

Kinetics

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

$$\frac{\Delta n_A}{-a} = \frac{\Delta n_B}{-b} = \frac{\Delta n_C}{+c} = \frac{\Delta n_D}{+d}$$

extent of Rx: ξ

def: $\Delta \xi = \frac{\Delta n_A}{\nu_A}$

ν_A = stoichiometric number
for any species A

(-ve for reactants)

(+ve for products)

Rate of reaction:

def: $r = \frac{d\xi}{dt}$

def: $r = \frac{1}{\nu_A} \frac{dn_A}{dt}$

BUT n_A is an extensive property
↳ depends upon system size
[need redefinition]

⇒ divide by volume

$$r = \frac{1}{\nu_A} \frac{dn_A}{dt} = \frac{1}{\nu_A} \frac{d[A]}{dt}$$

- rate of given Rx must be independent of the species monitored
- rate has to be a transferable number
↳ independent of sys size
[intensive quantity]

Concentration dependence of rate

for $A + B \rightarrow C + D$

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Experimentally:

$$r = k[A]^\alpha[B]^\beta$$

rate constant
(strictly coeff)

α : order w.r.t. A } $\alpha + \beta$ = overall order
 β : order w.r.t. B }

Molecularity:

of reactants involved in the
written Rx



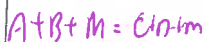
2

bimolecular



1

unimolecular



3

termolecular

★

using (=) for an overall strict Rx
→ for an elementary Rx



$$r = k[A]^\alpha[B]^\beta$$

✗ ✗ make this assumption for an overall Rx

Expt. Kinetics

→ to characterise R_x kinetics

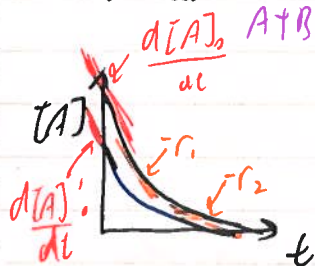
measure conc. rather than rate
generally:

1. Start R_x (t=0)
2. Measure property as f(t)
3. Convert property to reactant or R

product conc. as f(t)

4. Analyse kinetic data

Initial rates method



a.) can measure from $\frac{d[A]}{dt}|_{t=0} = r_0$
 $r_0 = -\text{gradient}$
 $r_0 = k[A]_0^\alpha [B]_0^\beta$

b.) 2nd expt: w/ $[A]_0$
 & const $[B]_0$

$$r_0' = -\text{gradient} = k[A]_0'^\alpha ([B]_0)^\beta$$

getting ratio:

$$\frac{r_0}{r_0'} = \left[\frac{[A]_0^\alpha}{[A]_0'^\alpha} \right]$$

$$= \left[\frac{[A]_0}{[A]_0'} \right]^\alpha$$

∴ measuring r_0 & r_0' for known $[A]_0$ & $[A]_0'$ (or known ratios) gives alpha

⇒ repeat by changing $[B]_0$ to get β

if know $\alpha, \beta, [A]_0', [B]_0$
 $[k]$ can be determined

Differential method: [drawing tangents to give rate @ any pt]

$t = 0$

$$r_t = -\frac{d[A]}{dt}|_{t=t} = k[A]_t^\alpha$$

↓ record r_t for a series of $[A]_t$

$$\ln r_t = \ln k + \alpha \ln [A]_t$$

↓ plot in graph to get k & α

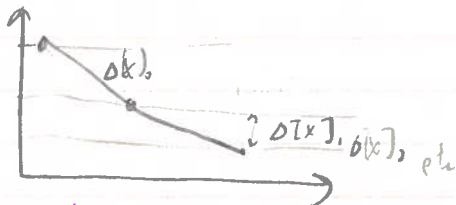
↳ Ostwald's isolation method

↳ having a great excess of B, so that the rate is only governed by [A]

Numerical integration:

assume $\frac{d[x]}{dt} \approx \frac{\Delta[x]}{\Delta t}$ for small Δt

$$[x]_0, \Delta[x] = \left(\frac{d[x]}{dt} \right) \Delta t$$



↳ then $[x]_1 = [x]_0 + \Delta[x]$

$$\Rightarrow [x]_{n+1} = [x]_n + \Delta[x]_n$$

\Rightarrow simulated $[x]_n$ is then fitted to exp't traces to determine kinetic parameters

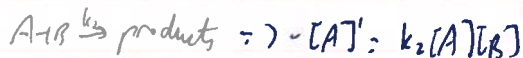
Drawbacks:

- computationally time consuming
- variable timescale for Rx
- sensitivity in complex (real world) situations,
[is $[x]_n$ only controlled by one Rx?]

