1.1 & 1.2 Reaction rate & mole balances

Let us begin our mathematical analysis of the system with the general mole balance.

$$\begin{bmatrix}\text{Rate of}\\\text{accumulation}\\\text{of species}\end{bmatrix} = \begin{bmatrix}\text{Rate of}\\\text{inflow of}\\\text{species}\end{bmatrix} - \begin{bmatrix}\text{Rate of}\\\text{outflow}\\\text{of species}\end{bmatrix} + \begin{bmatrix}\text{Rate of}\\\text{generation}\\\text{of species}\end{bmatrix} - \begin{bmatrix}\text{Rate}\\\text{of}\\\text{consumpt}^{n}\\\text{of spec}\end{bmatrix}$$

mole balance ⇒ units are $\frac{\text{moles}}{\text{time}}$

also called 'rate of change of species'

$$\underset{\text{rate}}{\left\{\frac{d\overset{\text{moles}}{N}}{dt}\right.} = \underbrace{F_{in} - F_{out}}_{\substack{\text{for macroscopic}\\\text{systems} \equiv \text{flow}}} + \underbrace{\overbrace{R_{gen}}^{\text{TB uses } G} - R_{cons}}_{\substack{\text{fn. of reaction}\\\text{rates}}}$$

{for molecular analysis ≡ flux

mass transfer

For reactants:

$$\frac{dN^R}{dt} = -R_{cons}$$

Reactants diminish over time

$\therefore$ $\frac{dN^R}{dt}$ is negative

$\therefore$ $-R_{cons}$ is negative

$\therefore$ R_{cons} is positive

$$R_{cons} = (-r_R)\,V \quad \text{.... } \underline{\underline{\text{convention}}}$$

$\therefore$ $(-r_R) \equiv$ positive

this convention confuses a lot of people

The convention:

$$\left.\begin{array}{l}\text{Reactants, rate} = -r \\ \text{Products, rate} = r\end{array}\right\} \text{both are positive}$$

Signs must be adjusted in the mole balance.

Consider: $A \longrightarrow B$

What does $-r_A$ mean?

$-r_A \equiv$ rate of reaction that consumes A

Generally,

$$\begin{Bmatrix}\text{Reaction}\\ \text{rate}\end{Bmatrix} = \underbrace{\begin{Bmatrix}\text{Reaction}\\ \text{rate}\\ \text{constant}\end{Bmatrix}}_{\text{or simply `rxn. const.'}} \times f(\text{conc.})$$

How does this term come about?

$$\boxed{\text{Rate} \propto \text{Driving force}}$$

e.g. speed of car $\propto$ engine power

population growth $\propto$ # of fertile individuals

In $A \longrightarrow B$

If $-r_A \propto C_A$ .... the more A, the more B is produced

$$\therefore \overbrace{\underbrace{-r_A}_{\substack{\text{+ve number (imp.)} \\ \left\{\frac{\text{moles}}{\text{vol. time}}\right\}}} = \underbrace{k}_{\substack{\text{rate constant} \\ \left(\text{units here} \equiv \frac{1}{\text{time}}\right) \\ = A\exp\left(-\frac{E_a}{RT}\right)}}\, C_A}^{\text{rate expression}} \longrightarrow \text{conc. of A} \left(\frac{\text{moles}}{\text{vol.}}\right)$$

The exponent of C_A is called the order of the reaction.

$-r_A = k\,C_A$ ..... 1st order reaction

$-r_A = k\,C_A^2$ ..... 2nd order reaction

The number of species involved in the rate expression gives us the 'molecularity' of the reaction

