

# Week 11 Recitation

Chapter 9: Kinetics cont.

# Updates

- Average (excluding non-submissions) = 73%
- Assignments 8 and 9 will be graded by this weekend.
- Doodle poll: Office hours will be held on Tuesday from 12-1:30 pm
- November 25<sup>th</sup>: Last day of in-person lectures – considering case spikes, should move online next week...
- We have heard your complaints about the recitations and will include more practice problems and examples.

Questions?

# Objectives

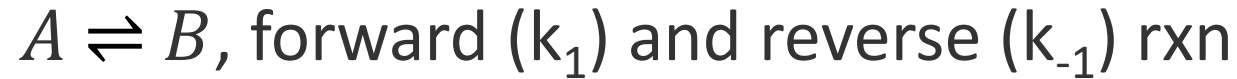
1. Reverse processes and interpreting mechanisms
2. Approximations and their meaning
  - Initial-rate approximation
  - Pre-equilibrium approximation
  - Steady-state approximation
2. Arrhenius and temperature dependence of kinetics
3. Transition state theory and collision theory (Ch. 8 and 9)

# Kinetics and Equilibrium

Up to this point, examples have consisted of single-step, stoichiometric reactions:

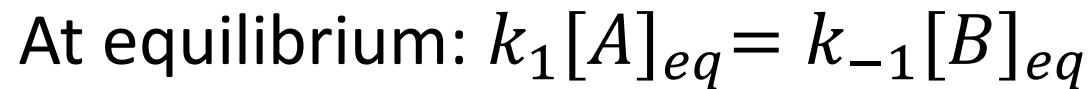


Complete reactions are a simplification - consider an equilibrium:

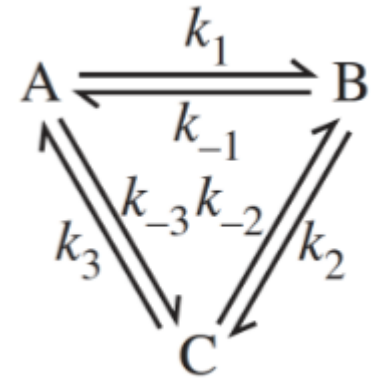


Rate of the disappearance of reactant A given by:

$$-\frac{d[A]}{dt} = k_1[A] - k_{-1}[B]$$



$$\frac{k_1}{k_{-1}} = \frac{[B]_{eq}}{[A]_{eq}} = K_{eq}$$



## Example: 9.15a

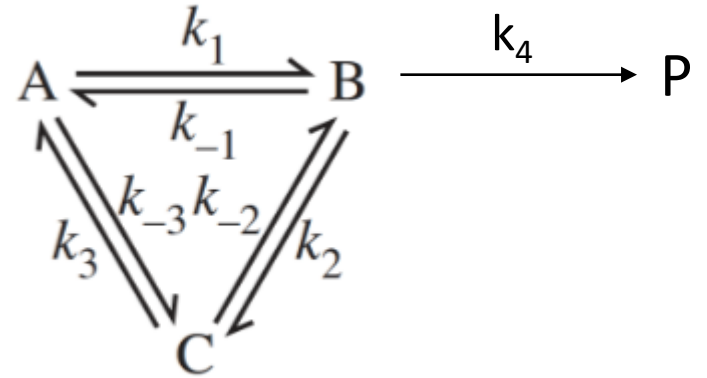
a. Write a differential equation for the rate of the formation of B.

Identify which species are consumed to produce B:

A ( $k_1$ ) and C ( $k_{-2}$ )

B is consumed to produce:

A ( $k_{-1}$ ), C ( $k_2$ ), and P ( $k_4$ , irreversible)



Related note:

$$\frac{d[B]}{dt} = k_1[A] + k_{-2}[C] - k_{-1}[B] - k_2[B] - k_4[B]$$

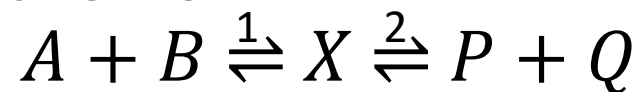
$$\frac{d[B]}{dt} = k_1[A] + k_{-2}[C] - (k_{-1} + k_2 + k_4)[B]$$

