

KINETICS : REVIEW OF CONCEPTS

1. Stoichiometry, progress variables, etc.

• You should know this by now!

2. Thermodynamics of Chemical Rxns.• Equilibrium : $\Delta G = \sum \nu_i \mu_i = 0$ check for
multiple rxns• Eq Constant : $K_a = \prod a_i^{\nu_i}$

- diff. expressions for activities of solids, liquids, gases.

- determine equilibrium compositions

$$\Delta G^0 = -RT \ln K_a$$

- temperature effect :

$$\left\{ \frac{\partial (-\Delta G^0 / T)}{\partial T} \right\}_P = \left(\frac{R \partial \ln K_a}{\partial T} \right)_P = \frac{\Delta H^0}{T^2}$$

$$\text{or} \quad \left(\frac{\partial \ln K_a}{\partial T} \right)_P = \frac{\Delta H^0}{RT^2}$$

$$\text{or} \quad \left(\frac{\partial \ln K_a}{\partial (1/T)} \right)_P = - \frac{\Delta H^0}{R}$$

• Effects of Rxn. conditions :

1. Pressure : look at change in number of gaseous moles in rxn.2. Temperature : changes value of K_a via relation given above.3. Inert gases : Again, depends on the change in # of gaseous moles. Addition of inert gases has same effect AS A pressure decrease.4. Catalyst : Eq. constant and yield is

3. REACTION RATE EXPRESSIONS: $r = kF(C_i, T)$

$$r_i = \frac{1}{V} \frac{dn_i}{dt}$$

• be warned: $r = \frac{1}{\nu_i} \frac{dC_i}{dt}$
only in constant
Volume systems!

• Variables that influence reaction rates

1. T, P , composition of system (NO SHIT!)
2. catalysts (increase rate) and inhibitors (decrease rate) — do not appear in stoichiometric eqn.
3. Rate generally decreases monotonically with time or extent of rxn.

4. Rate constant:

Arrhenius Law

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

where A is pre-exponential factor
(or Frequency factor), assumed
to be Temp. independent.

5. Very often use power law to describe $F(C_i)$

$$F(C_i) = \prod C_i^{\beta_i}$$

$\beta_i \sim$ order of
rxn. w/ resp. to

6. Forward and reverse rxn. may be
important: $r = \vec{r} - \overleftarrow{r}$

• Experimental Aspects - interpretation
and evaluation of kinetic data.

Must First

- a) properly identify system, side reactions, stoichiometry, experimental conditions.
- b) obtain significant, reproducible data.

INTERPRETATION of DATA -

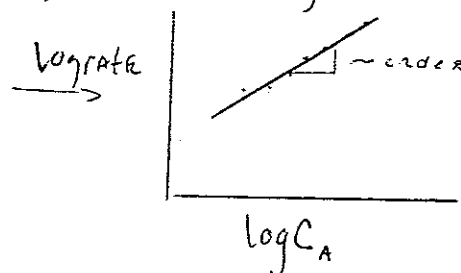
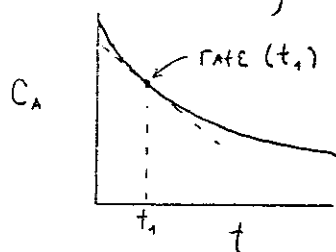
- ① Differential methods - based on differentiation of experimental C vs. t data
 \rightarrow gives actual rate of rxn.

• 2 methods:

a) single experimental run

• Assume $r = k C_A^{\beta_A} C_B^{\beta_B} \dots$

$$\log r = \log k + \beta_A \log C_A + \beta_B \log C_B + \dots$$



b) initial rates - vary initial reactant concentration; focuses on conditions prevailing at beginning of rxn.

$$r_0 = k (C_{B_0}^{\beta_B} C_{C_0}^{\beta_C} \dots) C_{A_0}^{\beta_A}$$

$$r_0' = k (C_{B_0}^{\beta_B} C_{C_0}^{\beta_C} \dots) C_{A_0'}^{\beta_A}$$

$$\rightarrow \beta_A = \frac{\log (r_0 / r_0')}{\log (C_{A_0} / C_{A_0'})}$$

- can handle more complex rate expressions
- can neglect reverse reactions.

- ② Integral methods - guess form of rate expression based on stoichiometry and assumptions concerning mechanism.

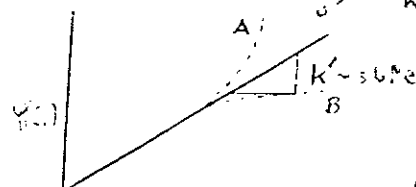
• propose $\frac{1}{v} \frac{d\xi}{dt} = k F(C_i) \rightarrow t = \int_0^{\xi} \frac{d\xi}{k v F(C_i)}$

A \rightarrow Assumed order greater than true order
 B \rightarrow Assumed order less than true order

i.e. $r = k C_A^2$
 $k' = k C_B C_C \dots$

$kt = \psi(C_i)$

• linear?



