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CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #11

Kinetic Theory: Encounter Model, Transition State Model & Ionic Strength Effects

Brezonik, pp. 130-158

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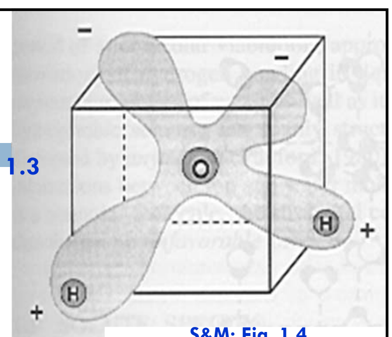
Introduction

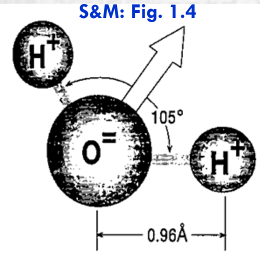
Structure of Water

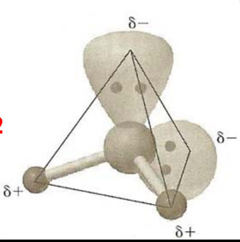


S&M: Fig. 1.3

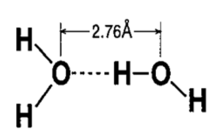
- sp^3 hybridization
  - 2 bonding and 2 non-bonding orbitals
- Dipolar Character
- Origin of Water's Unusual properties
  - High melting and boiling point
  - High heat of vaporization
  - Expands upon freezing
  - High surface tension
  - Excellent polar solvent

S&M: Fig. 1.4





B: Fig 1.2



Water's intermolecular structure

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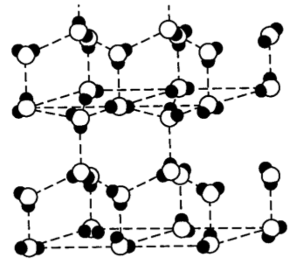

Fig. 1.5a
Pg. 8

- Dominated by Hydrogen Bonds
- Ice
  - Open tetrahedral structure
- Water
  - Flickering cluster model
    - 100 ps lifetime
    - 0.1 ps molecular vibration
  - Avg cluster size
    - 65 molecules @ 0°C
    - 12 molecules @ 100°C

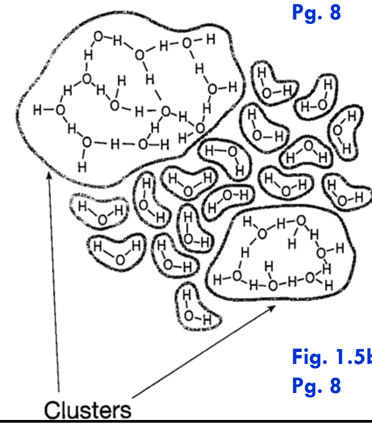

Fig. 1.5b
Pg. 8

Solutes in Water

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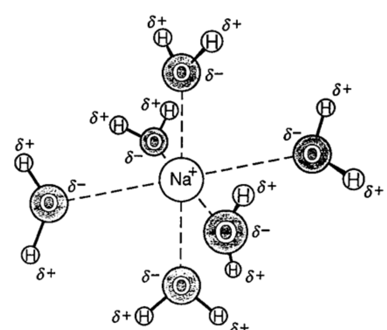
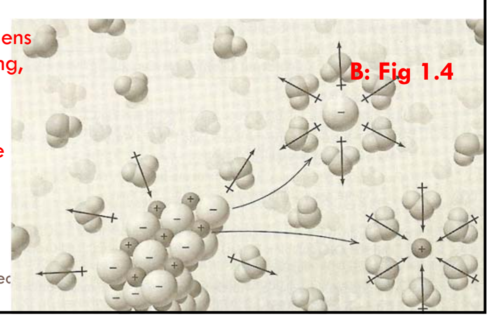
- Great solvent for ionic or ionizable substances
- Ion-dipole bonds improves stability
  - Energy increases with charge of ion anc decreases with size
  - Solvent hole model
    - As solute-water bonding strengthens compared to water-water bonding, solubility goes up
      - Hydrophilic solute
    - Weak solute-water bonds reduce solubility
      - Hydrophobic solutes