Mechanisms:

→ combining kinetic expressions:

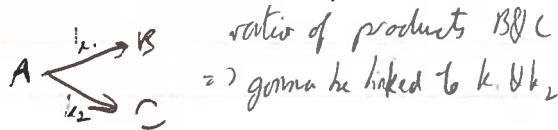
* rates of change of $[x]$ ($\frac{d[x]}{dt}$) are additive



overall:

$$\frac{d[A]}{dt} = -k_1[A] - k_2[A][B]$$

1 concurrent Rx (competition)



$$\frac{d[A]}{dt} = -k_1[A] - k_2[A] = -k_s[A]$$

$k_s = k_1 + k_2$

$$\frac{d[A]}{dt} = k_1[A] = k_1[A]_0 \exp(-k_s t)$$

$$\Rightarrow [B]_t = \left(\frac{k_1[A]_0}{k_s} \right) (1 - e^{-k_s t})$$

as $t \rightarrow \infty$: $[B]_{\infty} \rightarrow \left(\frac{k_1[A]_0}{k_s} \right) = \frac{k_1[A]_0}{k_1 + k_2}$

Branching ratio: $\frac{k_1}{k_s}$

$f(B) = \frac{k_1}{k_s} = \frac{k_1}{k_1 + k_2}$
 $f(C) = \frac{k_2}{k_s} = \frac{k_2}{k_1 + k_2}$

→ Branching dictates the effect of overall Rx

$$t \in [0, t]$$

by integration:

$$[B]_t = \left\{ \frac{k_1[A]_0}{k_2 - k_1} \right\} \cdot \{ \exp(-k_1 t) - \exp(-k_2 t) \}$$

can get $[C]_t$ from mass balance

$$[A]_t + [B]_t + [C]_t = [A]_0$$

if only $[B]$ present @ $t=0$

$$\begin{aligned} [C]_t &= [A]_0 - [A]_t - [B]_t \\ &= [A]_0 - [A]_0 e^{-k_1 t} - \left\{ \frac{k_1[A]_0}{k_2 - k_1} \right\} \cdot \exp(-k_1 + k_2)t \end{aligned}$$

$$[C]_t = [A]_0 \left\{ 1 + \frac{k_1 e^{-k_2 t} - k_2 e^{-k_1 t}}{k_2 - k_1} \right\}$$

t when $[B]$ stops constant:

$$\frac{d[B]}{dt} = 0$$

$$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0$$

$$\frac{1}{2} = \exp[(k_2 - k_1)t_{max}]$$

$$t_{max} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$

Kinetic conditions to apply SSA

Kinetic: $k_2 \gg k_1$

Temporal: past t_{max}

both are met for reactive

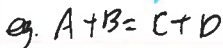
intermediates (atoms, ions, free radicals)

Applying steady state:

1. Characterise kinetics
- ↓
2. propose mechanism
- ↓
3. write required observation
- ↓
4. Use SSA for intermediates
- ↓
5. Predict kinetics
- ↓
6. Compare \rightarrow V/I if good

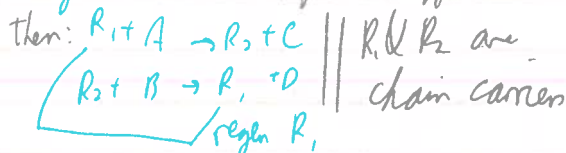
Chain Rx's: \rightarrow elementary reactions which
eg. combustion
pyrolysis of hydrocarbons
atmospheric ozone depletion
take place repeatedly

\Rightarrow then representations of radicals



w/ radical intermediate R_1, R_2

eg. Initially: $A \rightarrow 2R_1$ [requires energy]



R_x would continue until A & B are all consumed

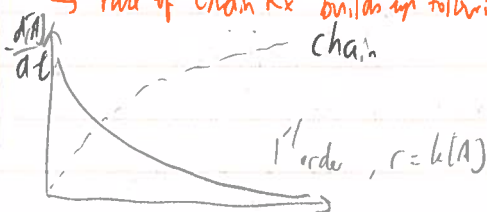
⊗ competing Rx's present eg. $R_1 + R_2 \rightarrow$ minor products

gradually diminish the conc of radicals

features:

\rightarrow v. large R_x rates

\rightarrow rate of chain Rx builds up following initiation



- Simple collision theory:
for an $A+B \rightarrow R_x$:

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for an $A+B \rightarrow R_x$:

$$\text{rate} = \text{freq of molecular collisions} \times \text{fraction of collisions w/ enough energy to react}$$

$$Z_{AB} = \sigma_{AB} \langle S \rangle_{rel} \frac{N_A}{2V} \frac{N_B}{V} \quad \left| \quad f(E > E_a) = e^{-\frac{E_a}{kT}}$$

$$r_{An} = \sigma_{AB} \langle S \rangle_{el} \frac{N_A}{2V} \frac{N_A}{V} e^{-\frac{E_g}{RT}}$$

$$r_{AB} = \sigma_{AB} \left(\frac{[A][B]}{2} \right)^{\frac{1}{2}} e^{-\frac{E_A}{RT}}$$