1 species ≡ unimolecular

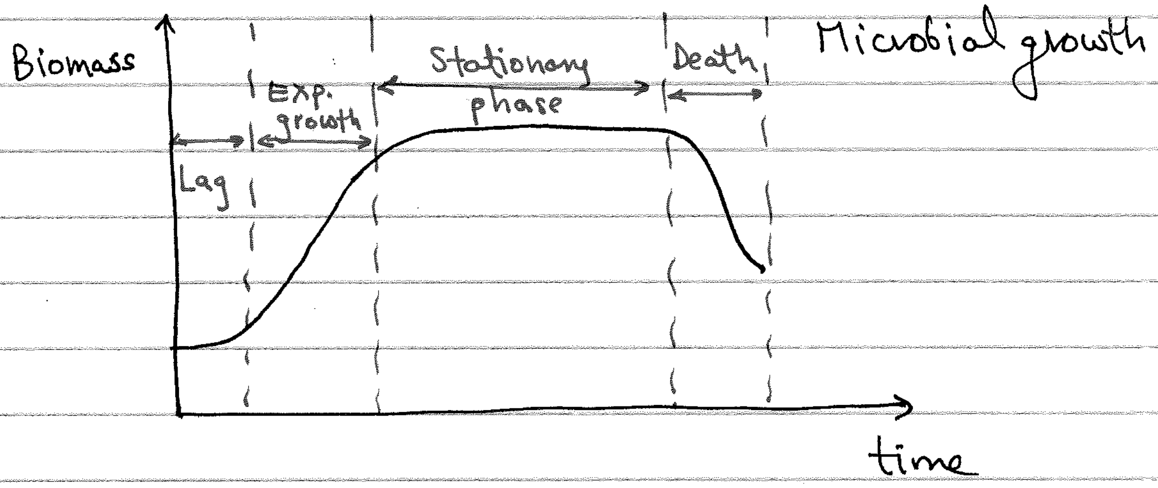
2 species ≡ bimolecular

$\therefore \quad -r_A = kC_A^2$ .... 2nd order unimolecular reaction

What happens if the rate of reaction is constant?

i.e. $-r_A = k$ .... 0th order reaction

Can you think of a 0th order reaction?



Stationary phase 'growth' is 0th order.

* 0th order reaction rates are common in heterogeneous catalytic reactions where the catalytic sites are saturated ('plateau' effect)

For $A + B \longrightarrow C$

The reaction rate might depend on C_A & C_B

Here,
$$-r_A = \underbrace{k \underbrace{C_A}_{\text{1st order in A}} \underbrace{C_B}_{\text{1st order in B}}}_{\text{2nd order overall}}$$

This rxn. is a 2nd order, bimolecular rxn.

Similarly,
$$\underbrace{-r_A = k C_A^3 C_B}_{\text{4th order overall, bimolecular rxn.}}$$

How does one know what the order of the reaction is?

By <u>experimentation</u> ⇒ we will learn this later in the course

<u>No one</u> can predict what the rate expression is without experimentation.

Experimentation identifies all the variables that influence the reaction rate.

Have you heard of World Cup Widows?

Generally,

$$\begin{pmatrix}\text{rate of} \\ \text{population} \\ \text{growth}\end{pmatrix} \propto \begin{pmatrix}\text{\# of sexually} \\ \text{active, fertile} \\ \text{individuals}\end{pmatrix}$$

But this is not true during World Cups?

The same is also true at the molecular level.

Eg. $H_2 + Br_2 \rightleftharpoons 2HBr$

stoichiometry !!

$$-r_{H_2} = -r_{B_2} = \left(\frac{1}{2}\right) r_{HBr} = \left(\frac{1}{2}\right)\frac{k_1 [H_2][Br_2]^{1/2}}{1 + k_2\left(\frac{[HBr]}{[Br_2]}\right)}$$

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

Stoichiometry is important.

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

$$-r_{H_2} = -r_{Br_2} = \frac{1}{2} r_{HBr}$$

In general,

$$aA + bB \rightarrow cC + dD$$

$$A + \left(\frac{b}{a}\right)B \rightarrow \left(\frac{c}{a}\right)C + \left(\frac{d}{a}\right)D$$

$$-r_A = \frac{-r_B}{(b/a)} = \frac{r_C}{(c/a)} = \frac{r_D}{(d/a)}$$

"For every mole of A that is consumed, (b/a) moles of B are consumed"

↳ Say it out loud!

How do we know the rate expression even after experimentation?

Experiments help us identify the sequence of steps in a reaction.

→ Remember Haber-Bosch

The effective rate of the process is the rate of the slowest step.

→ rate-limiting (or rate-determining step)

Real-life example:

Student writes exam	→	Professor grades exam	→	UBC posts grade
3 hours		let's not get into this 😛		1 hour

The professor is the 'rate-limiting' step

The overall rate & not time, therefore, will be the rate at which he grades your exams.

* We will consider an example in the 1st tutorial session

TYPES OF REACTORS

Let's return to our general mole balance:

For species i,

$$\frac{dN_i}{dt} = F_{in}^{i} - F_{out}^{i} + R_{gen}^{i} - R_{cons}^{i}$$

Assume no flows in/out of system

$$\boxed{\therefore \quad \frac{dN_i}{dt} = R_{gen}^{i} - R_{cons}^{i}} \Longrightarrow$$ Governing equation of a batch reactor

Assume the system is homogeneous (well-mixed)

e.g. of batch reactor ≡ cooking

80% of reactors in pharma industry are batch reactors

Consider an example

$$aA \longrightarrow bB$$

$$A \longrightarrow (b/a)\, B$$

For A: $$\frac{dN_A}{dt} = R_{gen}^{A} - R_{cons}^{A}$$

$$R_{gen} = \underset{\substack{\text{reaction}\\\text{rate}}}{\underset{\swarrow}{r_{gen}}} \cdot \underset{\substack{\text{volume}\\\text{of}\\\text{system}}}{\underset{\searrow}{V}}$$

$$\left[\frac{\text{moles}}{\text{time}} = \frac{\text{moles}}{\text{vol.} \times \text{time}} \cdot \text{volume}\right] \Longrightarrow \text{units are very important}$$