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{[B]_{eq}[C]_{eq}}{[C]_{eq}[A]_{eq}}$$

$$K = \frac{k_1}{k_{-1}} = \frac{k_{-2}k_{-3}}{k_2k_3}$$

# Complex Reactions and Approximations

Consider a complex reaction scheme:



Initial-rate approximation: At  $t = 0$ ,  $[P] = 0$  and -2 step can be ignored,

$$\frac{d[P]}{dt} = k_2[X]$$

Pre-equilibrium approximation: If step 1 rapidly reaches eq. and step 2 is slow,

$$k_1[A][B] = k_{-1}[X]$$

$$\frac{d[P]}{dt} = k_2[X] \equiv \frac{k_2 k_1}{k_{-1}} [A][B]$$

## Example: 9.15b

b. Write a diff. eq. for the formation of P in terms of [A],  $K_{eq}$ , and  $k_4$ .

Identify the appropriate approximation:

ABC fast,  $B \rightarrow P$  **slow**  $\therefore$  **pre-equilibrium approximation**

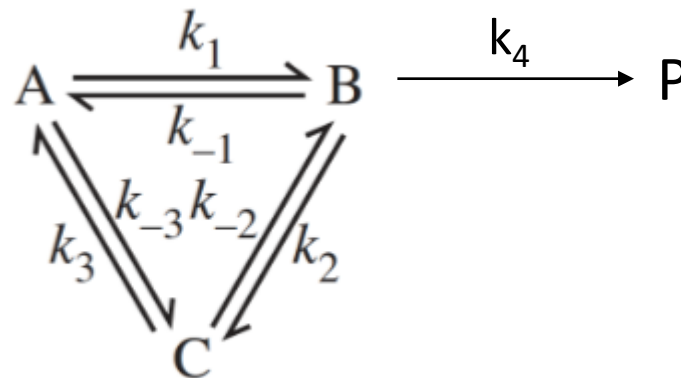
Define  $K_{eq}$ :

$$K_1 = \frac{k_1}{k_{-1}}, K_2 = \frac{k_{-2}}{k_2}, K_3 = \frac{k_{-3}}{k_3}$$

Ans:

$$\frac{d[P]}{dt} = k_4[B] = k_4 K_1 [A]$$

Work is on the following slide.



Recall:

$$K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{[B]_{eq}[C]_{eq}}{[C]_{eq}[A]_{eq}}$$

$$K = K_1 = K_2 K_3$$



b. Write a diff. eq. for the formation of P in terms of [A],  $K_{eq}$ , and  $k_4$ .

Recall:  $\frac{d[B]}{dt} = k_1[A] + k_{-2}[C] - k_{-1}[B] - k_2[B] - k_4[B]$

If  $K_2 = \frac{k_{-2}}{k_2} = \frac{[B]}{[C]}$ , then  $k_{-2} = k_2 \frac{[B]}{[C]}$

Substitute  $k_{-2}$ :

$$\frac{d[B]}{dt} = k_1[A] + \left( k_2 \frac{[B]}{[C]} \right) \cancel{[C]} - k_{-1}[B] - k_2[B] - k_4[B]$$

$$\frac{d[B]}{dt} = k_1[A] + \cancel{k_2[B]} - k_{-1}[B] - \cancel{k_2[B]} - k_4[B]$$

If  $B \rightarrow P$  is slow, then  $k_4[B] = 0$ :

$$\frac{d[B]}{dt} = k_1[A] - k_{-1}[B], \text{ apply pre-eq. approximation: } [B] = \frac{k_1}{k_{-1}} [A] \equiv K_1[A]$$

$$\frac{d[P]}{dt} = k_4[B] = k_4 K_1[A]$$

c. Write an expression for P as a function of time given:

$$[A] = [A]_0 \text{ and } [B] = [C] = [P] = 0$$

Work:

$$[P] = [A]_0 - ([A] + [B] + [C])$$

$$\text{Recall: } [B] = \frac{k_1}{k_{-1}} [A] \equiv K_1 [A] \therefore [C] = \frac{k_{-3}}{k_3} [A] \equiv K_3 [A]$$

$$\text{Substitute into mass balance: } [P] = [A]_0 - ([A] + K_1 [A] + K_3 [A]) = [A]_0 - [A](1 + K_1 + K_3)$$

