Print version

CEE 697K
ENVIRONMENTAL REACTION KINETICS

Lecture #11

Kinetic Theory: Encounter Model, Transition State Model & Ionic Strength Effects
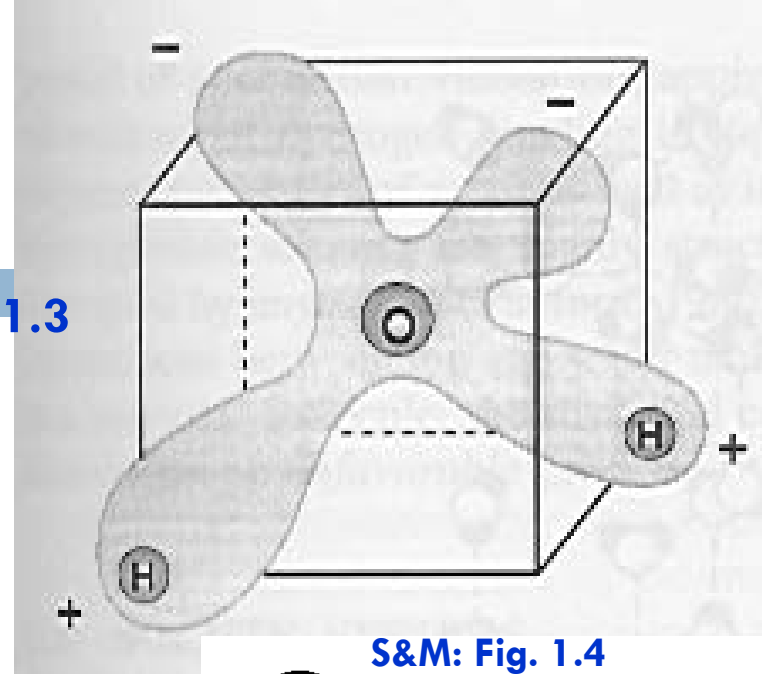
Brezonik, pp. 130-158
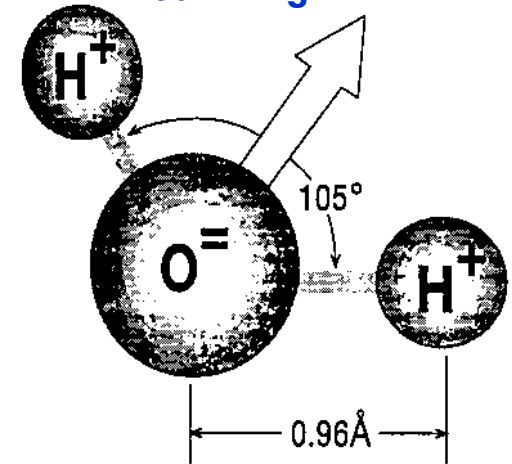
David A. Reckhow

Introduction

Structure of Water

S&M: Fig. 1.3

- sp³ 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
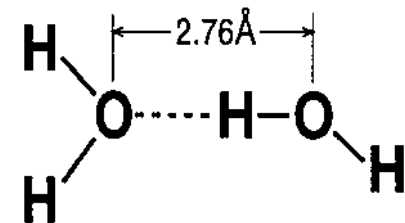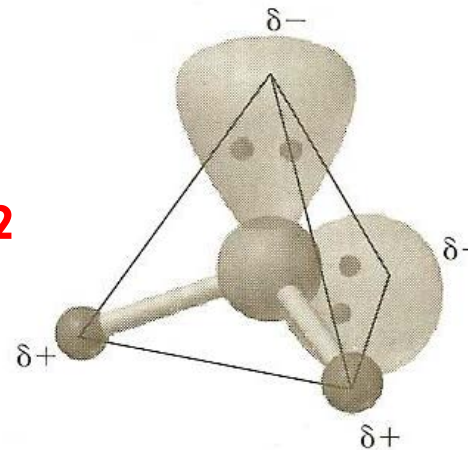 - High surface tension
  - Excellent polar solvent

S&M: Fig. 1.4

B: Fig 1.2

CEE697K Lec

Water's intermolecular structure

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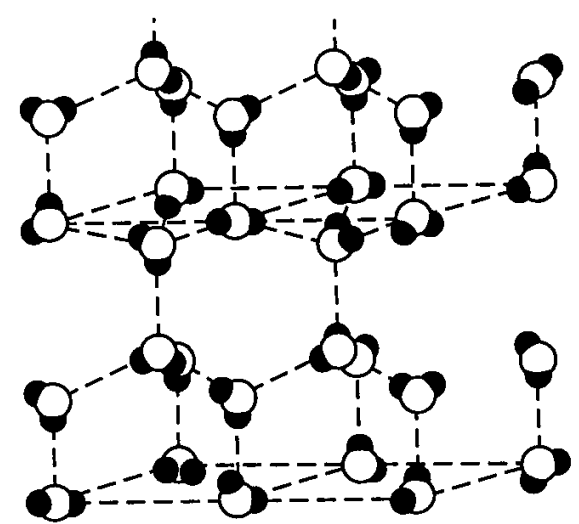   - 65 molecules @ 0°C
    - 12 molecules @ 100°C

