt} = k\,\frac{N_{A0}(1-X_A)\left(C_{B0}vt - \frac{N_{A0}X_A b}{a}\right)}{V_0+vt}$$

$$\boxed{\therefore \quad \frac{dX}{dt} = \frac{k(1-X_A)\left(C_{B0}vt - \frac{N_{A0}X_A b}{a}\right)}{V_0+vt}}$$

→ solve a single equation numerically

$$\therefore \quad \frac{X_{t_{i+1}} - X_{t_i}}{t_{i+1}-t_i} = \frac{k(1-X_{A_{t_i}})\left(C_{B0}vt_i - \frac{N_{A0}X_{A_{t_i}} b}{a}\right)}{V_0+vt_i}$$

Conclusions:

* Both approaches are correct

* You need numerical methods to solve the problem

* Conversion ⇒ 1 ODE

* Concentration ⇒ System of ODEs

The Algorithm

① Write mole balance

$\downarrow$

② Derive design equation

$\downarrow$

③ Account for changes in P, V & n

(we have not looked @ T yet)

$\downarrow$

④ Solve the system

* Implicit is the understanding that k is given

i.e. $-r_A = kC_A$ or $-r_A = kC_A^2$ etc.

* What if I don't tell you what k or the order of the reaction is?

$$aA + bB \longrightarrow cC + dD$$

Remember: you cannot make any assumptions regarding the order

$$-r_A = k\, C_A^{\alpha}\, C_B^{\beta}\, C_C^{\gamma}$$

↑ this is also possible

Remember the rate expression for HBr formation.

$$r_{HBr} = \frac{k_1 C_{H_2} C_{Br_2}^{1/2}}{1 + k_2 \frac{C_{HBr}}{C_{Br_2}}}$$

How does one find α, k etc.?

Step 1 : simplify the system

↓

Experimentally = take all reactants barring 1 in great excess

$$\therefore\ -r_A = k\, C_A^{\alpha}\, \underbrace{C_B^{\beta}\, C_C^{\gamma}}_{\text{take in large excess}}$$

$$\therefore \quad C_B^{\beta} C_C^{\gamma} \approx \text{constant}$$

$$\therefore \quad -r_A = k' C_A^{\alpha} \qquad \text{.... wait, } C_C?$$

For the [HBr] system:

Initially, when [HBr] is very small,

$$r_{HBr} = \frac{k_1 C_{H_2} C_{Br_2}^{1/2}}{1 + k_2 \underbrace{\left(\frac{C_{HBr}}{C_{Br_2}}\right)}_{\text{very small}}}$$

$$\therefore \quad r_{HBr_{ini}} \approx k_1 C_{H_2} C_{Br_2}^{1/2}$$

If we take H_2 in large excess, then

$$r_{HBr_{ini}} \approx k_1' C_{Br_2}^{1/2}$$

$$\therefore \quad -r_A = k' C_A^{\alpha}$$

But these rates are evaluated in a batch reactor.

General mole balance gives us:

$$\frac{dC_A}{dt} = r_A$$

$$\therefore \frac{dC_A}{dt} = -k' C_A^{\alpha}$$

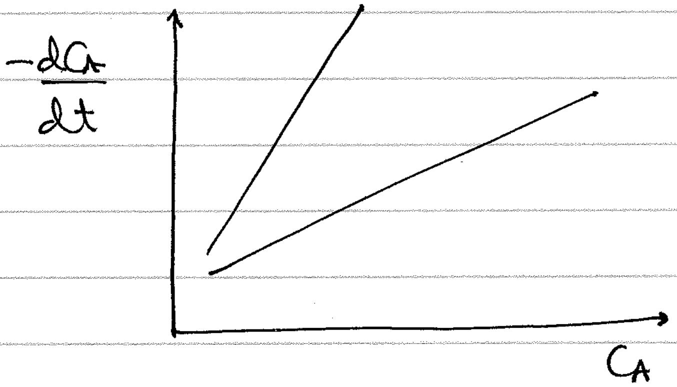
and $k' \approx k \times C_{B0}$

$$\ln\left(\frac{dC_A}{dt}\right) = \ln\left(-k' C_A^{\alpha}\right)$$

$$\boxed{\therefore \ln\left(-\frac{dC_A}{dt}\right) = \ln k' + \alpha \ln C_A}$$