S&M: Fig. 1.6



B: Fig 1.4

Activation Energy

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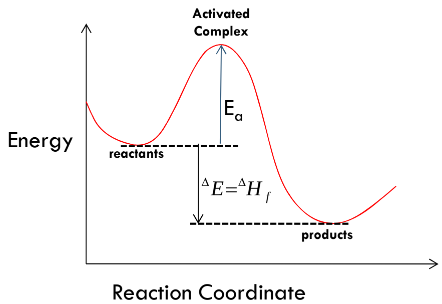
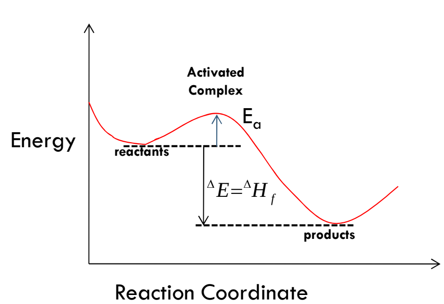
- Activation Energy must always be positive
  - Unlike ΔH, which may be positive or negative
- Differing reaction rates





Encounter Theory I

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- Uncharged Solutes
  - Nature of diffusion in water
    - Encounter within a solvent cage
    - Random diffusion occurs through elementary jumps of distance Molecular diameter $\lambda = 2r$ Molecular radius

Average time between jumps

More appropriate for water

- For a continuous medium: $D = \lambda^2 / 2\tau$ or $\tau = \lambda^2 / 2D$
- For a semi-crystalline structure: $D = \lambda^2 / 6\tau$ or $\tau = \lambda^2 / 6D$

For water, D ~ $1\text{x}10^{-5}$ cm^{2}s^{-1}, and λ = $4\text{x}10^{-8}$ cm, so τ ~ $2.5\text{x}10^{-11}$ s

If time between vibrations is ~ $1.5\text{x}10^{-13}$ s, then the average water molecule vibrates 150 times ($2.5\text{x}10^{-11}/1.5\text{x}10^{-13}$) in its solvent cage before jumping to the next one.

Encounter Theory II

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- Probability of Encounter
  - If A and B are the same size as water
    - They will have 12 nearest neighbors
  - Probability that "A" will encounter "B" in a solvent cage of 12 neighbors is:
    - Proportional to the mole fraction of "B"

$$P_{B/A} = 6X_B$$

With each new jump, "A" has 6 new neighbors

Where: $$X_B = \frac{n_B}{\left(1/\gamma\lambda^3\right)}$$

n_B: # molecules of "B" per cm³

$\left(1/\gamma\lambda^3\right)$: # molecules of solvent per cm³

γ: Geometric packing factor

λ^3: Molecular volume (cm³)

Encounter Theory III

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- And combining the rate of movement with the probability of encountering "B", we get an expression for the rate of encounter with "B"

$$1/\tau_{AB} = \left[6D/\lambda^2\right] P_{A/B}$$

- Then substituting in for the probability

$$1/\tau_{AB} = 6D(6n_B\gamma\lambda^3)/\lambda^2$$
$$= 36\gamma\lambda n_B D$$

  - For water, γ=0.74, and the effective diffusion coefficient, $D_{AB} = D_A + D_B$, and $\lambda = r_{AB}$, the sum of the molecular radii
    - Then we get:

$$1/\tau_{AB} = 25 r_{AB} D_{AB} n_B$$

# of encounters/sec for each molecule of "A"

Encounter Theory IV

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- Now the total # of encounters between "A" and "B" per cm^3 per second is:

$$n_A / \tau_{AB} = 25 r_{AB} D_{AB} n_A n_B$$

- In terms of moles of encounters (encounter frequency) this becomes:

$$Z_{e,AB} = \frac{1000 \frac{cm^3}{L}}{N_o \frac{molecules}{Mole}} \left(\frac{n_A}{\tau}\right) = 25 r_{AB} D_{AB} \left(\frac{1000 \frac{cm^3}{L}}{N_o \frac{molecules}{Mole}}\right) n_A n_B$$

$$= 25 r_{AB} D_{AB} [A] n_B$$

$n_B=[B]/N_0/1000$

L/cm^3 cm cm^2s^{-1} #/Mole $M^{-1}s^{-1}$

$$Z_{e,AB} = 2.5x10^{-2} r_{AB} D_{AB} N_0 [A][B]$$

Encounter Theory V

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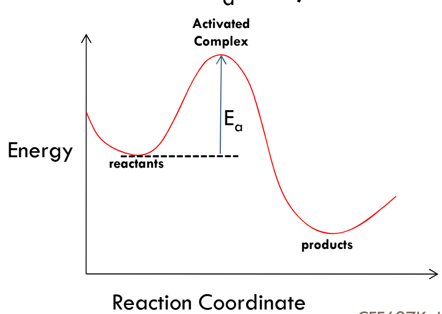
- Frequency Factor