CEE697K Lecture
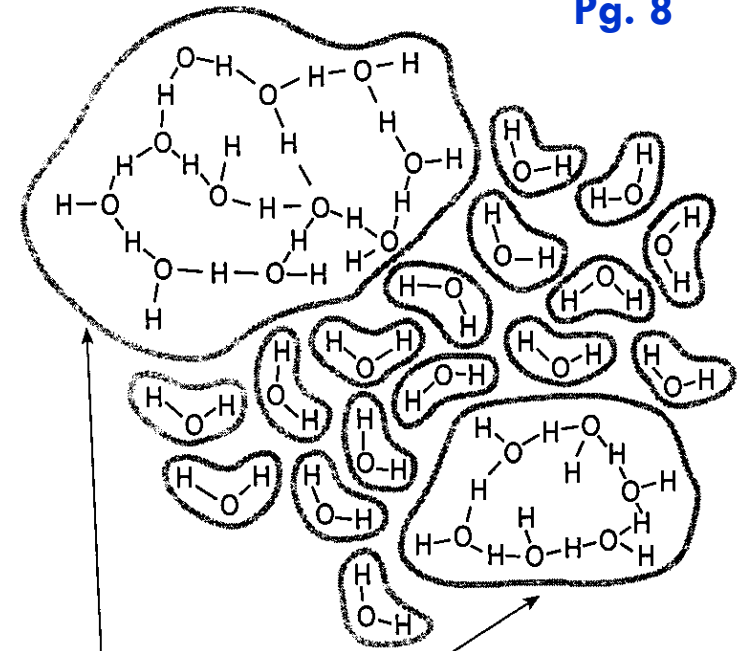
Fig. 1.5a
Pg. 8

Fig. 1.5b
Pg. 8

Clusters

Solutes in Water

□ Great solvent for ionic or ionizable substances

□ Ion-dipole bonds improves stability

   □ Energy increases with charge of ion and 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
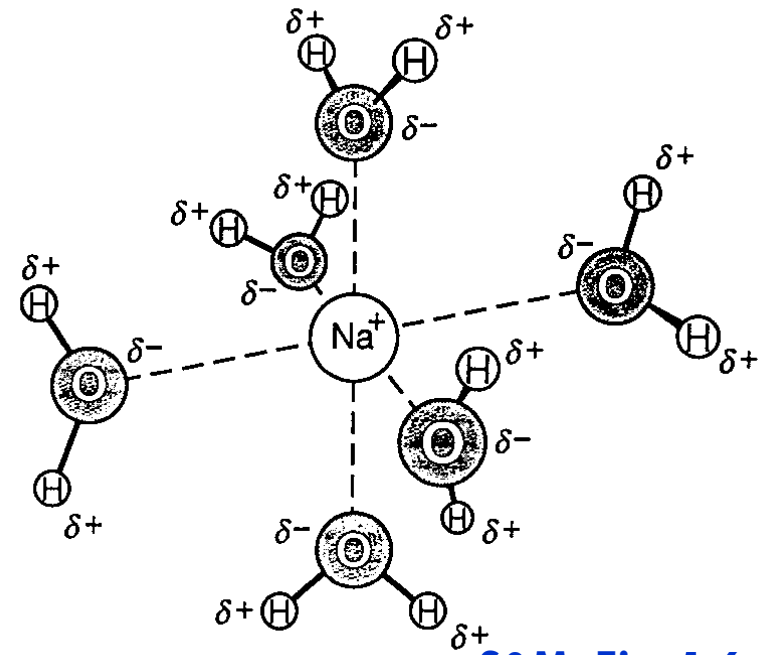
S&M: Fig. 1.6
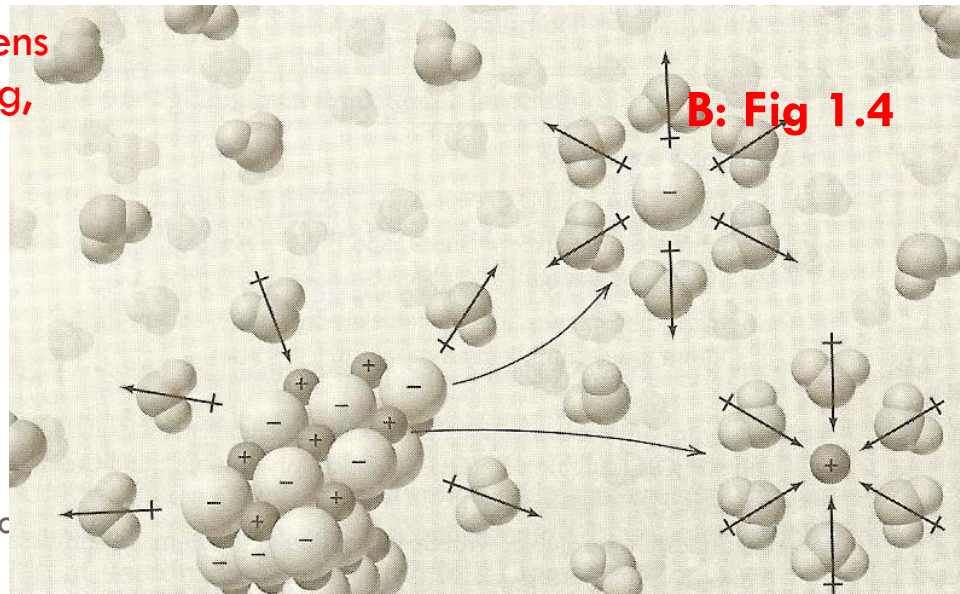
B: Fig 1.4

