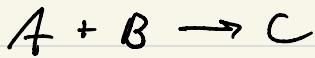


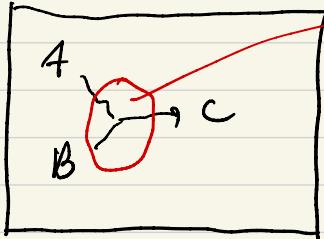
Essential Kinetics

The thermodynamics deals with endpoints and is summable.

Kinetics deals with how we get from A + B. Generally impossible to infer a priori, mutable



$$\text{rate} = \frac{\# \text{events}}{\text{time} \cdot \text{s.t.}}$$



What's going on here could be complicated + difficult to infer

where s.t. could be volume, area, mass catalyst, ...

Difficult to observe individual events. Rather, typically observe effect on amounts of A, B, C

Connection to stoichiometry

A disappearing equivalent to C appearing event A = - event C

In general define a rate r s.t.

$$r_j = z_j r$$

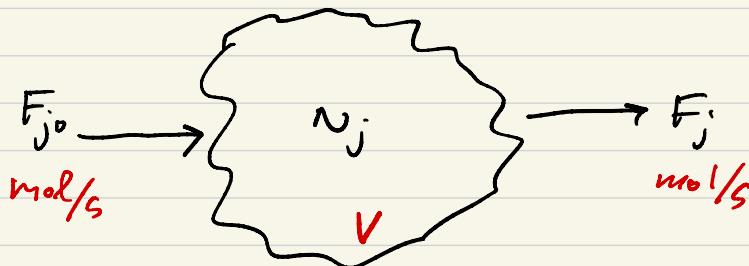
r thus becomes independent of stoic factor.

Will often talk about forward & reverse rate.

$$r_f = r_c \quad r_r = r_A = r_B$$

$$r_f - r_r = r_{\text{net}} = 0 \text{ @ equilibrium}$$

Relation to mass balances



$$\frac{dn_j}{dt} = F_{j0} - F_j + \int r_j dV$$

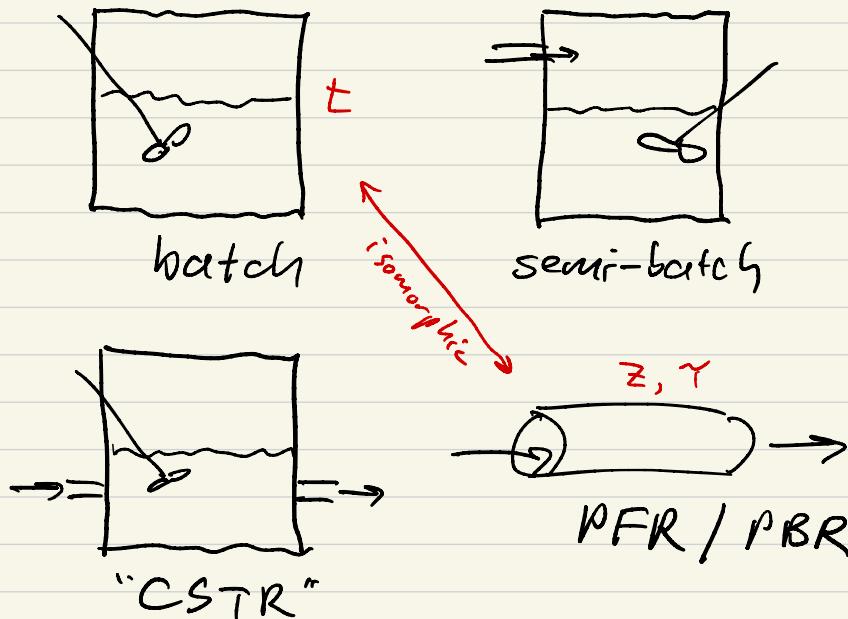
accum in out gen/cons.

$$\text{single rxn} \quad = F_{j0} - F_j + z_j \int r dV$$

multiple
reactions

$$= F_{j_0} - F_j + \sum_i \gamma_{ij} \int r_i dV$$

simple reactors



In batch, closed system, reduces to

$$\frac{dN_j}{dt} = \gamma_j \int r dV$$

If well-mixed / homogeneous

$$\frac{dN_j}{dt} = \gamma_j r V$$

- or -

$$\frac{dC_j}{dt} = \gamma_j r$$

$$c_j = c_{j0} + \gamma_j \xi \quad \xi \text{ volume normalized}$$

$$\boxed{\frac{d\xi}{dt} = r}$$

r expression cannot be written down from stoich, in general.

