Ch. 13 Chemical Kinetics

- "we can predict reaction products, + energetics, now we want to learn about speeds"
- some reactions faster than others!

"What controls how fast:

- car rusts
- medicine reacts
- TNT explodes?
- milk sours
- ice cream metabolizes
- sugar in candy bar $\Rightarrow CO_2 + H_2O$ + energy

Factors (other than chems themselves)

① concentrations

② temperature

③ "catalysts"

13.1 Reaction Rate

↓

change (in x) per time interval $$\frac{\overset{\text{"change in"}}{\Delta} x \leftarrow \text{"thing changing"}}{\Delta t}$$

Ex: mph

Any average rate can be determined between measurements at 2 points in time

Rate: change in something (x) per time interval $= \frac{\Delta x}{\Delta t}$

Ex: What is average speed of car that between 10:00 (t_1) and 10:30 (t_2) travels from point 0 (x_1) to 30 miles away (x_2)?

$$\frac{\Delta x}{\Delta t} = \frac{x_2 - x_1}{t_2 - t_1} = \frac{30\text{ mi} - 0\text{ mi}}{10{:}30 - 10{:}00} = \frac{30\text{ mi}}{30\text{ min}} = \boxed{\frac{1\text{ mile}}{\text{minute}}}$$

$$\frac{1\text{ mile}}{\text{min}} \Big| \frac{60\text{ min}}{1\text{ hour}} = \frac{60\text{ miles}}{1\text{ h}} = \boxed{60\text{ mph}}$$

Ex $A \longrightarrow B$

Chemical rates defined by changes in concentration (M) per time interval

$$rate = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

Notes

① rates can be written based on products or reactants, which are linked by stoich.
$\Rightarrow$ [B] increases as [A] decreases (Fig 15.1)

② rate (of change) decreases with time
- declines as S.M. is depleted
(T-110, Table 14.2, Brown)

③ Rate Can be Found from:
a. 2 Time Points (T-110, Table 14.2, Brown)
b. Known rate of change for another chemical (factor coefficients!)
c. Graphical analysis (not tested)
- tangent slope, or calculus ($rate_t = \frac{d[B]}{dt}$)
(T-111, Fig 15.2, Brown)

④ The Relative rate of change for reactants/products has stoichiometric relationship.