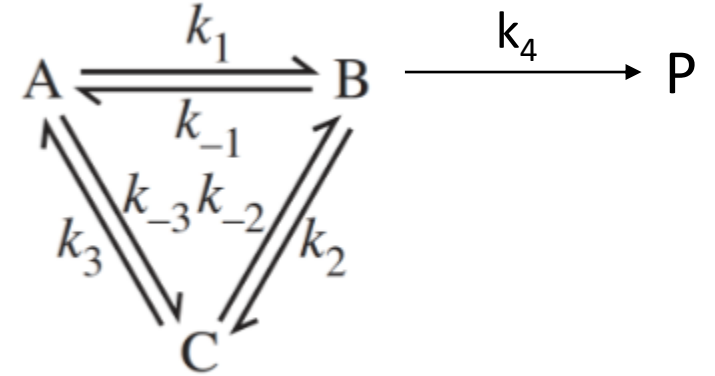
Recall rate expressions:

$$\frac{d[P]}{dt} = k_4 K_1 [A] = -\frac{d[A]}{dt} (1 + K_1 + K_3) \therefore \frac{d[A]}{dt} = -k [A], \text{ where } k = \frac{k_4 K_1}{(1 + K_1 + K_3)}$$

$$\int \frac{d[A]}{[A]} = -k \int dt \equiv \ln([A]) = -kt + C, \text{ exponentiate: } [A] = [A]_0 e^{-kt}$$

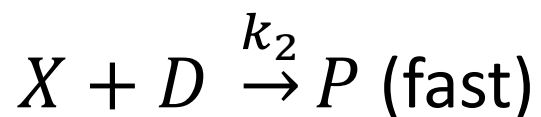
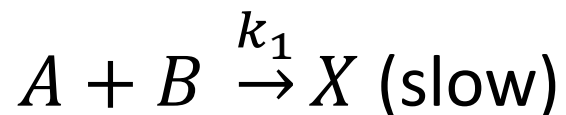
$$\text{Substitute: } [P] = [A]_0 - [A]_0 e^{-kt} = [A]_0 (1 - e^{-kt})$$

$$\text{Ans: } [P] = [A]_0 (1 - e^{-kt})$$



# Steady-state Approximation

Rather than a slow conversion from intermediate to product, assume the intermediate is produced slowly and consumed rapidly:



Therefore, the rate of the first, slow step approximates that of the second step:

$$k_1[A][B] \cong k_2[X][D]$$

$$\frac{d[P]}{dt} = k_2[X][D] = k_1[A][B], \text{ and if represented in terms of the intermediate:}$$

$$\frac{d[X]}{dt} = -k_2[X][D] + k_1[A][B] \cong 0 \text{ (approx. 0 b/c [X] treated as constant)}$$

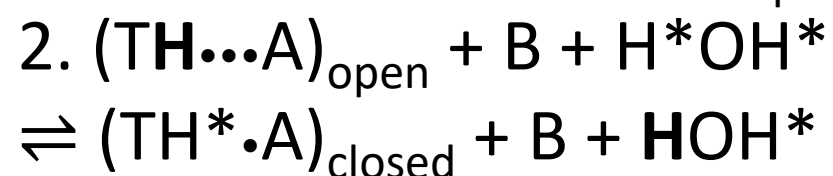
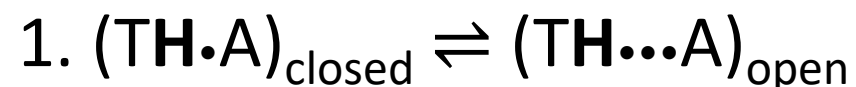
## Example: 9.17a

a. Use the steady-state approximation for  $[(\text{TH}\cdots\text{A})_{\text{open}}]$  to obtain initial rate of exchange.