Rate $r = f(T, P, c_j)$ algebraic

c_j most commonly written as C_j or P_j and can be represented in terms of ξ .

Common observations

1) r is a decreasing function of ξ reactions generally slow as reactants are consumed

2) r can often be factored:

$$r = k(T) f(T, P, c_j)$$

$$-or- = k(T) f(c_j)$$

T dep. comp dependence

3) $k(T)$ called the rate constant,
 is generally a strong function of
 T , and often follows Arrhenius
 form

$$k(T) = A e^{-E_a/RT}$$

A : pre factor

E_a : activation energy

Can be written $\ln k = \ln A - \frac{E_a}{RT}$

Recalls equilibrium expression

4) $f(c_j)$ can often be written as
 a polynomial factor in c_j / p_j

$f = c_A^a c_B^b$ in general a & b are
not the stoichiometric
 coefficients

a : "order" in a , fractional or
 $a+b$: overall order integer

No guarantee of this form

$$\text{eq } k_1 C_A^2 / (1 + k_2 C_B)$$

2nd order in A
indeterminant in B

Units: rates always $\frac{\#}{\text{L} \cdot \text{s}}$. Units
on rate expression components must
match.

apparent order + activation energy

$$\alpha_{app} = \left(\frac{\partial \ln r}{\partial \ln C_A} \right)_{C_j=A,T} \quad \text{in general}$$

$$r = k C_A \quad \ln r = \ln k + \ln C_A \quad \alpha_{app} = 1$$

$$r = \frac{k_1 C_A^2}{1 + k_2 C_B} \quad \left(\frac{\partial \ln r}{\partial C_A} \right) = 2 = \alpha_{app}$$

$$k_2 C_B \ll 1 \quad \left(\frac{\partial \ln r}{\partial C_B} \right) = 0 = b_{app} \quad \} \text{varies w/C_B}$$

$$k_2 C_B \gg 1 \quad \left(\frac{\partial \ln r}{\partial C_B} \right) = 1 = b_{app}$$

Similarly

$$E_{a,app} = -R \left(\frac{\partial \ln r}{\partial' T} \right)$$

$$r = k C_A = A e^{-E_a/RT} C_A$$

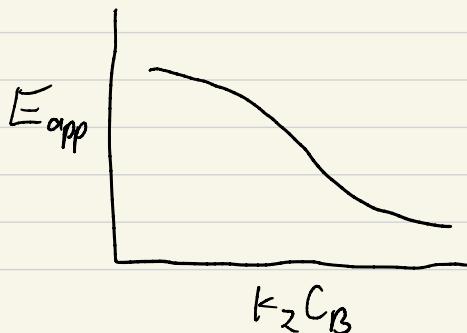
$$\ln r = \ln A - E_a/RT + \ln C_A$$

$$\frac{\partial \ln r}{\partial' T} = -E_a/R$$

$$r = \frac{k_1 C_A^2}{1 + k_2 C_B}$$

$$k_2 C_B \ll 1 \quad \left(\frac{\partial \ln r}{\partial' T} \right) = \left(\frac{\partial \ln k_1}{\partial' T} \right) = -\frac{E_{a,app,1}}{R}$$

$$k_2 C_B \gg 1 \quad \left(\frac{\partial \ln r}{\partial' T} \right) = \left(\frac{\partial \ln k_1}{\partial' T} \right) - \left(\frac{\partial \ln k_2}{\partial' T} \right) \\ = -\frac{E_{app,1}}{R} + \frac{E_{app,2}}{R}$$