CEE697K Lec

Activation Energy

- ☐ Activation Energy must always be positive
  - ☐ Unlike $^{\Delta}H$, which may be positive or negative
- ☐ Differing reaction rates
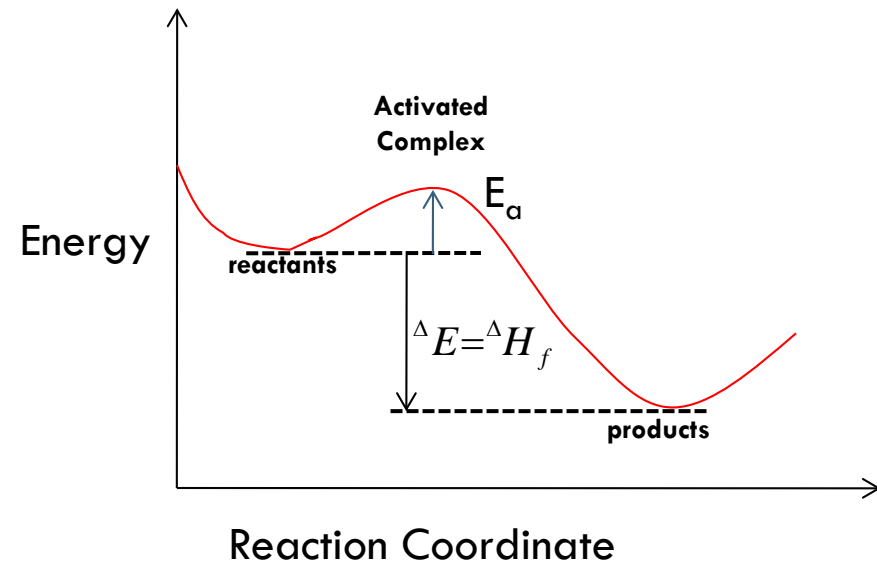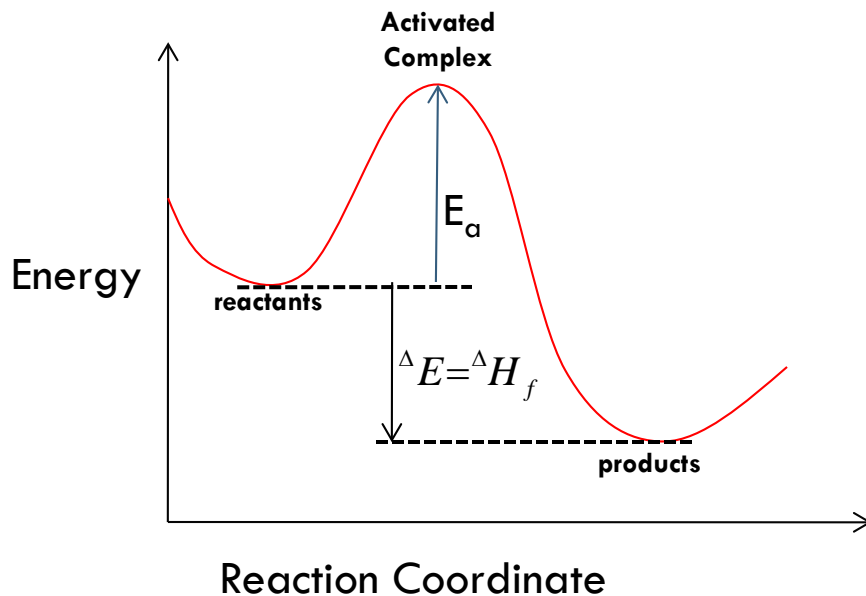
Activated
Complex

E_a

Energy

reactants

$^{\Delta}E = {}^{\Delta}H_f$

products

Reaction Coordinate

Activated
Complex

E_a

Energy

reactants

$^{\Delta}E = {}^{\Delta}H_f$

products

Reaction Coordinate

David A. Reckhow

Encounter Theory I

□ 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 ~ 1x10^{-5} cm^{2}s^{-1}, and λ = 4x10^{-8} cm, so τ ~ 2.5x10^{-11} s

If time between vibrations is ~ 1.5x10^{-13} s, then the average water molecule vibrates 150 times (2.5x10^{-11}/1.5x10^{-13}) in its solvent cage before jumping to the next one.

Encounter Theory II

□ 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:

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

← # molecules of "B" per cm^3

← # molecules of solvent per cm^3

Geometric packing factor   Molecular volume (cm^3)

CEE697K   Lecture #11

David A. Reckhow

Encounter Theory III

□ 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, $\gamma=0.74$, and the effective diffusion coefficient, $D_{AB} = D_A + D_B$, and $\lambda=r_{AB}$, the sum of the molecular radii

▪ Then we get:

