Kinetics (Summary) - basics only

Burghaus 2006

rate of conversion

$$J = -\frac{1}{a}\frac{dn_A}{dt} = \frac{1}{b}\frac{dn_B}{dt}$$

⊖ A disappears

⊕ B is formed

n_A, n_B: particle number
t: time

reaction rate

$$r = J/V = -\frac{1}{a}\frac{d[A]}{dt}$$

V: volume
$[A]$: concentration

rate laws

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

α: reaction order with respect to A

$\alpha+\beta+\ldots$: total reaction order

k: rate coefficient

examples:

$aA \rightarrow bB$

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$N_2 + 3H_2 \rightarrow 2NH_3$

$$r = -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = \frac{1}{2}\frac{d[NH_3]}{dt}$$

—

$$O_{ad} + CO_{ad} \xrightarrow[Pt]{k_r} CO_{2,gas}$$

$$r_{CO_2} = k_r[O][CO] = \frac{d[CO_2]}{dt}$$

1st order kinetics

$$r = -\frac{1}{a}\frac{d[A]}{dt} = k[A]$$

$$[A](t) = [A]_0 e^{-kt}$$

$$t_{1/2} = \ln(2)/k$$

2nd order kinetics

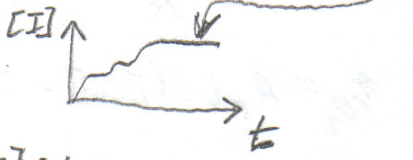
$$r = k[A]^2$$

$$[A] = \frac{[A]_0}{1 + k_A[A]_0 t}$$

$$t_{1/2} = 1/(k_A[A]_0)$$

steady-state approx.

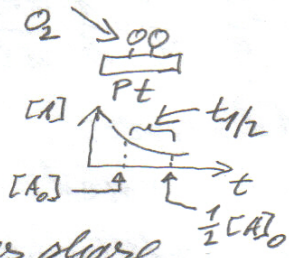
$\frac{d[I]}{dt} \approx 0$ for large t



[I]: Intermediate

examples:

$O_2(gas) \xrightarrow{k/Pt} 2O(ads)$



gas phase

$2I \rightarrow I_2$

$2NOBr \rightarrow 2NO + Br_2$

liquid $H^+ + OH^- \rightarrow H_2O$

surface reaction

$CO_{ads} + O_{ads} \rightarrow CO_2$ gas

⊙ $R \xrightarrow{k_a} I \xrightarrow{k_b} P$

R: reactant

P: product

⊙ $O_{ad} + CO_{ad} \rightarrow CO_2$ gas

$$\frac{d[CO]_{ad}}{dt} = 0$$

rate determining step

$R \xrightarrow{k_1} I \xrightarrow{k_2} P$

$k_2 \gg k_1$

$\Rightarrow$ $R \to I$ determines the total rate (slow step)

pre-equilibrium

$A + B \rightleftarrows I \to P$

fast — slow

$\Rightarrow \frac{d[I]}{dt} \approx 0$

Arrhenius-eq.

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

- E_a: activation energy
- A: pre exponential factor

examples:

- $C_6H_5N_2^+$ formation
  Levine p. 546
- $A \rightleftarrows B \rightleftarrows C \rightleftarrows D$

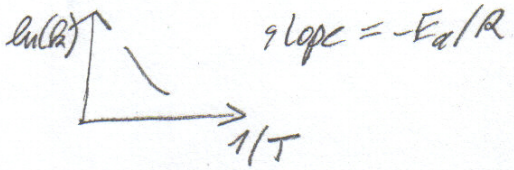
  $B \rightleftarrows$ slow step

  $\Rightarrow \frac{d[D]}{dt} \sim [C]$

$CO_{ads} + O_{2\,ad} \underset{rt}{\rightleftarrows} (CO \cdots O_2)^{\#}_{ad}$

$\to \cdots \to CO_2$ (gas)

intermediate $(CO \cdots O_2)^{\#}$ acts as a buffer



slope $= -E_a/R$

intercept $= \ln(A)$