Common rate laws

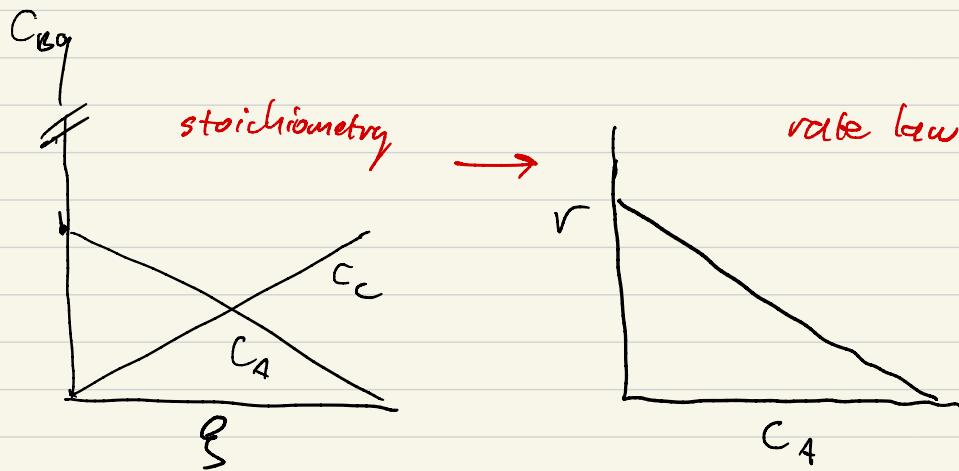
1st order



(perhaps B in great excess)

constant V, batch reactor

$$C_A = C_{A0} - \xi \quad C_B = C_{B0} - \xi \quad C_C = C_{C0} + \xi$$



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

$$\frac{dC_B}{dt} = -k C_A$$

$$\frac{dC_C}{dt} = k C_A$$

Initial value problem. Integrate from \$t_0, C_{A0}, C_{B0}, C_{C0}\$ to \$t\$

$$\frac{dC_A}{dt} = -k C_A \rightarrow C_A = C_{A0} e^{-kt}$$

$$\frac{dC_B}{dt} = -k C_{A0} e^{-kt} \rightarrow C_B = C_{B0} + C_{A0} (e^{-kt} - 1)$$

$$C_B = C_{B0} + C_{A0} \int_0^t e^{-kt} dt$$

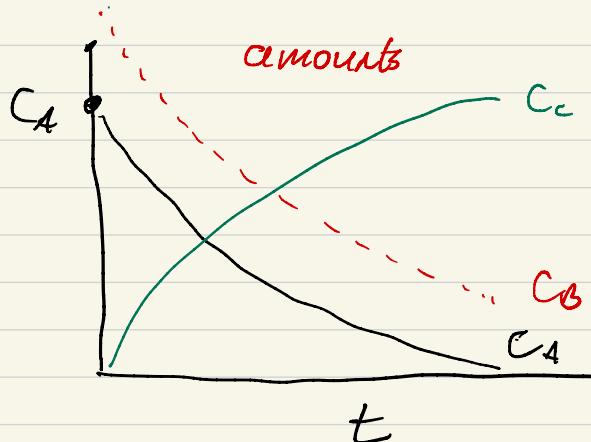
$$C_B - C_{B0} = C_{A0} e^{-kt} \Big|_{t=0}^t = C_{A0} (e^{-kt} - 1)$$

$$C_B = C_{B0} + C_{A0} (e^{-kt} - 1)$$

double check

$$C_B = C_{B0} - \xi = C_{B0} - C_{A0} + C_A$$

$$\frac{dC_C}{dt} = k C_{A0} e^{-kt} \rightarrow C_C = C_{C0} + C_{A0} (1 - e^{-kt})$$



Can equivalently solve in ξ or X

$$\frac{dC_A}{dt} = -kC_A \Rightarrow -\frac{d\xi}{dt} = -k(C_{A0} - \xi)$$

$$\frac{d\xi}{dt} = k(C_{A0} - \xi)$$

$$\int \frac{d\xi}{C_{A0} - \xi} = \left[kt - \ln(C_{A0} - \xi) \right]_0^\xi = kt$$