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

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

CEE697K Lecture #11

David A. Reckhow

Encounter Theory IV

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

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

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

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

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

$n_B = [B]/N_o/1000$

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

$$Z_{e,AB} = 2.5 x 10^{-2} r_{AB} D_{AB} N_0 [A][B]$$

CEE697K Lecture #11   David A. Reckhow

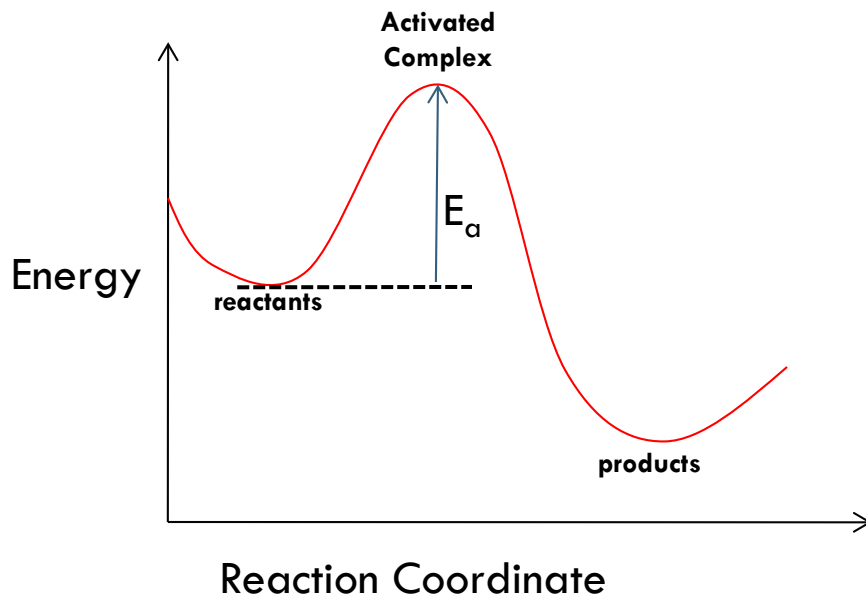# Encounter Theory V

□ Frequency Factor

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

▫ When $E_a = 0$, $k = A$

A

Activated Complex

E_a

Energy

reactants

products

Reaction Coordinate

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

David A. Reckhow

Transition State Theory I

- Consider the simple bimolecular reaction

$$A + B \xrightarrow{\quad k \quad} C$$
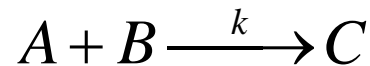
- Even though it is an elementary reaction, we can break it down into two steps

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

"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:

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

CEE697K Lecture #11

Activated Complex

E_a

Energy

reactants

products

Reaction Coordinate
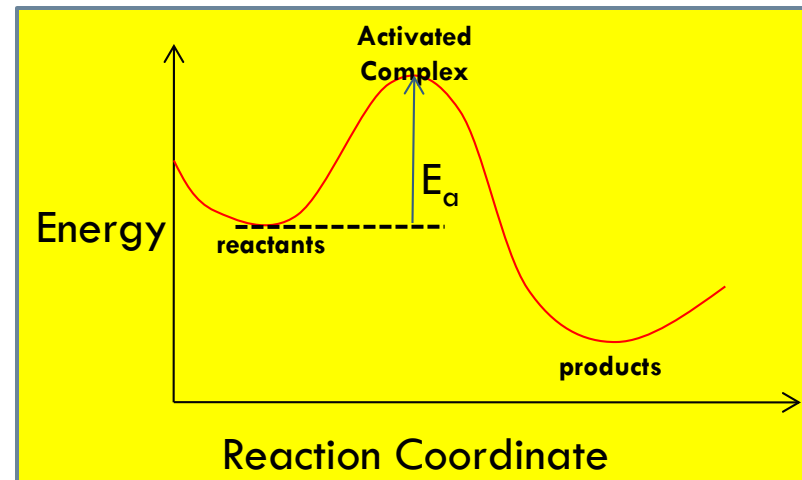
Transition State Theory II

☐ Now the transition state is just one bond vibration away from conversion to products

    ▫ Planks Law:

vibrational energy → $E_{vib} = h\nu$ ← Frequency of vibration (s^{-1})

Planck's constant (6.62 x 10^{-27} ergs·s)

    ▫ Bond energy must be in the thermal region:

Temperature (°K)

Bond energy → $E_{bond} \approx kT$

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

    ▫ So equating, we get:

$$h\nu = kT \qquad \nu = \frac{kT}{h}$$

    ▫ And since conversion occurs on the next vibration:

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

Transition State Theory III

☐ Now from basic thermodynamics:

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

▪ And also $\quad ^\Delta G^o = {^\Delta H} - T {^\Delta S}$

▪ So: $\quad K = e^{\Delta S/R} e^{-\Delta H/RT}$

☐ And combining: $\quad k = \dfrac{kT}{h} e^{\Delta S^{\neq}/R} e^{-\Delta H^{\neq}/RT}$

▪ Recall: $\quad ^\Delta E = {^\Delta H} - P{^\Delta V} \approx {^\Delta H}$

☐ And substituting back in: $\quad k = \left(\dfrac{kT}{h} e^{\Delta S^{\neq}/R} \right) e^{-E_a/RT}$