$t\text{-BuBr} \xrightarrow{H_2O} t\text{-BuOH}$

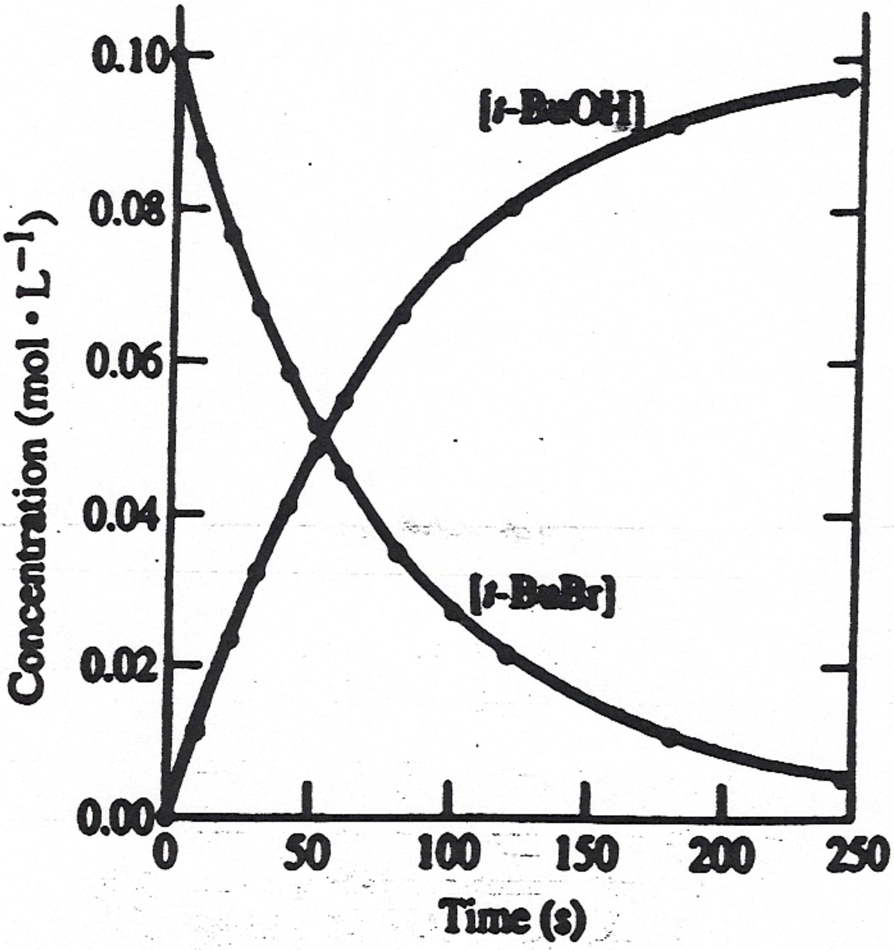


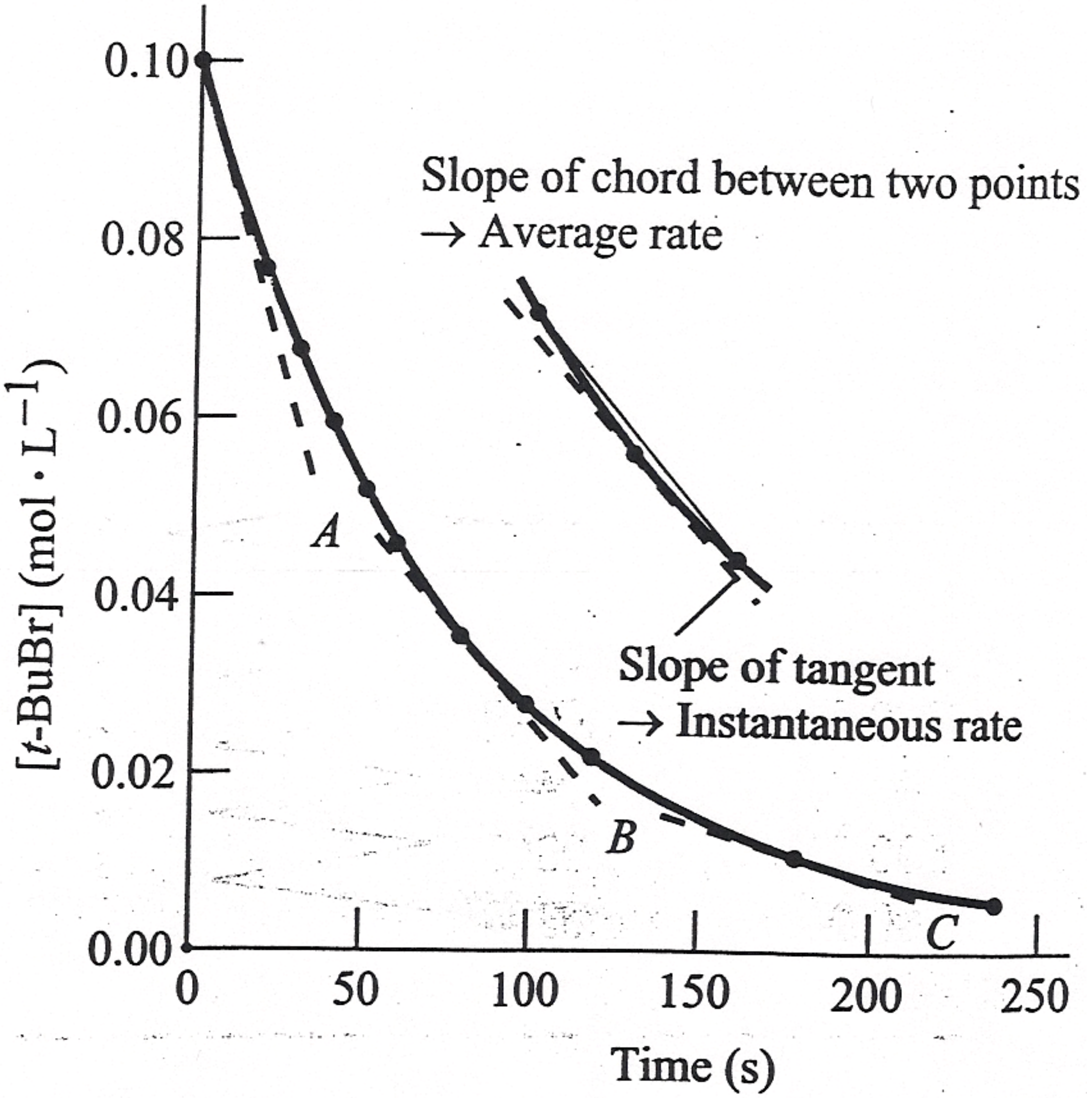
FIGURE 15.1 Concentration Changes during the Reaction of *t*-Butyl Bromide with Hydroxide Ion The reaction was carried out with excess water at 55°C in 20% aqueous ethanol.

TABLE 14.2 Rate Data for Reaction of C_4H_9Cl with Water

Time, *t* (s)	$[C_4H_9Cl]$ (*M*)	Average Rate (*M*/s)
0.0	0.1000	1.9×10^{-4}
50.0	0.0905	1.7×10^{-4}
100.0	0.0820	1.6×10^{-4}
150.0	0.0741	1.4×10^{-4}
200.0	0.0671	1.22×10^{-4}
300.0	0.0549	1.01×10^{-4}
400.0	0.0448	0.80×10^{-4}
500.0	0.0368	0.560×10^{-4}
800.0	0.0200	
10,000	0	

CHEMISTRY: The Central Science 7/e
by Brown/Lemay/Bursten

T 111 Fig. 15.2 Rate of Hydrolysis of *t*-Butyl Bromide



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$2A + 1B \rightarrow 1C + 2D$

① If the concentration of B is dropping at a rate of 0.5 M/min, what is the rate of change for the following?