$$- \ln(C_{A0} - \xi) + \ln C_{A0} = kt$$

$$\frac{C_{A0} - \xi}{C_{A0}} = e^{-kt}$$

$$\xi = C_{A0}(1 - e^{-kt})$$

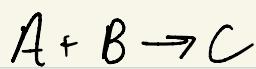
$\frac{1}{2}$ - life

time for C_A to reach $\frac{1}{2}$ initial value

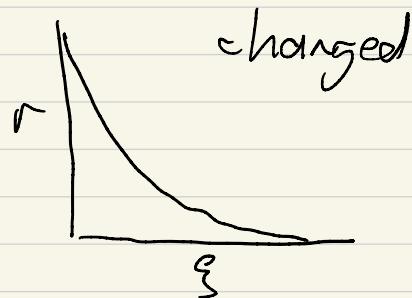
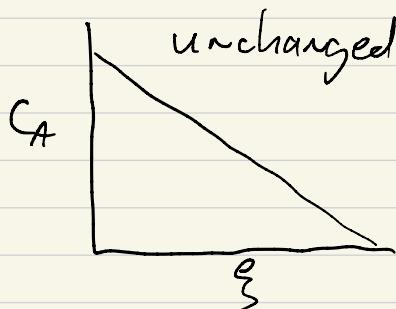
$$\frac{C_A}{C_{A0}} = \frac{1}{2} = \frac{C_{A0} e^{-kt/2}}{C_{A0}}$$

$$\Rightarrow t_{1/2} = \frac{\ln 2}{k}$$

independent
of C_{A0}

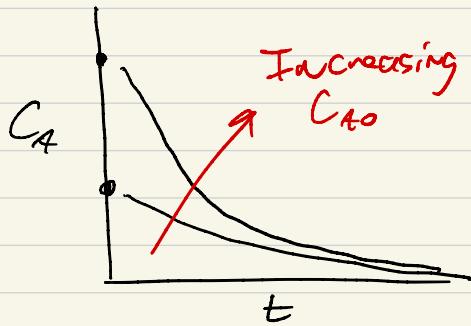


$$r = k C_A^2 \quad \text{2nd order}$$



$$\frac{dC_A}{dt} = -k C_A^2 \Rightarrow \frac{1}{C_A} = \frac{1}{C_{A0}} + k t$$

$$\Rightarrow C_A = C_{A0} \cdot \frac{1}{1 + k t C_{A0}}$$



$$C_A = C_{A0}/2$$

$$\frac{1}{2} = \frac{1}{1 + k t_{1/2} C_{A0}}$$

$$t_{1/2} = 1/k C_{A0}$$



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

How to solve?

- Use stoichiometry to relate C_B to C_A

$$C_A = C_{A0} - \xi \quad C_B = C_{B0} - \xi = C_{B0} - C_{A0} + C_A$$

analytical

- rewrite in terms of ξ

$$\frac{d\xi}{dt} = r = k (C_{A0} - \xi)(C_{B0} - \xi)$$

Z_1 $\frac{C_B/C_{B0}}{C_A/C_{A0}} = e^{-(C_{A0} - C_{B0})kt}$

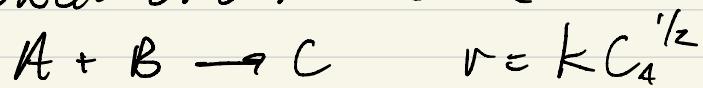
- solve simultaneously, numerically

numerical
integrate

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

$$\frac{dC_B}{dt} = -k C_A C_B$$

Fractional order? Sure!



$$\frac{dC_A}{dt} = -k C_A^{1/2}$$

$$\frac{dC_A}{C_A^{1/2}} = -k dt$$

$$2 C_A^{1/2} \left[\begin{matrix} C_A \\ C_{A0} \end{matrix} \right] = -kt$$

$$C_A^{1/2} = C_{A0}^{1/2} + e^{-kt/2}$$

did I do
that right?

$$t_{1/2} \stackrel{?}{=} \left(\frac{C_{A0}}{2} \right)^{1/2} = C_{A0}^{1/2} + e^{-kt_{1/2}/2}$$

$$C_{A0}^{1/2} \left(\frac{1}{\sqrt{2}} - 1 \right) = e^{-kt_{1/2}/2}$$

$$\frac{1}{2} \ln C_{A0} + \ln \left(\frac{\sqrt{2} - 1}{\sqrt{2}} \right) = kt_{1/2}/2$$

$$t_{1/2} = \frac{1}{k} \left(\ln C_{A0} + 2 \ln \left(\frac{\sqrt{2} - 1}{\sqrt{2}} \right) \right)$$

yeck!

