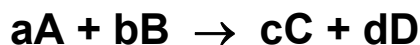


*Chem 344 – Experimental Kinetics, brief review — Wed, Sept 9, 2009*

Thermodynamics addresses Initial and Final states, Kinetics senses the path

Rates normalized to account for stoichiometry.



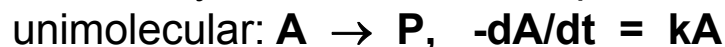
$$r = -1/a \, dA/dt = -1/b \, dB/dt = 1/c \, dC/dt = 1/d \, dD/dt$$

Observed reactions have **orders**:

$$r = k[A]^x [B]^y [C]^z [D]^w$$

order of reaction =  $x + y + z + w$ ,  $x$  = order w/r/t A etc.

Molecularity: if reaction one step, order reflect stoichiometry.



**Methods to determine order:**

Initial rates:  $R \rightarrow P$  Initial concentration is  $R_0$  or  $P_0$

so:  $r = k [R_0]^x = \text{slope} = dR/dt$

ratio rates with different concentrations to get  $x$

**Integrated rate laws** - find a linear form

1<sup>st</sup> order:  $\ln ([A]/[A_0]) = -kt$

2<sup>nd</sup> order:  $1/[A] - 1/[A_0] = kt$

$$kt = 1/\{[A_0] - [B_0]\} \ln \{[A][B_0]/[B][A_0]\}$$

Graphical Method  $\rightarrow$  plot:  $[A]$ ,  $\ln [A]$ ,  $1/[A]$ , etc. vs.  $t$

Half-life (best for 1<sup>st</sup> order)  $\tau_{1/2} = \text{time to go to } [A_0/2] = 0.693/k$

**Temperature variation** - Arrhenius -  $k = Ae^{-E_a/RT}$

Analysis - plot:  $\ln k$  vs  $1/T$  slope =  $-E_a/RT$  intercept =  $\ln A$

$E_a$  is barrier to reaction forward. Lower - reaction faster—catalyst role

**Mechanism** – series of single step reactions making up complex reaction

Reaction goes forward until equilibrium – reverse reaction equal rate

$$K_{eq} = [P_e]/[A_e] = (A_0 - A_e)/A_e = (A_0/A_e - 1) = k_1/k_{-1}$$

$$r = (k_1 + k_{-1}) \{ [A] - [A_e] \} \quad \ln(A - A_e)/(A_0 - A_e) = -(k_1 + k_{-1}) t$$

Chain Reaction – bottleneck/rate determining step --  $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

a)  $-d[A]/dt = k_1[A] \Rightarrow [A] = [A_0]e^{-k_1t}$

b)  $[B] = k_1[A_0]/(k_2 - k_1) [e^{-k_1t} - e^{-k_2t}]$

c)  $d[C]/dt = k_1e^{-k_1t} - [k_1/(k_2 - k_1)] (-k_1e^{-k_1t} + k_2e^{-k_2t})$  - induction

a) if  $k_2 \gg k_1$  B concentration assume small steady value

$$d[B]/dt \sim 0 = k_1[A] - k_2[B] \quad \text{-- steady state approx. - } [B] = k_1/k_2[A]$$

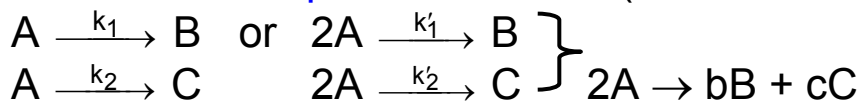
$$d[C]/dt = k_2[B] = k_2[k_1/k_2[A]] = k_1[A] \quad \text{- looks 1<sup>st</sup> in A but i time}$$

b) if  $k_1 \gg k_2$  – [B] builds up and approaches equilibrium

$$d[B]/dt \approx k_1[A] = k_1[A_0]e^{-k_1t} \quad \text{-- } [B] = [A_0] - [A]$$

$$d[C]/dt = k_2[B] = k_2\{ [A_0] - [A] \} \quad \text{-- looks 1<sup>st</sup> order in A}$$

c) Alternate case – parallel reaction (A forms independent products)



$$r = -1/2 d[A]/dt = k'_1[A]^2 + k'_2[A]^2 = (k'_1 + k'_2) [A]^2$$

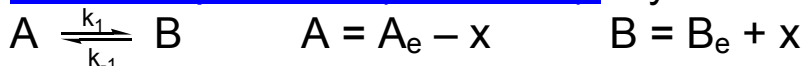
Determine complexity – for above cases:

c) – see 2 products whose ratio is non-stoichiometric or T-dependent

a) – see induction period in [C] or b) – detect intermediate [B]

**Methods** -- follow [A] -- Absorbance, fluorescence, whatever ~ conc.

Disturb equilibrium (relaxation) - system must relax to new equilibrium



$$x = x_e e^{-t/\tau} \quad \text{relaxation time: } 1/\tau = k_1 + k_{-1}$$

Since  $K_{eq} = k_1/k_{-1}$  get both values  $k_1, k_{-1}$  from  $\tau$  &  $K_{eq}$