Steady-state approximation:  $d[(\text{TH}\cdots\text{A})_{\text{open}}]/dt = 0$

Write out full expression based on mechanism:

Mechanism: Imino H ex.



$$\frac{d[(\text{THA})_{\text{open}}]}{dt} = k_{op}[(\text{THA})_{\text{closed}}] - k_{cl}[(\text{THA})_{\text{open}}] - k_{tr}[(\text{THA})_{\text{open}}][\text{B}] = 0$$

$$k_{op}[(\text{THA})_{\text{closed}}] = k_{cl}[(\text{THA})_{\text{open}}] + k_{tr}[(\text{THA})_{\text{open}}][\text{B}]$$

$$\frac{k_{op}[(\text{THA})_{\text{closed}}]}{k_{cl} + k_{tr}[\text{B}]} = [(\text{THA})_{\text{open}}], \text{ substitute: } \frac{d[(\text{TH}^*\text{A})_{\text{closed}}]}{dt} = k_{tr}[(\text{THA})_{\text{open}}][\text{B}]$$

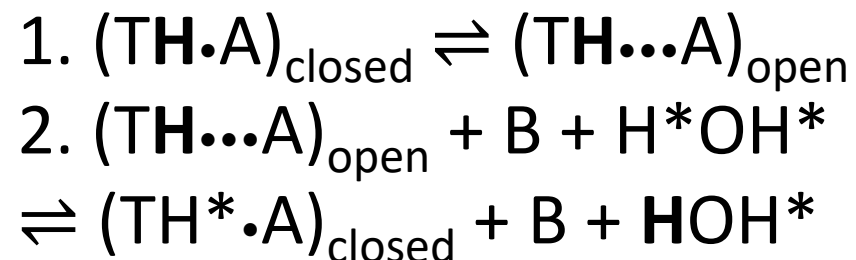
## Example: 9.17a cont.

a. Use the steady-state approximation for  $[(\text{TH}\cdots\text{A})_{\text{open}}]$  to obtain initial rate of exchange ( $k_{\text{ex}}$ ).

$$\frac{d[(\text{TH}^*\text{A})_{\text{closed}}]}{dt} = k_{tr}[(\text{THA})_{\text{open}}][\text{B}]$$

$$\frac{d[(\text{TH}^*\text{A})_{\text{closed}}]}{dt} = \frac{k_{tr}k_{op}[(\text{THA})_{\text{closed}}][\text{B}]}{k_{cl}+k_{tr}[\text{B}]}$$

Mechanism:



Note that  $[\text{B}]$  is consumed and regenerated in second step!

Ans:

$$k_{\text{ex}} = \frac{k_{tr}k_{op}[\text{B}]}{k_{cl}+k_{tr}[\text{B}]}$$

# Arrhenius and Temperature Dependence

$T \propto KE$  and chemistry occurs when particles collide with sufficient energy ( $E_A$ ) and in the correct orientation ( $p$ ) i.e. related to collision theory (Ch. 8)

Arrhenius and contemporaries observed the following:

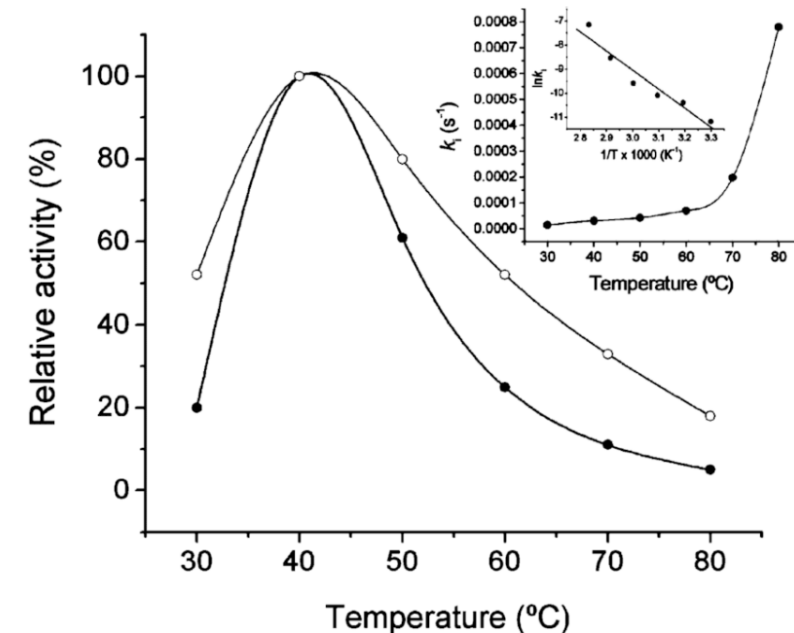
$$\ln(k) = -\frac{E_A}{RT} + \ln(A)$$

Therefore, one can plot  $\ln(k)$  as a function of  $1/T$  to determine  $E_A$ !