Variable volume

Rate laws are natural fractions of concentration ("/_V).

If volume varies along course of reaction, must account for in mass balances.

$$C_j = \frac{n_j(\ell)}{V} \rightarrow \frac{n_j(\ell)}{V(\ell)}$$

$$V = \sum_j n_j \bar{v}_j(T, P, n_j)$$

\bar{v} (partial molar volume)

liquid, solid \sim constant

gas - EOS

$$\text{ideal} \quad \bar{v}_j = \frac{RT}{P}$$

$$V(\ell) = \frac{RT}{P} \sum_j (n_{j0} + \gamma_j \ell)$$

$$= \frac{RT}{P} (n_{\text{tot}, 0} + \underbrace{\left[\sum_j \gamma_j \right] \ell}_{\Delta \gamma_j})$$

rate laws from experiment

Goals

- extract rate parameters
- infer form of rate law

Methods

- differential methods

- fit $r = f(C_A)$
- requires observation of r
- $\Delta C_j / \Delta t$ in batch
- $\Delta C_j / \Delta \tau$ in flow

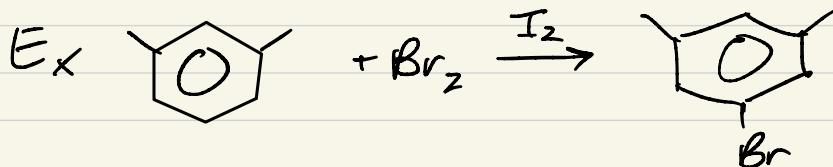
- integral methods

- model $C_j = f(C_j, t)$

- obs 1/2 lives

Differential

(see course outline)



17°C, xylene solvent

$$r = f(T, C_x, C_{Br_2}, C_{I_2})$$

isothermal $\rightarrow T$ constant

xylene solvent $\rightarrow C_x$ constant

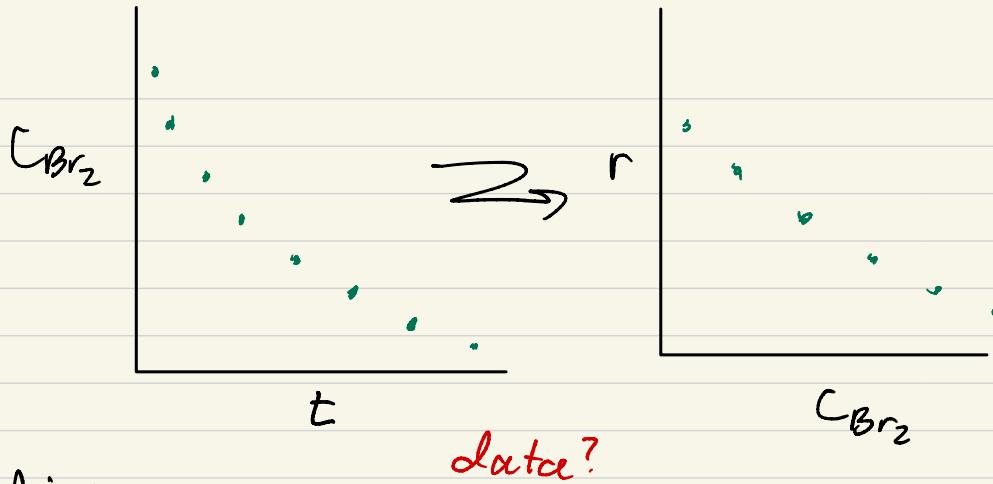
method of isolation

I₂ catalyst $\rightarrow C_{I_2}$ constant

$$\rightsquigarrow r = f(C_{Br_2})$$

How to observe C_{Br_2} ??