A:

C:

D:

② If A is dropping at 0.8 M/min, what is the rate of change for:

B:

C:

D:

③ Write the rate law, relative to each, beginning with B. Put +/– signs so that rate ends up being positive.

13.3 Rate Law and Order of Reaction:

A. The "Overall Order" of a reaction is the sum of the individual orders (practice 13-7)

B. Calculations for 1st Order Reactions

$r = k[A] = -\frac{\Delta[A]}{\Delta t}$

Calculus, integrate

$\ln[A]_t = -kt + \ln[A]_0$ $y = mx + b$ form!

(useful for graphical analysis) - linear plot of $\ln[A]_t$ vs. time gives slope $= -k$

u13.2a ∴ only 1st order as straight line

Or $\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$ Used for 2-point analysis

Application: find
1. $[A]_t$ at any time
2. time for $[A]_0 \rightarrow [A]_t$
3. k

Handling "ln"

① enter $[A]_0 / [A]_t$ ratio, then hit LN button

② "antiln" $\ln \frac{100}{x} = 1.83$ find x

enter 1.83, hit e^x

result: $6.23 = \frac{100}{x}$ $\boxed{x = \text{[redacted]}}$

$x = 100/6.23 = \boxed{16}$

$$\boxed{2A} + 1B \longrightarrow 1C + 2D$$

① If the concentration of B is dropping at a rate of 0.5 M/min, what is the rate of change for the following?

A: ↓ 1.0 $\bar{M}$

C: ↑ 0.5 $\bar{M}$

D: ↑ 1.0 $\bar{M}$

② If A is dropping at 0.8 M/min, what is the rate of change for:

B: ↓ 0.4 $\bar{M}$

C: ↑ 0.4 $\bar{M}$

D: ↑ 0.8 $\bar{M}$

③ Write the rate law, relative to each, beginning with B. Put +/– signs so that rate ends up being positive.

$$\text{rate} = \frac{\Delta[B]}{\Delta t} = \frac{\Delta \frac{1}{2}(A)}{\Delta t} = \frac{-\Delta 1(C)}{\Delta t} = \frac{-\Delta \frac{1}{2}(D)}{\Delta t}$$

(13-5)

$2A \rightarrow B$

① If $\frac{\Delta A}{\Delta t} = -0.10$ M/s, what is $\frac{\Delta B}{\Delta t}$?

② $A \rightarrow B$

a. Calculate the average rate from 0 → 10 sec if [A] goes from 0.1000 → 0.0876 M?

b. If [B] = 0 at 0 sec, what is $\underset{[B]}{\text{it}}$ after 5 sec?

13-5

$2A \rightarrow B$

① If $\frac{\Delta A}{\Delta t} = -.010\ M/s$, what is $\frac{\Delta B}{\Delta t}$?

$$\boxed{+.05\ M/s}$$

② $A \rightarrow B$

a. Calculate the average rate from $0 \rightarrow 10$ sec if $[A]$ goes from $0.1000 \rightarrow 0.0876\ M$?

$$\frac{\Delta A}{\Delta t} = \frac{.1000 - .0876}{10s - 0s} = \frac{.00124\ M}{10 sec} - rate = \boxed{\frac{+.00012\ M}{1\ sec}}$$

b. If $[B] = 0$ at 0 sec, what is it after 5 sec? $[B]$

$$B: \frac{.000124}{sec} \times 5\ sec = \boxed{.00062\ M}$$

(13-6)

13.2 Effect of Concentrations on Rates

- since reactants must collide to react, rates depend on concentrations

A. General "Rate Law"

$rate = k[A]^x[B]^y[C]^z \cdots$ A, B, C reactants or catalyst

① describes dependence of rate on each conc.

$rate \propto [A]^x$ $rate \propto [B]^y$ $rate \propto [C]^z$

- ex: if $x = 0$ then doubling [A] ⇒ no change in rate
  - $x = 1$ " " ⇒ rate doubles (direct proportion
  - $x = 2$ ⇒ ×4

② k is "rate constant": rate changes with time & conc, but k does not

③ each reaction has own rate law and constant

- both must be determined experimentally
- can't tell from eqn stoichiometry

13.7-1 $\boxed{\text{problem: find k given rate law, rate + conc.}}$

④ given rate law and k, can find rate given conc

problem 13.7-2

⑤ Examples of rate laws - wide variety, can't deduce from balanced eqn

⑥ "Order" = exponent for reactant $x=1 \Rightarrow$ first $2 \Rightarrow$ second, etc.

$\text{rate} = k[A]^2$

① If rate is 3.6×10^{-3} M/s when $[A] = 0.20$ M, what is k?

② If $k = 0.090\ M^{-1}s^{-1}$ and $[A] = 0.60$ M, what is the rate?

