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.

$aA + bB \rightarrow cC + dD$

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

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.

unimolecular: **$A \rightarrow P$, $-dA/dt = kA$**

bimolecular: **$2A \rightarrow P$, $-1/2\ dA/dt = kA^2$**

$A + B \rightarrow P$, $-dA/dt = kAB$

Methods to determine order:

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

so: **$r = k [R_0]^x$** = slope = dR/dt

ratio rates with different concentrations to get x

Integrated rate laws - find a linear form

1st order: **$\ell n ([A]/[A_0]) = - kt$**

2nd order: **$1/[A] - 1/[A_0] = kt$**

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

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

Half-life (best for 1st order) $\tau_{1/2}$ = 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

$\mathbf{E_a}$ 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

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

$\mathbf{r = (k_1 + k_{-1}) \{[A] - [A_e]\}}$ $\ell n(A-A_e)/(A_0-A_e) = -(k_1+k_{-1})\,t$

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

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 $\mathbf{k_2 >> k_1}$ B concentration assume small steady value

$d[B]/dt \sim 0 = k_1[A] - k_2[B]$ – steady state approx. - $[B] = k_1/k_2[A]$

$d[C]/dt = k_2[B] = k_2[k_1/k_2[A]] = k_1[A]$ - looks 1st in A but i time

b) if $\mathbf{k_1 >> k_2}$ – [B] builds up and approaches equilibrium

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

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

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

$A \xrightarrow{k_1} B$ or $2A \xrightarrow{k'_1} B$

$A \xrightarrow{k_2} C$ $2A \xrightarrow{k'_2} C$ } $2A \rightarrow bB + cC$

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

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

$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$ $A = A_e - x$ $B = B_e + x$

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

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