$$Z_{e,AB} = \underbrace{2.5x10^{-2} r_{AB} D_{AB} N_0}_{A} [A][B]$$

- When E_a = 0, k=A



$$k = Ae^{-E_a/RT}$$

Transition State Theory I

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- Consider the simple bimolecular reaction

$$A + B \xrightarrow{k} C$$

- Even though it is an elementary reaction, we can break it down into two steps

$$A + B \Leftrightarrow AB^{\neq} \xrightarrow{k^{\neq}} C$$

"Activated Complex"

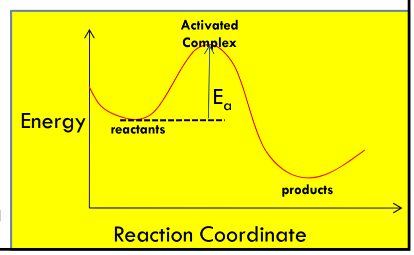
- Where the first "equilibrium" is:

$$K^{\neq} = \frac{[AB^{\neq}]}{[A][B]}$$

$$[AB^{\neq}] = K^{\neq}[A][B]$$

- So the forward rate is:

$$\frac{d[C]}{dt} = k^{\neq}[AB^{\neq}] = \underbrace{k^{\neq}K^{\neq}}_{k}[A][B]$$



Transition State Theory II

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- Now the transition state is just one bond vibration away from conversion to products
  - Planks Law:

$$E_{vib} = h\nu$$

vibrational energy; Frequency of vibration (s^{-1}); Planck's constant (6.62 x 10^{-27} ergs-s)

  - Bond energy must be in the thermal region:

$$E_{bond} \approx kT$$

Bond energy; Temperature (°K); Boltzman constant (1.3807×10^{-16} ergs °K^{-1})

  - So equating, we get:

$$h\nu = kT \qquad \nu = kT/h$$

  - And since conversion occurs on the next vibration:

$$k^{\neq} = \nu \quad \text{and} \quad k = k^{\neq}K^{\neq} = \frac{kT}{h}K^{\neq}$$

Transition State Theory III

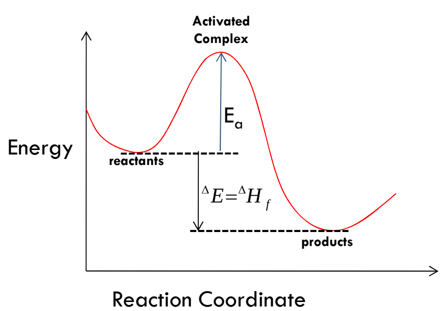
- Now from basic thermodynamics:

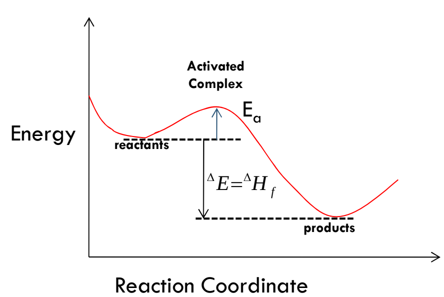
$$\Delta G^o = -RT \ln K \quad \text{or} \quad K = e^{-\Delta G^o / RT}$$

  - And also $\Delta G^o = \Delta H - T\Delta S$
  - So: $K = e^{\Delta S / R} e^{-\Delta H / RT}$
- And combining: $$k = \frac{kT}{h} e^{\Delta S^{\neq} / R} e^{-\Delta H^{\neq} / RT}$$
  - Recall: $\Delta E = \Delta H - P\Delta V \approx \Delta H$
- And substituting back in: $$k = \underbrace{\left(\frac{kT}{h} e^{\Delta S^{\neq} / R} \right)}_{A} e^{-E_a / RT}$$

Activation Energy

- Activation Energy must always be positive
  - Unlike ΔH, which may be positive or negative
- Differing reaction rates





Temperature Effects

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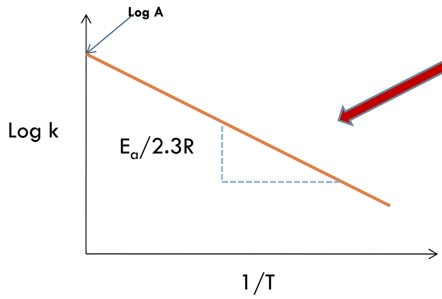
- Arrhenius Equation