Rate Law Examples	Effect on Rate when [A] is		"Order" of A	Overall Rxn Order	Rate Constant Units
	doubled	tenfold			
$r = k[A]$					
$r = k[A][B]$					
$r = k[A]^2[B]$					
$r = k[A]^3[B]$					
$r = k[B]$					
$r = k[A]^{1/2}[B]$					

$\text{rate} = k[A]^2$

① If rate is 3.6×10^{-3} M/s when $[A] = 0.20\,M$, what is k?

$3.6 \times 10^{-3} \frac{M}{s} = k\,(0.20\,M)^2$

$k = \frac{3.6 \times 10^{-3}\ M/s}{.040\ M^2}$

$\boxed{k = 0.090\ M^{-1}s^{-1}}$

② If $k = 0.090\ M^{-1}s^{-1}$ and $[A] = 0.60\,M$, what is the rate?

$r = (0.090\ M^{-1}s^{-1})(.60\,M)^2 = \boxed{0.324\ M \cdot s^{-1}}$

Rate Law Examples	Effect on rate when [A] is doubled	tenfold	"Order" of A	Overall Rxn Order	Rate Constant Units
$r = k[A]$	x2	x10	1st	1st	s^{-1}
$r = k[A][B]$	x2	x10	1st	2nd	$M^{-1}s^{-1}$
$r = k[A]^2[B]$	x4 (2^2)	x100 (10^2)	2nd	3rd	$M^{-2}s^{-1}$
$r = k[A]^3[B]$	x8 (2^3)	x1000 (10^3)	3rd	4th	$M^{-3}s^{-1}$
$r = k[B]$	no	change	zero	1st	s^{-1}
$r = k[A]^{1/2}[B]$	$1.4 = \sqrt{2}$	$\sqrt{10} =$	1/2	1½	$M^{-1/2}s^{-1}$

6. Determining Rate Laws
need either
① known mechanism (13.7)
or ② systematic variation of each reactant, with experimental measurement of rate
* each reactant, one at a time
* only one reactant should vary
(practice 13-9.1)

General determination of "order", when numbers aren't simple:

$$\text{ratio of 2 rates}\left\{\frac{r_2}{r_1} = \underbrace{\left[\frac{[A]_2}{[A]_1}\right]}_{\text{ratio of 2 concentrations}}^{x} \leftarrow \text{"order" for } [A]\right.$$

Rate effect when A is doubled: ~~and the~~

Rate		Order of [A]	Means
doubles	$2 = 2^x$	1	$r \propto [A]^1$
x 4	$4 = 2^x$	2	$r \propto [A]^2$
x 8	$8 = 2^x$	3	$r \propto [A]^3$
unchanged	$1 = 2^x$	0	$r \propto [A]^0 \equiv 1$

① $A + B \longrightarrow C + D$

	[A]	[B]	rate
1.	0.20	0.20	0.0078
2.	0.40	0.20	0.0156
3.	0.20	0.40	0.0078

order of A:

B:

Rate law:

k (number + units):

what is rate when [A] = 0.80, [B] = 0.80

② $A + B \longrightarrow C + D$

[A]	[B]	rate
0.20	0.20	0.15
0.40	0.20	0.30
0.20	0.40	0.30
0.40	0.40	0.60
0.80	0.40	
0.80	0.80	

Rate Law:

number for k:

① $A + B \longrightarrow C + D$

	[A]	[B]	rate
1.	0.20	0.20	0.0078
2.	0.40	0.20	0.0156
3.	0.20	0.40	0.0078

) A×2 ⇒ double rate

B×2 ⇒ no rate change

order of A: 1

B: 0

Rate law: $r = k[A]$

k (number + units): $.0078 = k(0.20\,M) = \boxed{0.039\,s^{-1}}$

What is rate when $[A] = 0.80$, $[B] = 0.80$

$r = (.039)(0.80) = \boxed{0.0312\,M/s}$

② $A + B \longrightarrow C + D$

[A]	[B]	rate
0.20	0.20	0.15
0.40	0.20	0.30
0.20	0.40	0.30
0.40	0.40	0.60
0.80	0.40	$\boxed{1.20}$
0.80	0.80	$\boxed{2.40}$

Rate Law: $r = k[A]^1[B]^1$

number for k: $0.15 = k\,(0.20)(0.20)$ $\boxed{k = 3.75\,M^{-1}s^{-1}}$

③ $A + B + C \longrightarrow D + 2E$

[A]	[B]	[C]	rate
0.20	0.20	0.2	0.15
0.40	0.2	0.2	0.60
0.20	0.4	0.2	0.30
0.20	0.2	0.4	0.15

k=

④ $A + B \longrightarrow C$

[A]	[B]	rate
0.1	0.1	1
0.2	0.1	4
0.1	0.2	1

⑤

[A]	[B]	rate
0.1	0.1	3
0.2	0.1	6
0.1	0.2	24

⑥ $r = k[A][B]$

moles A	moles B	Liters of Solvent	Relative Rate
.5	.5	1	1
.5	.5	2	
.5	.5	0.5	

$\boxed{\text{Answers}}$ (13-10)