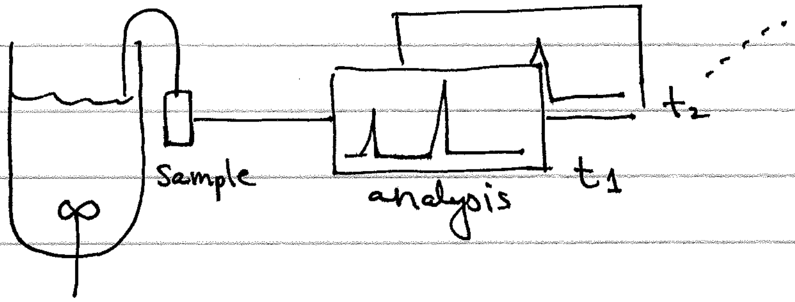
If I plot $\underbrace{-\frac{dC_A}{dt}}_{y\text{-axis}}$ versus $\underbrace{C_A}_{x\text{-axis}}$, $\alpha = \text{slope}$

$\ln k' = \text{intercept}$



We need to find $-\frac{dC_A}{dt}$ for the batch reactor

What are we measuring in experiments?



t	0	t_1	t_2	...
C_A	C_{A_0}	C_{A_1}	C_{A_2}	...

} we are collecting this

We need to calculate $-\frac{dC_A}{dt}$ from the data

<u>Numerical method recap:</u>

Area under the curve → crude rectangles
→ Trapezoidal Rule
→ Simpson's 1/3rd Rule
→ Simpson's 3/8th Rule

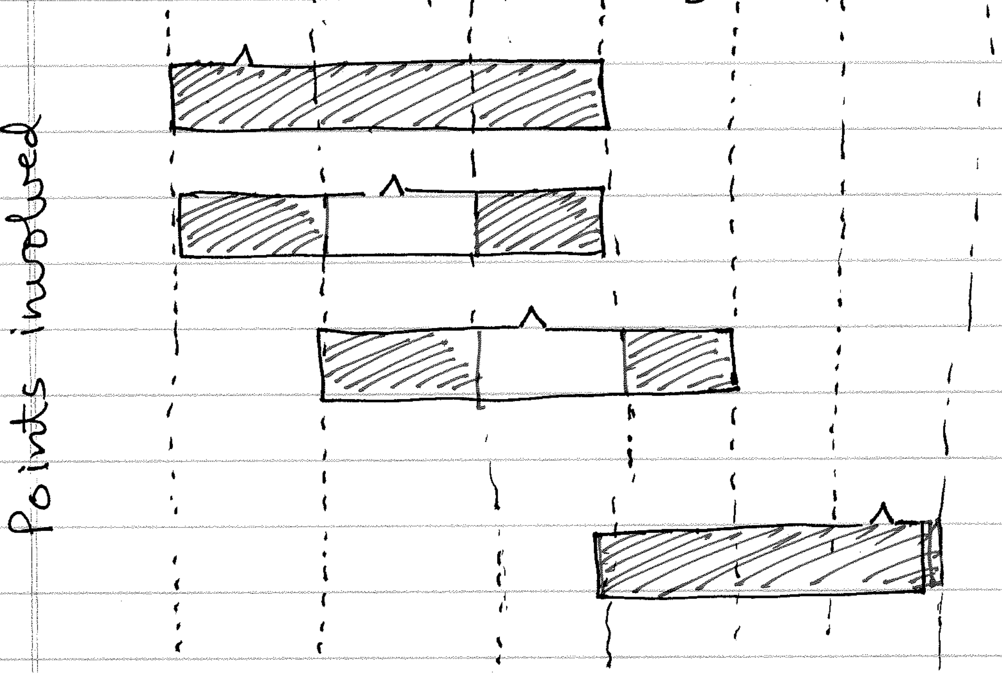
Solving system of ODEs → $\frac{dy}{dt} = f(y)$

$$\therefore y_{t_2} = y_{t_1} + (t_2 - t_1) f(y_{t_1})$$

Let's look @ the 3rd type of numerical estimation technique

↳ find differentials

Time	t_0	t_1	t_2	t_3	t_4	t_5	(time units)
Conc.	C_{A_0}	C_{A_1}	C_{A_2}	C_{A_3}	C_{A_4}	C_{A_5}	(conc. units)



first: $$\left(\frac{dC_A}{dt}\right)_{t_0} = \frac{-3C_{A_0} + 4C_{A_1} - C_{A_2}}{2(t_1 - t_0)}$$

internal: $$\left(\frac{dC}{dt}\right)_{t_1} = \frac{C_{A_2} - C_{A_0}}{2(t_2 - t_1)}$$