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \qquad k = Ae^{-E_a/RT} \qquad \ln\frac{k_2}{k_1} = \frac{(T_2 - T_1)E_a}{RT_1T_2}$$



$$\ln\frac{K_2}{K_1} = \frac{(T_2 - T_1)^{\Delta}H_0}{RT_1T_2}$$

Analogous to Van't Hoff Equation for Equilibria

Ionic Strength Effects

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- Ion-ion Reactions
  - Based on activated complex theory

$$A + B \Leftrightarrow AB^{\neq} \xrightarrow{k^{\neq}} C \qquad \frac{d[C]}{dt} = k^{\neq}[AB^{\neq}] = k^{\neq}K^{\neq}[A][B]$$

  - So let's look at the equilibrium constant

$$K^{\neq} = \frac{\{AB^{\neq}\}}{\{A\}\{B\}} = \frac{[AB^{\neq}]\gamma_{AB^{\neq}}}{[A]\gamma_A[B]\gamma_B} \quad \text{or} \quad [AB^{\neq}] = K^{\neq}[A][B]\left(\frac{\gamma_A\gamma_B}{\gamma_{AB^{\neq}}}\right)$$

  - Which means:

$$\frac{d[C]}{dt} = \underbrace{\frac{kT}{h}K^{\neq}}_{K_2^{\circ}\ (\text{for } I=0)}[A][B]\left(\frac{\gamma_A\gamma_B}{\gamma_{AB^{\neq}}}\right)$$

Reactions with charged ions

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- Using the Debye-Huckel Equation $-\log\gamma_i = 0.55 z_i^2 I^{0.5}$
  - I<0.005

$$\log k_2 = \log k_2^o + \left\{-0.51 z_A^2 - 0.51 z_B^2 + 0.51\underbrace{(z_A + z_B)^2}_{z_A^2 + 2z_A z_B + z_B^2}\right\} I^{0.5}$$

$$= \log k_2^o + 1.02 z_A z_B I^{0.5}$$

- Using the Guntelberg Approximation $-\log\gamma_i = \dfrac{0.55 z_i^2 I^{0.5}}{(1+I^{0.5})}$
  - I<0.01

$$\log k_2 = \log k_2^o + 1.02 z_A z_B \frac{I^{0.5}}{(1+I^{0.5})}$$

I corrections (cont.)

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- Neutral species

$$-\log\gamma_i = b_i I$$

$$\log k_2 = \log k_2^o + \{b_A + b_B - b_{AB^{\neq}}\} I$$

- Some case studies:

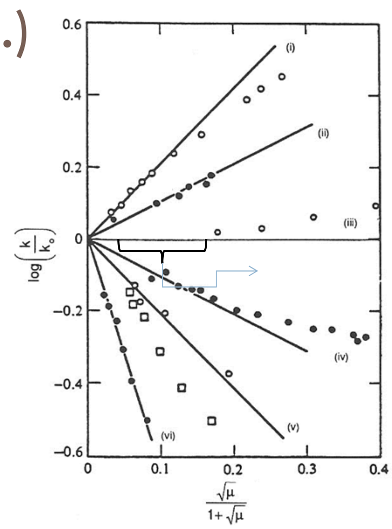

Figure 3-13. Effect of ionic strength on rate constants: (i) $BrCH_2COO^- + S_2O_3^{2-}$; (ii) $e^-_{aq} + NO_2^-$; (iii) $H_3O^+ + C_{12}H_{22}O_{11}$ (inversion of sucrose); (iv) $H_3O^+ + Br^- + H_2O_2$; (v) $OH^- + Co(NH_3)_5Br^{2+}$ (ionic strength varied with NaBr [circles] and Na_2SO_4 [squares]); (vi) $Fe(H_2O)_6^{2+} + Co(C_2O_4)_3^{3-}$. (From Weston, R. E., Jr. and H. A. Schwarz, *Chemical Kinetics*, Prentice-Hall, Englewood Cliffs, NJ, 1972. With permission.)