③ $A + B + C \rightarrow D + 2E$

[A]	[B]	[C]	rate
0.20	0.20	0.2	0.15
0.40	0.2	0.2	0.60
0.20	0.4	0.2	0.30
0.20	0.2	0.4	0.15

A: $\frac{0.60}{0.15} = 4 = \left(\frac{0.4}{0.2}\right)^x$

$4 = 2^x$ $\boxed{x=2}$

$\boxed{r = k[A]^2[B]^1[C]^0}$

$0.15 = k(0.2)^2(0.2)$

$k = \frac{0.15}{0.008}$

$\boxed{k = 18.75\ M^{-2}s^{-1}}$

④ $A + B \rightarrow C$

[A]	[B]	rate
0.1	0.1	1
0.2	0.1	4
0.1	0.2	1

$\boxed{r = k[A]^2}$

⑤

	[A]	[B]	rate
A^1	0.1	0.1	3
	0.2	0.1	6
	0.1	0.2	24

$\boxed{r = k[A]^1[B]^3}$

B: $\frac{r_2}{r_1} = \frac{24}{3} = 8 = \left(\frac{0.2}{0.1}\right)^x = 2^x$

$x = 3$

⑥ $r = k[A][B]$

moles A	moles B	Liters of Solvent	Relative Rate
.5	.5	1	1
.5	.5	2	$\boxed{1/4}$
.5	.5	0.5	$\boxed{4}$

both conc 1/2

both conc double

13-12

① In practice

a. $\ln 1.8 = 0.59$ $\ln\left(\frac{100}{18}\right) = \ln 5.56 = 1.7$ $\ln\left(\frac{18}{7.2}\right) = 0.91$

b. $\ln x = 1.43$ $\ln \frac{14}{x} = 1.86$ $\ln \frac{100}{x} = 1.13$

$14/x = 6.42$ $100/x = 3.10$

$x = 4.18$ $x = 2.18$ $x = 32.3$

Assume 1st Order Rate Laws for the Following

② What is the rate constant k if [A] goes from $1.0\,\bar{M} \rightarrow 0.32\,\bar{M}$ in 46 sec?

$kt = \ln \frac{A_0}{A_t}$

$k\,46 = \ln(1/.32) = 1.14$

$k = \frac{1.14}{46} = \boxed{0.025\ s^{-1}}$

③ If $k = 113\ \text{years}^{-1}$, how long will it take for 10% of A to react?

Hint: $A_0 = 100\%$

$A_t = 100\% - 10\% = 90\%$

$113t = \ln \frac{100\%}{90\%} = .105$

$t = 9.32 \times 10^{-4}$ years

$= \boxed{8.1\ \text{hours}}$

④ If $k = 0.061\ \text{days}^{-1}$, what % of a spilled poison remains after 12 days?

Set $A_0 = 100\%$

$A_t = x\%$

$(0.061)(12) = \ln \frac{100}{x}$

$.732 = \ln 100/x$

$2.08 = 100/x$

$\boxed{x = 48\%}$

C. Half-life $t_{1/2}$: Time for Concentration to Drop by Half (for 1st order reaction)

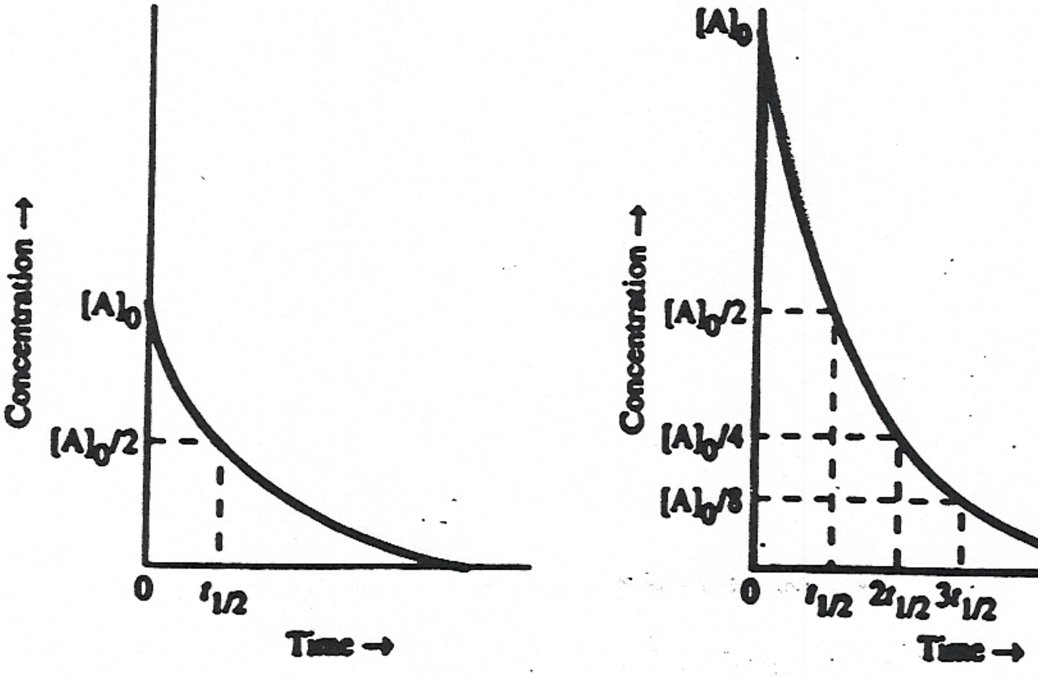
at $t_{1/2} \Rightarrow [A]_{t_{1/2}} = \frac{1}{2}[A]_0$