A

Activation Energy

☐ Activation Energy must always be positive

  ☐ Unlike $^\Delta H$, which may be positive or negative

☐ Differing reaction rates

CEE697K Lecture #11   David A. Reckhow
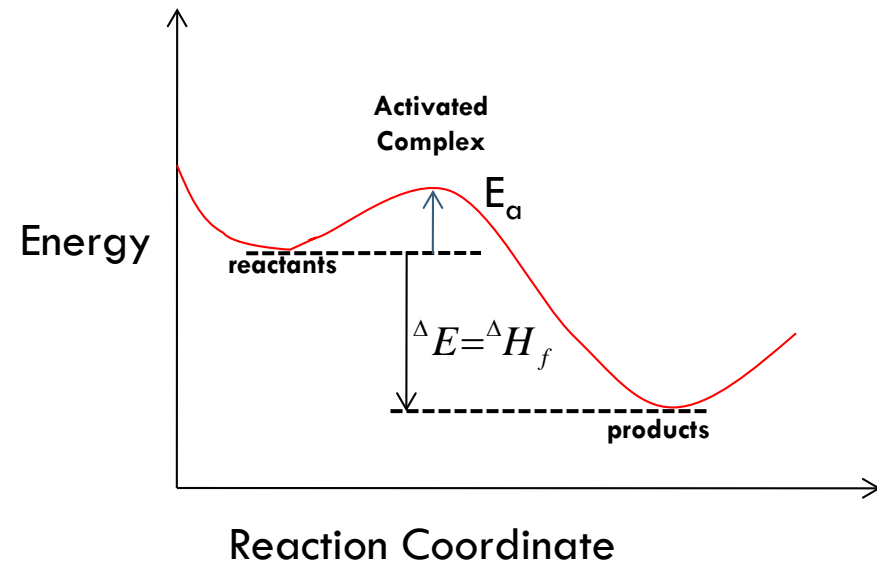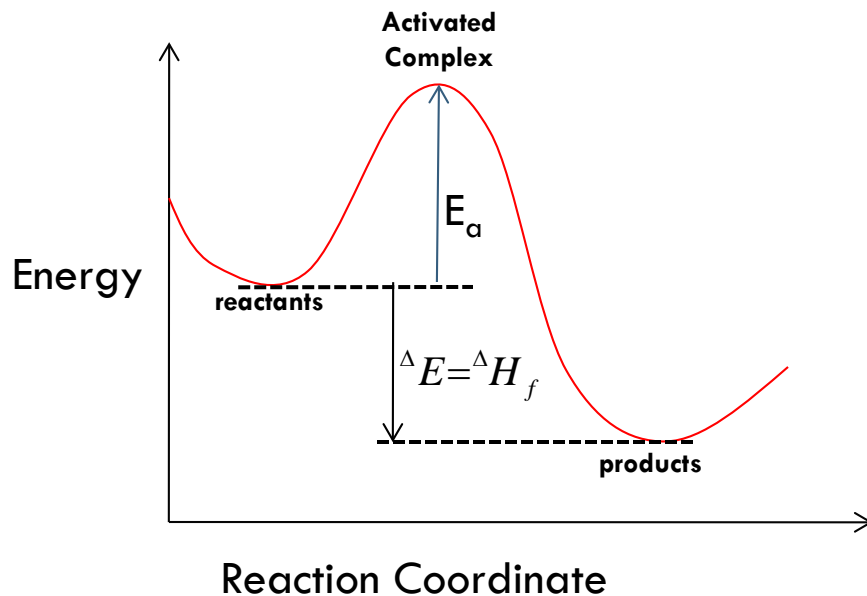
Temperature Effects

☐ Arrhenius Equation

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}$$
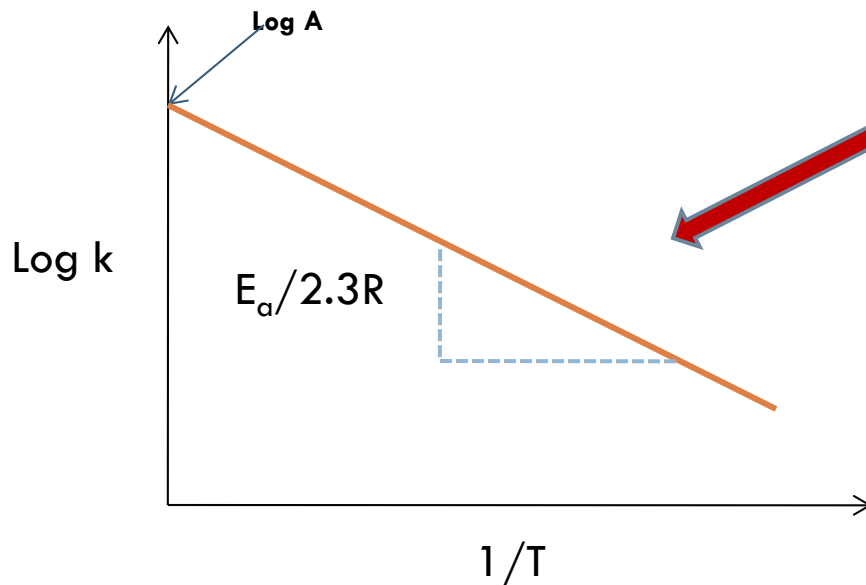
⟶