does not matter what time you take

↓

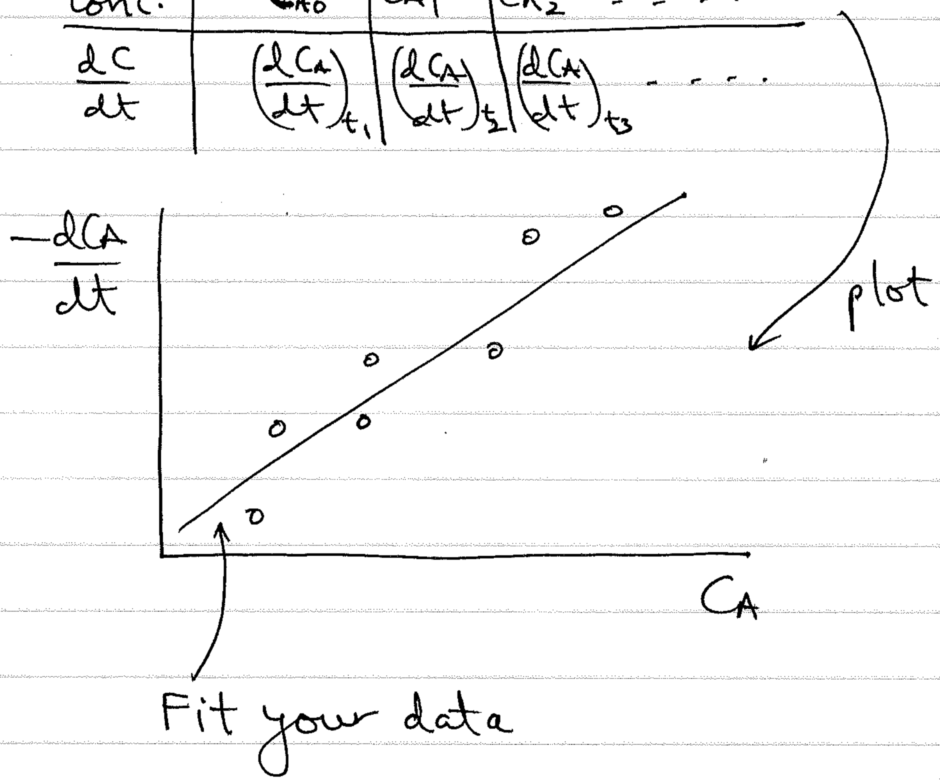
Make sure sampling is consistent

$$\left(\frac{dC}{dt}\right)_{t_2} = \frac{C_{A_3} - C_{A_1}}{2(\Delta t)}$$

last: $$\left(\frac{dC}{dt}\right)_{t_5} = \frac{C_{A_3} - 4C_{A_4} + 3C_{A_5}}{2\Delta t}$$

∴

Time	t_0	t_1	t_2	. . . .
Conc.	C_{A0}	C_{A1}	C_{A2}	- - - .
$\frac{dC}{dt}$	$\left(\frac{dC_A}{dt}\right)_{t_1}$	$\left(\frac{dC_A}{dt}\right)_{t_2}$	$\left(\frac{dC_A}{dt}\right)_{t_3}$	- - .



What happens if you want to fit the data manually?

→ statistics ≡ minimize the sum of the squares of the residuals!

→ very useful in fitting non-linear data

⇓

Michaelis-Menten (for eg.)

Graphical (integral) method:

Now, let us write out the general mole balance for a batch reactor:

$$\frac{dC_A}{dt} = r_A \quad \text{.... generic equation}$$

$$\underbrace{\frac{dC_A}{dt} = kC_A}_{1^{st}\text{ order}} \;, \quad \underbrace{\frac{dC_A}{dt} = kC_A^2}_{2^{nd}\text{ order}} \;, \quad \underbrace{\frac{dC_A}{dt} = kC_A^3}_{3^{rd}\text{ order}}$$

1st order case: $\frac{dC_A}{dt} = -kC_A$

$$\frac{dC_A}{C_A} = -k\,dt$$

$$\text{Also} \quad C_A(t=0) = C_{A0}$$

$$\therefore \left[\ln C_A\right] = -kt + C$$

$$\ln C_{A0} = C$$

$$\therefore \ln C_A = -kt + \ln C_{A0}$$

$$\boxed{\therefore \ln\left(\frac{C_A}{C_{A0}}\right) = -kt \quad \text{....} \; C_A < C_{A0}}$$