Measure  $k$  at two temperatures to determine  $E_A$ :

$$\ln(k_2) - \ln(k_1) = -\frac{E_A}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)$$

Biological systems begin to breakdown at higher  $T$ , thus rate of reaction decreases past a certain point.



# Transition State Theory: A conceptual description

Consider the free energy landscape of  $A + B \rightarrow P$ :

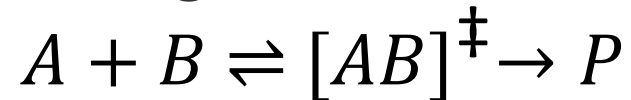
Transition state theory proposes a high energy intermediate  $[AB]^\ddagger$

$$d_r G = dG_F^\ddagger - dG_R^\ddagger$$

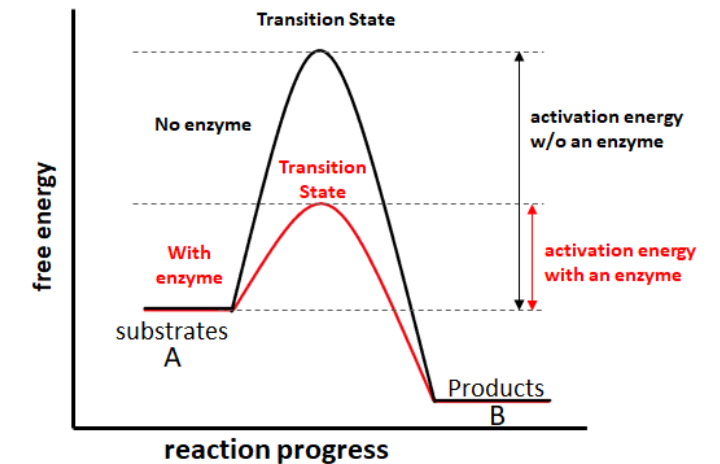
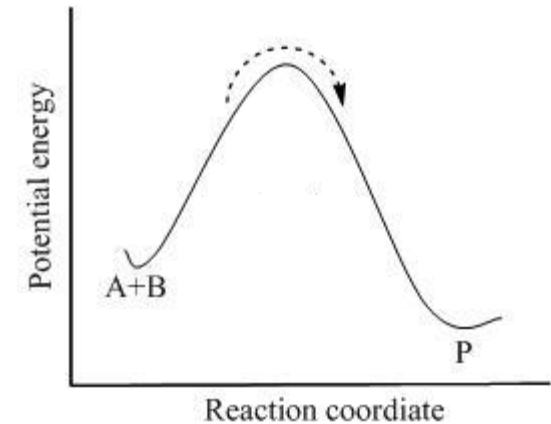
It is very difficult/impossible to determine  $[AB]^\ddagger$ :

- Very high E species, short lifetime
- Some transition states of gases (late 80s-early 90s)

Represented according to transition state theory:



Enzymes lower the activation energy of a reaction  
(Ch. 10)



# Concept Checks

When is it appropriate to make the initial-rate approximation?

When is it appropriate to make the pre-equilibrium approximation?

When is it appropriate to make the steady-state approximation?

What aspects of collision theory are present in the Arrhenius model?

Explain how the variables in the Arrhenius equation are related.

Explain how the Arrhenius equation can be used experimentally.

Under what conditions is the Arrhenius model a poor fit? Why is this the case?

An enzyme lowers the activation energy of a reaction. Using transition state theory, explain the consequences of this for: 1) The reaction kinetics and 2) The population levels for all species.



Questions?