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

⟶

$$\ln \frac{k_2}{k_1} = \frac{(T_2 - T_1)E_a}{RT_1 T_2}$$

$$\ln \frac{K_2}{K_1} = \frac{(T_2 - T_1)^{\Delta} H_0}{RT_1 T_2}$$

Analogous to Van't Hoff Equation for Equilibria

Log A

Log k

$E_a/2.3R$

1/T

David A. Reckhow

Ionic Strength Effects

□ Ion-ion Reactions

  ◘ Based on activated complex theory

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

  ◘ So let's look at the equilibrium constant

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

  ◘ Which means:

$$\frac{d[C]}{dt} = \underbrace{\frac{kT}{h}\, K^{\neq}}[A][B]\left(\frac{\gamma_A\gamma_B}{\gamma_{AB^{\neq}}}\right)$$

$$K_2^{\circ} \ \ (\text{for I=0})$$

CEE697K Lecture #11   David A. Reckhow

Reactions with charged ions

□ **Using the Debye-Huckel Equation** $\quad -\log \gamma_i = 0.55 z_i^2 I^{0.5}$

- I<0.005

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

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

$$\boxed{z_A^2 + 2 z_A z_B + z_B^2}$$

□ **Using the Guntelberg Approximation** $\quad -\log \gamma_i = 0.55 z_i^2 I^{0.5} \Big/ (1 + I^{0.5})$

- 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.)

☐ Neutral species

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

$$\log k_2 = \log k_2^o + \left\{ b_A + b_B - b_{AB^{\neq}} \right\} I$$
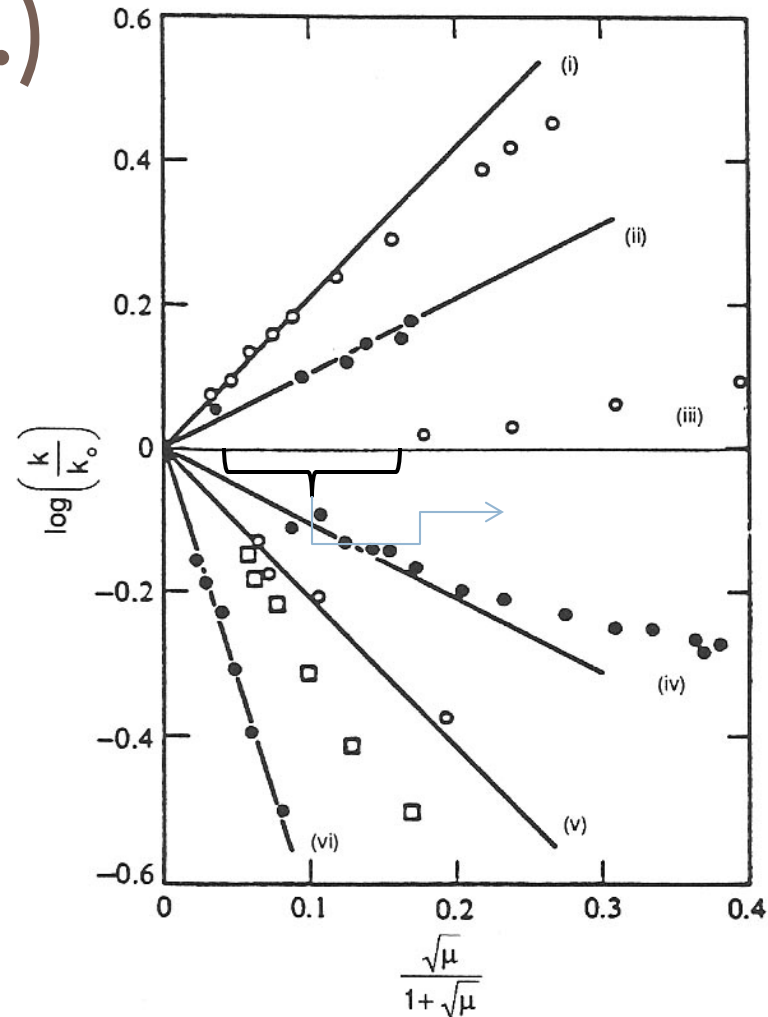
☐ Some case studies:

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.)

CEE697K Lecture #11

David A. Reckhow

Case Study: TCP

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

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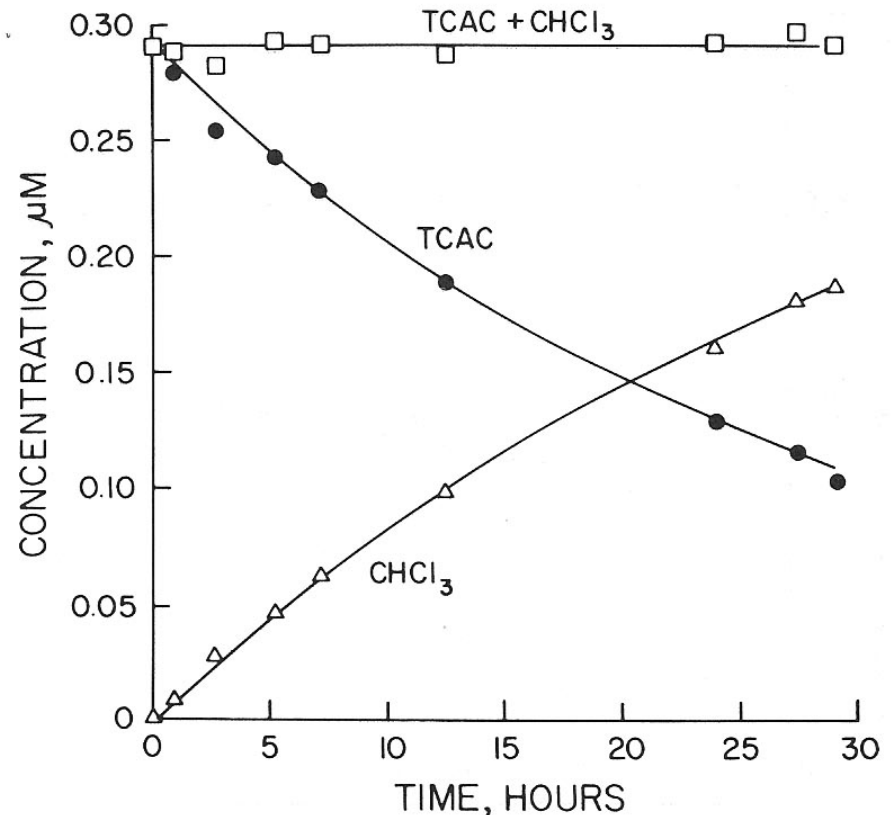 - Logically presumed to be a simple hydrolysis