so $kt_{1/2} = \ln \frac{[A_0]}{[A]_{t_{1/2}}} = \ln 2 = 0.693$

☆ $\boxed{kt_{1/2} = 0.693}$

D. Higher Order Rate

- time/concentration/$t_{1/2}$ relationships more complex
- not responsible



(a) (b)

FIGURE 15.4 Half-Life of a First-Order Reaction The half-life is independent of the initial concentration. The initial concentration of the reactant $[A]_0$ is less in (a) than it is in (b), but the time $t_{\frac{1}{2}}$ needed for the initial concentration to decrease to half its initial value is the same. The time needed for the initial concentration to decrease to one-quarter its initial value is $2t_{\frac{1}{2}}$ and to one-eighth its initial value is $3t_{\frac{1}{2}}$.

(13-14)

① The half-life for A is 30 sec. If you start with 128 A, how many will be left after:

t (sec)	Amount	t (sec)	Amount
0	128	120	
30		150	
60		180	
90		210	

② If k is 0.36 days^{-1}, what is $t_{1/2}$, and how long will it take for 75% to decay?

③ ^{14}C decomposes with $t_{1/2} = 5730$ years. What is k for decomposition?

$\boxed{\text{Assume 1st Order}}$

(13-14)

① The half-life for A is 30 sec. If you st
with 128 A, how many will be left after:

t (sec)	Amount	t (sec)	Amount
0	128	120	8
30	64	150	4
60	32	180	2
90	16	210	1

7 half-lives to hit 1%!

② If k is 0.36 $days^{-1}$, what is $t_{1/2}$, and how long will it take for 75% to decay?

$kt_{1/2} = 0.693$ $\quad 0.36\, t_{1/2} = 0.693$ $\quad t_{1/2} = 1.93$ days

75% = 2 half lives

so 2×1.93 days = $\boxed{\text{3.8 days total}}$

or $.36\, t = \ln \frac{100\%}{25\%}$

$\boxed{t = 3.8 \text{ days}}$

③ ^{14}C decomposes with $t_{1/2} = 5730$ years. What is k for decomposition?

$kt_{1/2} = 0.693$ $\quad k = \frac{.693}{5730} = \boxed{1.2 \times 10^{-4} \text{ years}^{-1}}$

13.4, 13.5 Reactions, Energetics, & Temp
"Q: Why are rates impacted by concentrations and temp?"