- Elementary rate: $r_{AD} = k[A][D]$

$$k_{\text{theoretical}} = \frac{\sigma_{AB}(s)_{\text{rel}} N_A^2}{e} e^{-\frac{E_a}{kT}}$$

$\Delta \epsilon_g (\text{J mol}^{-1})$ 2

$$\bar{E}_A = \sum_A \cdot N_A \quad ; \quad R = k_B \cdot N_A$$

$$\Rightarrow k_{\text{Arrhenius}} = A \exp\left(-\frac{E_a}{RT}\right) = A \exp\left(-\frac{E_a}{kT}\right)$$

Simple collision theory: predicts Arrhenius-like behaviour

BUT \Rightarrow SC7 usually overestimates k

∴ - distribution of intermolecular energy is ignored

- Molecular orientation not represented

steric factor: $P = \frac{A_{\text{exp}}}{A_{\text{theory}}}$

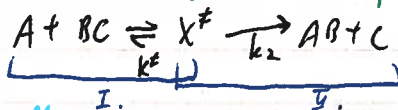
⇒ gives mechanistic info

4. need an improved theory of Rx kinetics

to represent a more realistic solution

Transition state theory / activated complex theory
[equation]

\Rightarrow postulates a state of eq^m between reactants & the activated complex



\Rightarrow allows quantification of articulated complexes $X \neq$

2) rate of breakdown of X^\ddagger = rate of product AB formation

$$I: K^f = \frac{[X^f]}{[A][BC]} \Rightarrow [X^f] = K^f [A][BC]$$

II. unimolecular dissociation of X^\ddagger , forming products

$$\frac{d[AQ]}{dt} = \frac{d[C]}{dt} = k_2 [X^\ddagger] = k_2 K^\ddagger [A][BC]$$

deriving:

K^\ddagger : from partition functions for reactants & activated complex

k_2 : from vibrational properties of the bond that breaks X^\ddagger
[taken as vib. freq.]

measuring:

reactants \Rightarrow SL right forward

using spectroscopic parameters,
vib freq etc

RT do not know exact structure of $X^\#$

- make assumptions on the structure

Q bonding of X^{\pm}

↳ then calc E_{rot} , E_{vib} , E_{elec} , E_{trans} to estimate K^{\ddagger}

* actual observation of X^F is near impossible (fs lifetime)

Applied Kinetics

Polar ozone depletion:

← sunlight from springtime



rate of ozone loss:

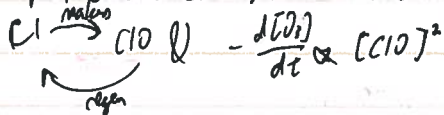
$$\frac{d[\text{O}_3]}{dt} = -k_1[\text{Cl}][\text{O}_3] = -r_1 \quad 2r_2$$

$$\frac{d[\text{ClO}]}{dt} = k_1[\text{Cl}][\text{O}_3] - 2k_2[\text{ClO}]^2[\text{M}] + 2k_2[\text{Cl}_2\text{O}_2][\text{M}] \approx 0 \text{ (SSA)}$$

$2r_2 \approx 0$ ∴ thermal decomposition inefficient @ low T

$$\frac{d[\text{O}_3]}{dt} = -2k_2[\text{ClO}]^2[\text{M}] = -2r_2$$

∴ polar ozone loss is a linear chain Rx



WITH ⇒ specific meteorological condⁿ

⇒ quadratic kinetic term

★ ClO can also interact w/ other free radicals in the stratosphere (eg. HO, HO₂)

↳ ozone loss will depend on rate constants & branching ratios

Thermal auto-acceleration

if Rx is exo ⇒ $\Delta H = -ve$

↓

adiabatically confined

energy is released (but can't all escape) ⇒ more T↑↑, k↑↑, rate ↑↑

- rate of enthalpy release:

$$\frac{d(\Delta H)}{dt} = \Delta H \cdot r = \Delta H \cdot \left\{ \frac{1}{k_a} \frac{d[r]}{dt} \right\} = Q_+$$

if: $Q_+ < \text{rate of heat loss}$

⇒ steady state T is eventually achieved, k stabilise ⇒ r stabilise

if $Q_+ > \text{rate of heat loss}$

⇒ T↑↑ → k↑↑ → r↑↑

↳ Rx rate becomes immeasurably fast

↳ T↑↑, p & V↑↑

↳ Thermal explosion

for a gas @ initial temp T w/ surr. T_s:

rate of heat loss:

$$Q_- = K_S(T - T_s)$$

coeff of thermal transfer → surface area of vessel

rate of heat production:

$$Q_+ = \Delta H \cdot r$$

⇒ can plot $Q_+ \text{ vs } Q_-$ as func of T to find explosion limits