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.

CEE697K Lecture #11

David A. Reckhow

TCP (cont.)

☐ **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

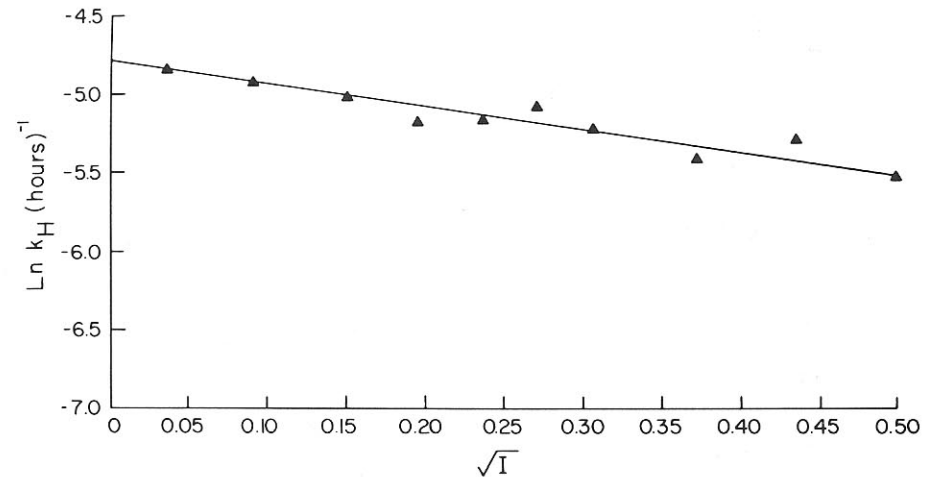 ■ High intercept

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

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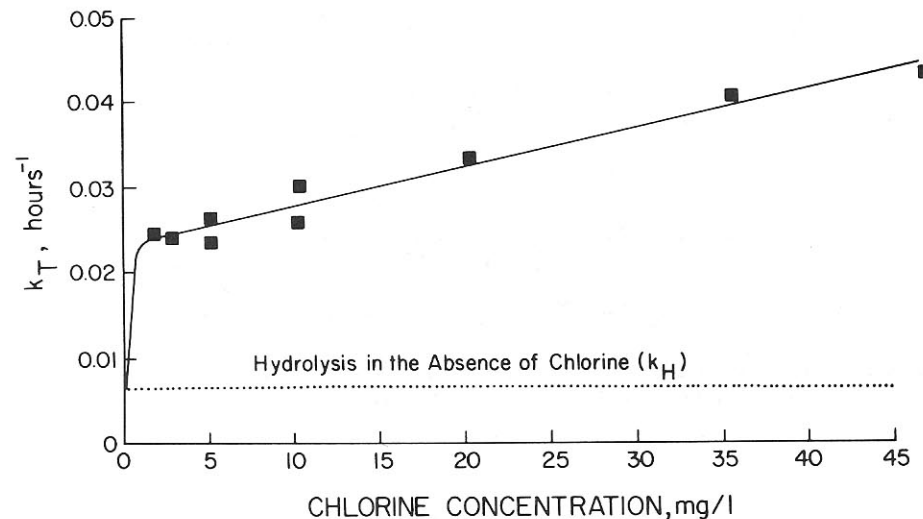

Hydrolysis in the Absence of Chlorine (k_H)