- Recall numerical procedures, fractional life methods, Guggenheim's method (for 1st order).

- Isolation method: $r = k C_A^{p_A} C_B^{p_B} C_C^{p_C} \dots$

- Use $C_{B_0} \gg C_{A_0}$, $C_{C_0} \gg C_{A_0}$, etc., so that

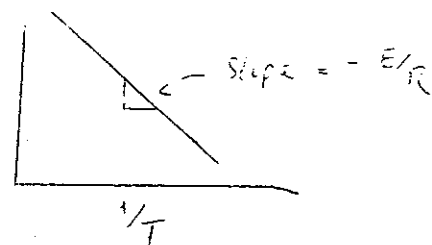
$$r = k' C_A^{p_A} \rightarrow \text{pseudo } p_A^{\text{th}} \text{ order reaction.}$$

- either integral or differentiation method.

- Activation energy: $k = A e^{-E/RT}$

$$\boxed{\frac{d \ln k}{d(1/T)} = -E/R}$$

$\ln k$



Molecular interpretations

- Features of a rxn mechanisms:

- Linear combination of steps must produce the stoichiometric reaction eqn.
- Each step must have reasonable energy reqs. i.e., ΔH 's not too positive. Larger ΔH 's are tolerated at high T or in initiation steps.
- High molecularity in gas phase is unusual. Termolecular rxns. are rare at best; higher molecularities aren't observed.
- Make a back only a few bonds per step.
- Rate expression must be consistent w/obsn.

- derivation of rate expression from a reaction mechanism is usually accomplished via assumptions. These assumptions are

1. Neglect reverse rxns. (irreversibility of a reaction). Valid during initial period of rxn - far removed from equilibrium.
2. Rate limiting step - one elementary rxn. occurs much slower than any of the others.
3. Bodenstein Assumption - concentration of intermediate species not changing very rapidly with time. (quasi-steady state).
4. Assumption of quasi-equilibrium of one or more elementary steps.
5. Surface rxns - Most abundant reactive intermediate (MARI)

$$\theta_x = 1 - \sum \theta_i \approx 1 - \theta_{\text{MARI}}$$

- Remember that different mechanisms can lead to the same rate expression.
- Guidelines in going from rate expressions and stoichiometry to mechanisms are given in H.C. very practical!

• Additional methods:

- ① Rxn. intermediates (especially on surfaces) - spectroscopy, etc.
- ② Isotopic substitution - gives knowledge of which bonds broken, different molecularity & order

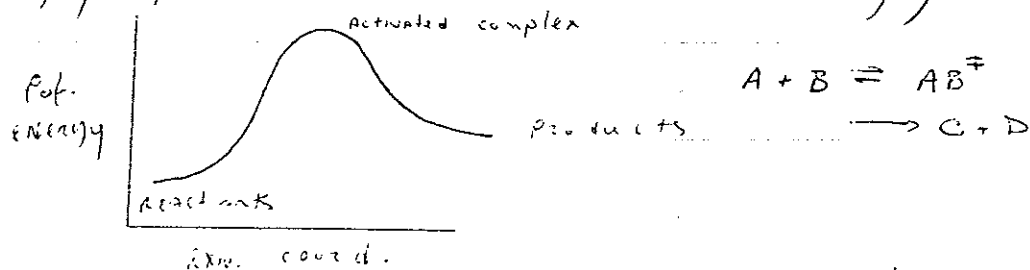
what happens if there are two slow rate limiting steps

Molecular theories of chemical kinetics

1. Collision theory - molecular collisions result in redistributions of energy and changes in geometric configurations.
 - link kinetics of rxns. to kinetic theory of gases. through use of theoretical expressions for bimolecular (or termolecular, depending on rxn. of interest) collision frequencies.
 - Only small # of bimolecular collisions lead to reaction. \rightarrow Energy requirement and geometric considerations (through a steric factor)
 - Energy requirement by far more important! Expect a threshold energy requirement below which rxn. will not occur.

2. Transition State Theory "activated complex"

- takes into account internal structure of molecules. Interested in reaction path along a multidimensional potential energy contour. \rightarrow different energies required for different paths. Lowest energy path \Rightarrow activation energy



- describe equilibrium by $K^\ddagger = \exp \frac{-\Delta G^\ddagger}{RT}$
 \Rightarrow statistical mechanics, partition func.