$\therefore$ r_{gen} has units of $\frac{\text{conc.}}{\text{time}}$ (so does $r_{cons.}$)

Products $\equiv$ r_{gen}

Reactants $\equiv$ $r_{cons.}$

Mole balance for products:

$$\frac{dN^P}{dt} = F_{in}^P - F_{out}^P + R_{gen} - \cancelto{\text{NO}}{R_{cons.}}$$

Assume the system is 'closed' = no flows

$$\frac{dN^P}{dt} = R_{gen}$$

$\left\{\begin{array}{l}\text{Remember:}\\ R_{gen} = r_{gen} \cdot V\end{array}\right\}$

Rember: if reactant, $R_{cons} = (-r)\cdot V$

$$\therefore \frac{dN_A}{dt} = -(-r_A)V$$

$$\boxed{\therefore \frac{dN_A}{dt} = r_A V} \Longrightarrow$$ Governing equation of a batch reactor

Assume reaction is first order in A

$$\therefore -r_A = kC_A$$

Assume reaction volume is <u>unchanging</u>

it doesn't always need to be this way
e.g. balloon

$$\therefore \frac{d(C_A V)}{dt} = r_A V$$

$$\boxed{\therefore \frac{dC_A}{dt} = -kC_A}$$ ..... 1st order ODE

Pause & check if the equation makes sense.

How do find C_B?

$$A \longrightarrow (b/a)\,B$$

For every mole of A that reacts, (b/a) of B is formed

$$\therefore \quad \frac{dC_A}{dt} = -kC_A$$

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

$$\therefore \quad \ln C_A = -kt + \underset{\substack{\uparrow \\ \text{const.}}}{a}$$

At $t = 0$, $C_A = C_{A_0}$

$$\therefore \; a = \ln C_{A_0}$$

$$\therefore \quad \ln C_A = \ln C_{A_0} - kt$$

$$\therefore \quad \ln\left(\frac{C_{A_0}}{C_A}\right) = kt$$

$$\frac{C_{A_0}}{C_A} = \exp(kt)$$

$$C_A = C_{A_0} \exp(-kt) \quad \ldots\ldots \quad C_A(t)$$

∴ moles A reacted = $C_{A0} - C_A$

∴ moles of B formed = $\left(\frac{b}{a}\right)\left(C_{A0} - C_A\right)$

$$\therefore \quad C_B = \frac{b}{a}\left[C_{A0}\left(1 - \exp(-kt)\right)\right]$$

$$\left.\begin{aligned} C_A &= C_{A0} \exp(-kt) \\ C_B &= \frac{b\,C_{A0}}{a}\left[1 - \exp(-kt)\right] \\ \text{As } t \to \infty, \quad C_B &= \frac{b\,C_{A0}}{a} \end{aligned}\right\} \text{Solution for constant volume case}$$

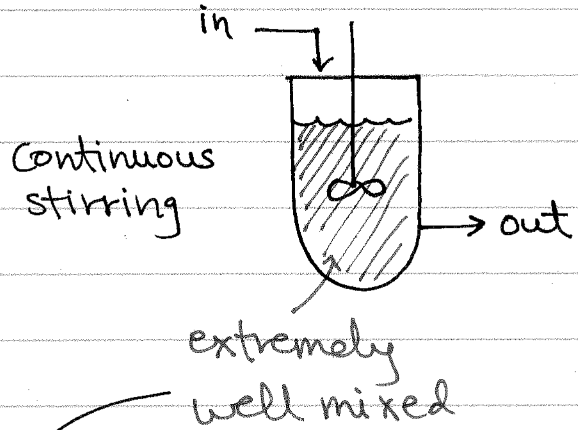
What were the important assumptions?

① no flows

② reaction mixture well-mixed

③ stoichiometry } used to solve ODEs
④ const. volume }

Now, consider a reactor with flows.



Volumetric flows

$\dot{V}_{in}$ = vol/time

$\dot{V}_{out}$ = vol/time

Think of a <u>red dye drop</u> falling into this reactor & the entire reacting mixture turning red <u>instantaneously</u>

Rxn:

$aA \longrightarrow bB$

$-r_A = kC_A$

Let concentration of A in inlet stream be C_{A_0}

Since the reactor is extremely well mixed,

$C_A \equiv$ concentration in reactor
↳ also concentration in outlet strea

So what happens to A inside the reactor?