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

CEE697

Disagreement with prior study

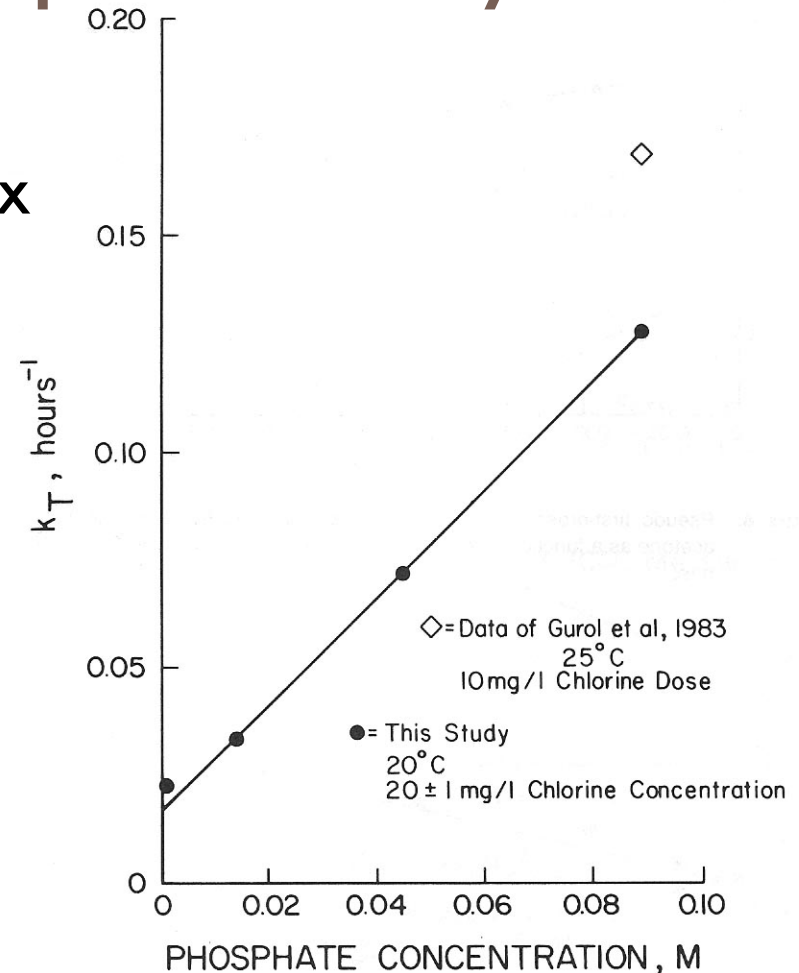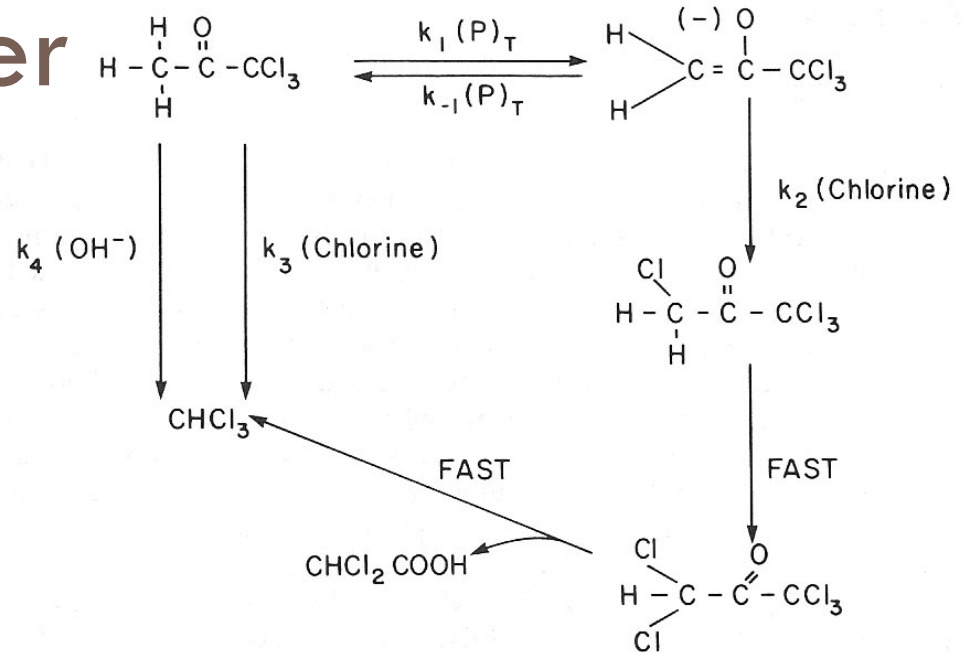- Gurol & Suffet showed 10x higher rate constants
- Phosphate?

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

David A. Reckhow

Putting it together

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

where
$k_1 = 1.25\ M^{-1}\ hr^{-1}$ $\qquad k_{-1} = 1.6 \times 10^{-7}/k_{TCAC}$
$k_3 = 32\ M^{-1}\ hr^{-1}$ $\qquad k_2 > 10^{-4}/k_{TCAC}$
$k_4 = 64,000\ M^{-1}\ hr^{-1}$

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

Figure 12. Hypothetical mechanism for the decomposition of trichloroacetone to chloroform in the presence of intermediate concentrations of phosphate at pH 7.
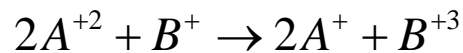
CEE697K Lecture #11   David A. Reckhow
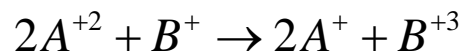
Catalysis

□ 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:

$$A^{+2} + C^{+} \rightarrow A^{+} + C^{+2}$$

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

$$C^{+3} + B^{+} \rightarrow C^{+} + B^{+3}$$

$$2A^{+2} + B^{+} \rightarrow 2A^{+} + B^{+3}$$
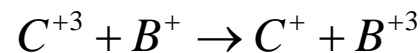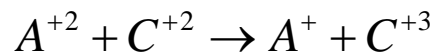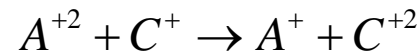
"C" serves as a sort of charge-transfer facilitator, since "B" does not exist in a divalent state

David A. Reckhow

Summary

Table 4-1. Mechanisms of Acid-Base Catalysis

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

- <u>To next lecture</u>

David A. Reckhow