Case Study: TCP

Note: both TCP and TCAC refer to the 1,1,1-trichloropropanone

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- Observed loss of 1,1,1-trichloropropanone in distribution systems
  - Lab studies show that chloroform is the product
  - Logically presumed to be a simple hydrolysis

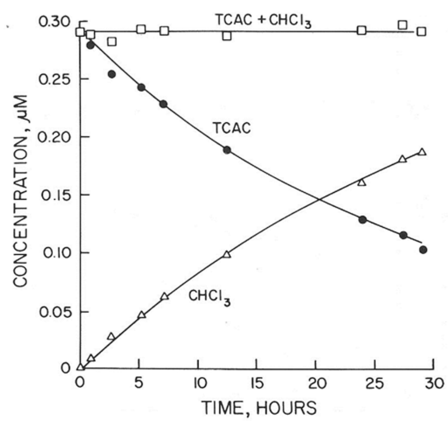

Figure 6. Chlorination of 1,1,1-trichloroacetone (TCAC). Conditions: 20.4 mg/L applied HOCl, $[PO_4]_T$ = 0.0145 *M*, pH 7.0, 20°C.

Reckhow & Singer, 1985
"Mechanisms of Organic Halide Formation During Fulvic Acid Chlorination and Implications with Respect to Preozonation", In Jolley et al., Water Chlorination; Chemistry, Environmental Impact and Health Effect, Volume 5, Lewis.

TCP (cont.)

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- Ionic strength effects

$$\ln k_H = -4.81 - 1.4\sqrt{I}$$

$$\log k_H = -2.08 - 0.6\sqrt{I}$$

- Rate with chlorine
  - Increases greatly
  - High intercept

$$k_T = 0.024 + 32[HOCl]_T$$

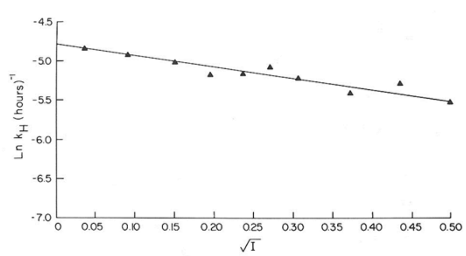

Figure 8. Pseudo first-order reaction rate constants for the hydrolysis of 1,1,1-trichloroacetone as a function of ionic strength. Conditions: pH 7.0, 20°C, no added chlorine.

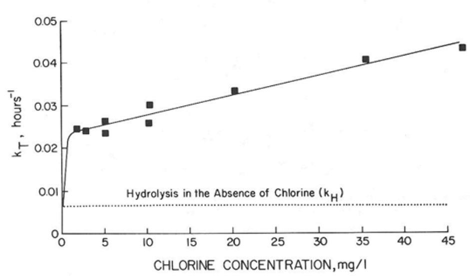

Figure 9. Pseudo first-order reaction rate constants for the disappearance of 1,1,1-trichloroacetone as a function of chlorine dose. Conditions: pH 7.0, 20°C, $[PO_4]_T$ = 0.0145 *M*.

Disagreement with prior study

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- Gurol & Suffet showed 10x higher rate constants
- Phosphate?

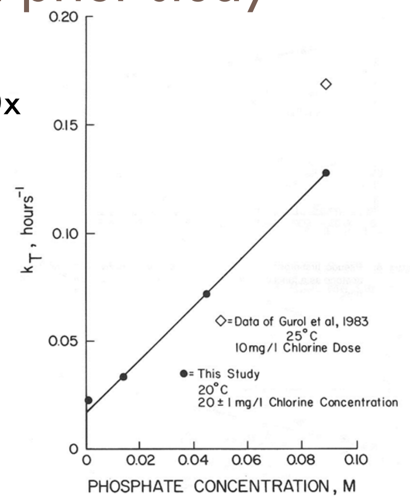

Figure 7. Pseudo first-order reaction rate constants for the chlorination of 1,1,1-trichloroacetone as a function of phosphate concentration at pH 7.0.