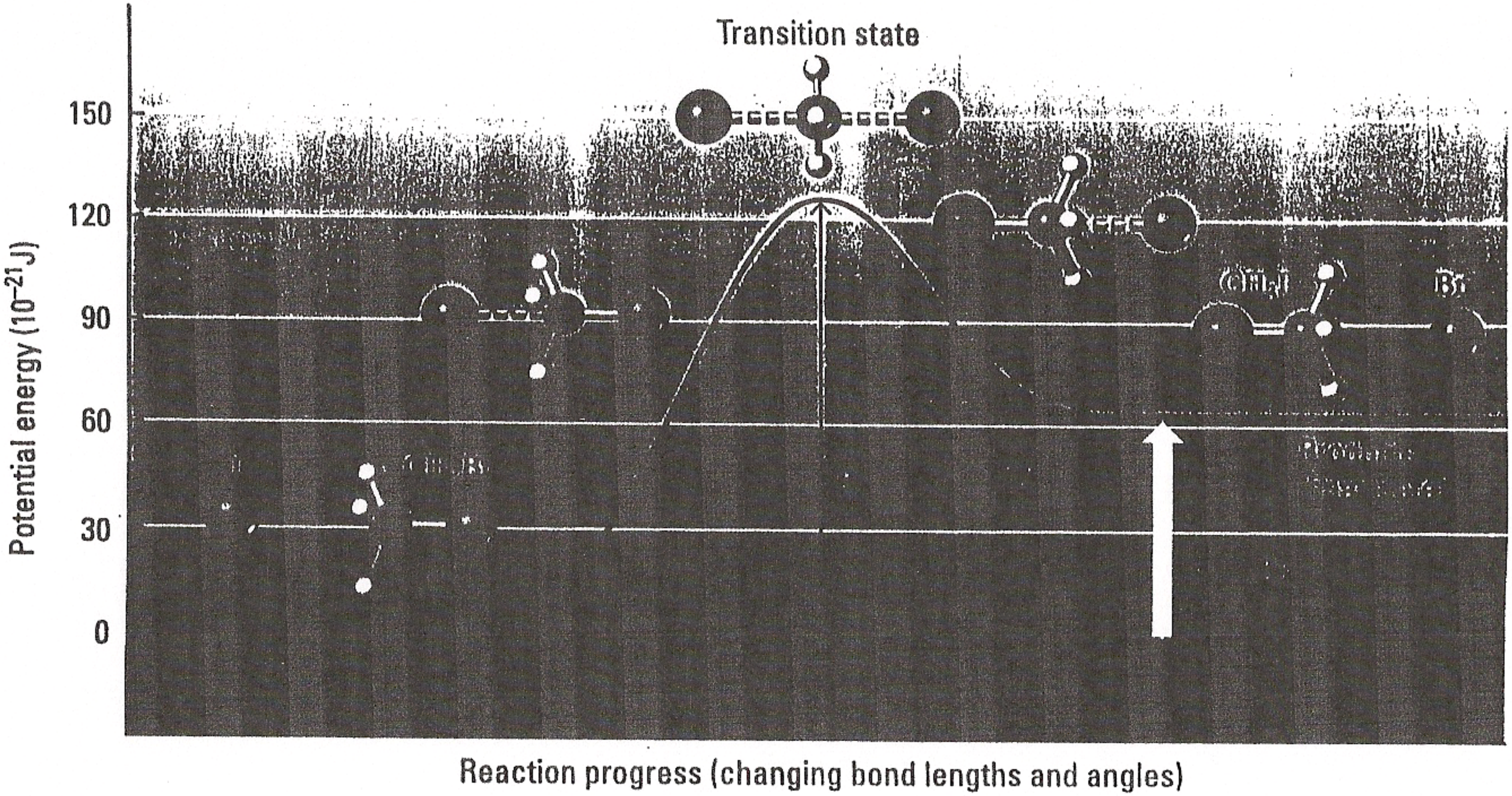
A. Nanoscale Reactions
– while an overall reaction may envolve many steps (13.7), elementary steps are either unimolecular or bimolecular
1. Unimolecular: a single molecule either rearranges or decomposes
– energy required!

$A \rightarrow B$ (Fig 13.7)

or $A \rightarrow B + C$

2. Bimolecular: 2 things collide
a. orientation, angle must be suitable!
Fig 13.8 Fig 13.8
– most collisions don't succeed
b. reactants must collide with enough energy
– called "activation energy, E_a"

higher conc → more collisions → faster rate Fig 13.12
higher temp → higher energy → more succeed
(also more collisions, but efficiency is key)