- spectrophotometric
- sampling



finite difference

$$r \left(\frac{C_{Br_2}(t_2) - C_{Br_2}(t_1)}{\Delta t} \right) \approx \frac{C_{Br_2}(t_2) - C_{Br_2}(t_1)}{t_2 - t_1}$$

n.p. ediff fd

- or - two sided

n.p. gradient

Postulate rate law

$$r = k C_{Br_2}^\alpha$$

linearize



$$\ln r = \ln k + \alpha \ln C_{Br_2}$$

$$b + m x$$

Or non-linear regression

Power is possibility to fit to complicated forms!

$$r = k C_{B_{I_2}}^\alpha C_{I_2}^\beta$$

$$\ln r = \ln k + \alpha \ln C_{B_2} + \beta \ln C_{S_2}$$

$$- \text{OR} -$$

$$V = \frac{k C_{Bz_2}^{\alpha} C_{I_2}^{\beta}}{1 + k' C_{x_{Bz}} \leftarrow \text{inhibition}}$$

Non-linear fit gives

$$k = 0.085 \text{ } M^{\frac{2}{3}} s^{-1} \quad \alpha = 1.45$$

integral approach

Same xylylene data

Non-linear fit suggests $r = k C_{Br_2}^{1.5}$

$$\text{Try rate} = k C_{Br_2}^{1.5} = - \frac{d C_{Br_2}}{dt}$$

$$\Rightarrow \frac{1}{C_{Br_2}^{1/2}} = \frac{1}{C_{Br_2,0}^{1/2}} + \frac{1}{2} k t$$

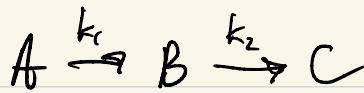
Could linearize data, $\frac{1}{C_{Br_2}^{1/2}}$ vs t
and do linear regression.

$$- \text{or} - \quad C_{Br_2}^{1/2} = \frac{2 C_{Br_2,0}^{1/2}}{2 + k t C_{Br_2,0}^{1/2}}$$

+ non-linear fit.

Gives excellent fit, same k

Don't have noise introduced by differentiating.



$$\frac{dC_A}{dt} = -k_1 C_A \quad \Rightarrow \quad C_A = C_{A0} e^{-k_1 t}$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \quad \Rightarrow \quad C_B = C_{B0} e^{-k_2 t}$$

$$\frac{dC_C}{dt} = k_2 C_B + C_{A0} \frac{k_1}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

$$C_C = C_{C0} + C_{A0} - C_A + C_{B0} - C_B$$

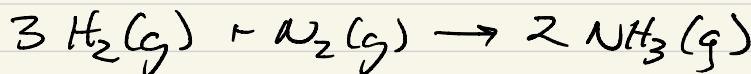
method of initial rates

A differential method

Rather than track rate change over the course of a reaction, set conditions & observe rate @ $t \approx 0$.

Semi-equivalent to a differential reactor.

ex Haber process



const T, V reactor

	$P_{\text{H}_2,0}$	$P_{\text{N}_2,0}$	$-\frac{dP}{dt}$ (torr)
1	100	1.00	0.010
2	200	1.00	0.040
3	400	0.50	0.080

$$\text{rate} = k P_{\text{H}_2}^a P_{\text{N}_2}^b$$

$$\left. \begin{array}{l} N_{NH_3} = 2\% \\ N_{H_2} = N_{H_2O} - 3\% \\ N_{N_2} = N_{N_2O} - \% \end{array} \right\} N_{tot} = N_{tot,0} - 2\%$$

$$-\frac{dP}{dt} = -\frac{RT}{V} \frac{dN}{dt} = \frac{2RT}{V} \frac{d\%}{dt}$$

\propto rate

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k}{k} \left(\frac{200}{100} \right)^a \left(\frac{1}{1} \right)^b$$

$$4 = 2^a \Rightarrow a=2$$

$$\frac{\text{rate}_3}{\text{rate}_2} = \frac{k}{k} \left(\frac{400}{200} \right)^2 \left(\frac{0.5}{1} \right)^b$$

$$2 = 4 \left(\frac{1}{2} \right)^b \Rightarrow b=1$$

$$r = k P_{H_2}^2 P_{N_2}$$

method of half-lives

integral method, best adapted
to 'simple rate' laws

$$0^{\text{th}} \text{ order} \quad t_{1/2} = \frac{1}{2} \frac{C_{A_0}}{k}$$

$$1^{\text{st}} \quad t_{1/2} = \frac{\ln 2}{k}$$

$$2^{\text{nd}} \text{ order} \quad t_{1/2} = \frac{1}{k C_{A_0}}$$