Putting it together

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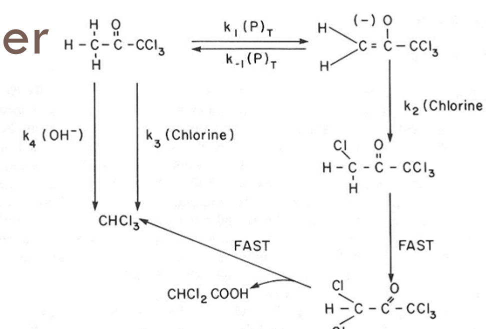

$$k_T = \frac{k_1 k_2 (\text{Chlorine})(P)_T}{k_{-1}(P)_T + k_2(\text{Chlorine})} + k_3(\text{Chlorine}) + k_4(OH^-)$$

where $k_1 = 1.25\ M^{-1}\ hr^{-1}$ $\quad k_{-1} = 1.6 \times 10^{-7}/k_{TCAC}$

$k_3 = 32\ M^{-1}\ hr^{-1}$ $\quad k_2 > 10^{-4}/k_{TCAC}$

$k_4 = 64{,}000\ M^{-1}\ hr^{-1}$

$$k_{TCAC} = \frac{(\text{Enolate})(H^+)}{(\text{Keto-enol})}$$

Figure 12. Hypothetical mechanism for the decomposition of trichloroacetone to chloroform in the presence of intermediate concentrations of phosphate at pH 7.

Catalysis

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- Homogeneous Catalysis
  - Definition
    - Liquid-phase substances which react with the main reactants or intermediates thereby providing an alternative pathway to products with a lower activation energy or a higher frequency factor. Catalysts are often regenerated over the course of the reaction.

$$2A^{+2} + B^{+} \rightarrow 2A^{+} + B^{+3}$$

termolecular reaction? – be skeptical

What really happens:

$$\begin{array}{c} A^{+2} + C^{+} \rightarrow A^{+} + C^{+2} \\ A^{+2} + C^{+2} \rightarrow A^{+} + C^{+3} \\ C^{+3} + B^{+} \rightarrow C^{+} + B^{+3} \\ \hline 2A^{+2} + B^{+} \rightarrow 2A^{+} + B^{+3} \end{array}$$

"C" serves as a sort of charge-transfer facilitator, since "B" does not exist in a divalent state

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- Summary

Table 4-1. Mechanisms of Acid-Base Catalysis

Type	Mechanism	Rate expression	Comments
I. Specific H^+	$S + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$ $SH^+ + H_2O \underset{slow}{\overset{k_3}{\rightarrow}} P + H_3O^+$	$P = k_1k_3[S][HA]/k_2[A^-]$ $= (k_1k_3/k_2K_a)[S][H^+]$ where $K_a = [H^+][A^-]/[HA]$	For protolytic case, expression applies when $k_3 << k_2[A^-]$ whether initial H^+ transfer is from Bronsted acid (HA) or H_3O^+.
II. General acid	$S + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$ $SH^+ + H_2O \underset{fast}{\overset{k_3}{\rightarrow}} P + H_3O^+$	$P = [S]\{\Sigma k_i[HA]_i\}$	Expression applies when $k_3 >> k_2[A^-]$; rate-controlling step is formation of intermediate SH^+. P written for presence of several Bronsted acids in system.
III. General acid	$S + HA \underset{k_2}{\overset{k_1}{\rightleftharpoons}} SH^+ + A^-$ $SH^+ + A^- \overset{k_3}{\rightarrow} P + HA$	$P = \frac{k_1k_3[S][HA]}{(k_2 + k_3)}$ or $P = k'[S][HA]$	Prototropic mechanism yields general acid catalysis regardless of relative sizes of k_2 and k_3.
IV. Specific OH^-	$HS + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S^- + BH^+$ $S^- + H_2O \underset{slow}{\overset{k_3}{\rightarrow}} P + OH^-$	$P = k_1k_3[S^-][B]/k_2[BH^+]$ $= (k_1k_3/k_2K_B)[S^-][OH^-]$	For protolytic case, expression applies when $k_3 << k_2[BH^+]$ regardless of nature of proton acceptor in first step.
V. General base	$HS + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S^- + BH^+$ $S^- + H_2O \underset{fast}{\overset{k_3}{\rightarrow}} P + OH^-$	$P = k[HS][B]$ $P = [HS]\{\Sigma k_i[B]_i\}$	Expression applies when $k_3 >> k_2[BH^+]$; rate-controlling step is formation of S^-; P written for presence of several Bronsted bases.
VI. General base	$HS + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} S^- + BH^+$ $S^- + BH^+ \overset{k_3}{\rightarrow} P + B$	$P = \frac{k_1k_3[S][HA]}{(k_2 + k_3)}$ or $P = k'[S][HA]$	Prototropic case yields general base catalysis regardless of relative sizes of k_2 and k_3.

Adapted from Laidler, K. J., *Chemical Kinetics*, McGraw-Hill, New York, 1965.

- To next lecture