Moore/Stanitski/Jurs, Chemistry: The Molecular Science
Figure 13

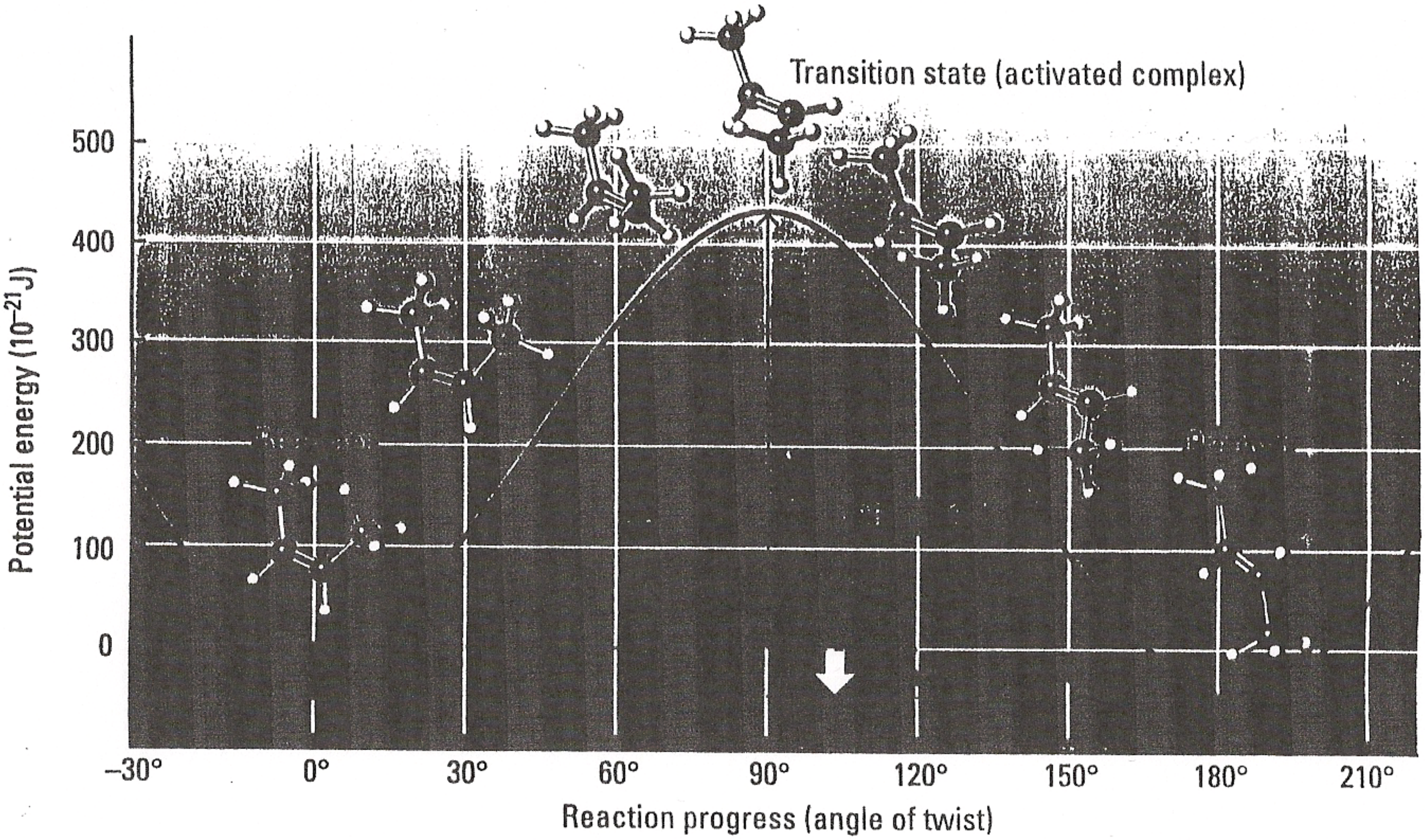


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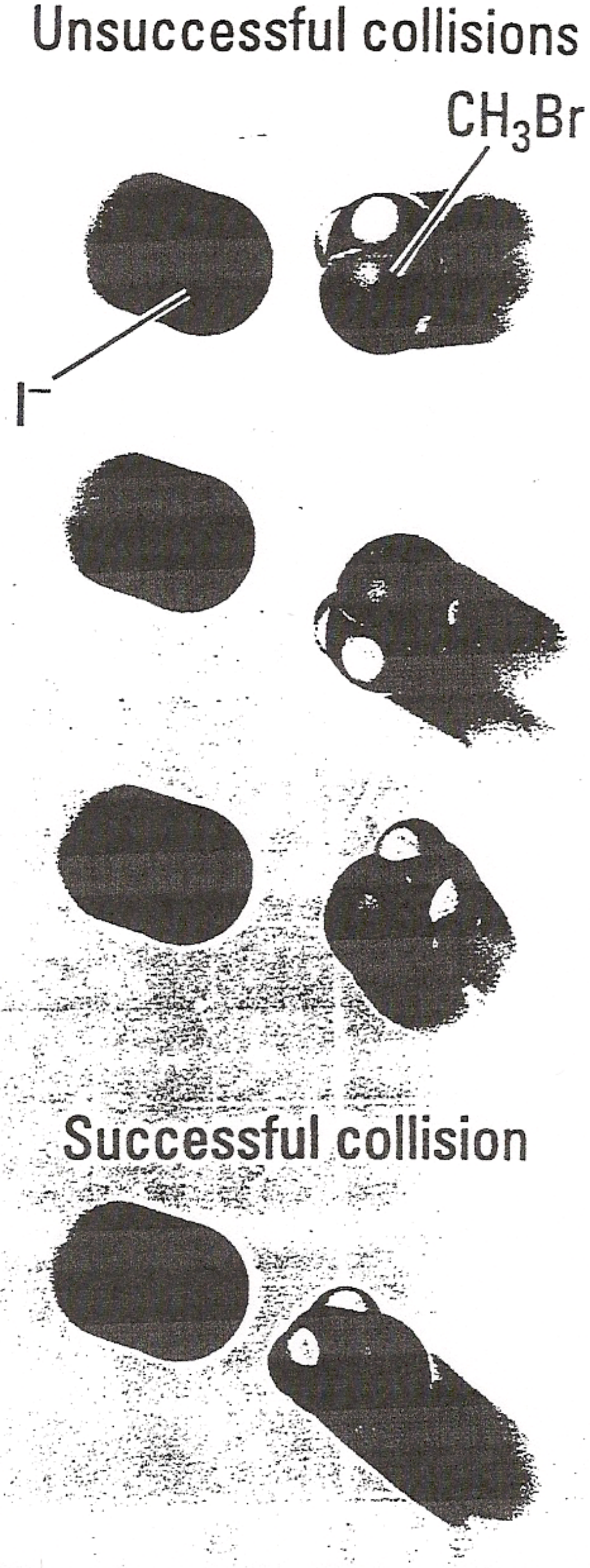
Figure 13.7



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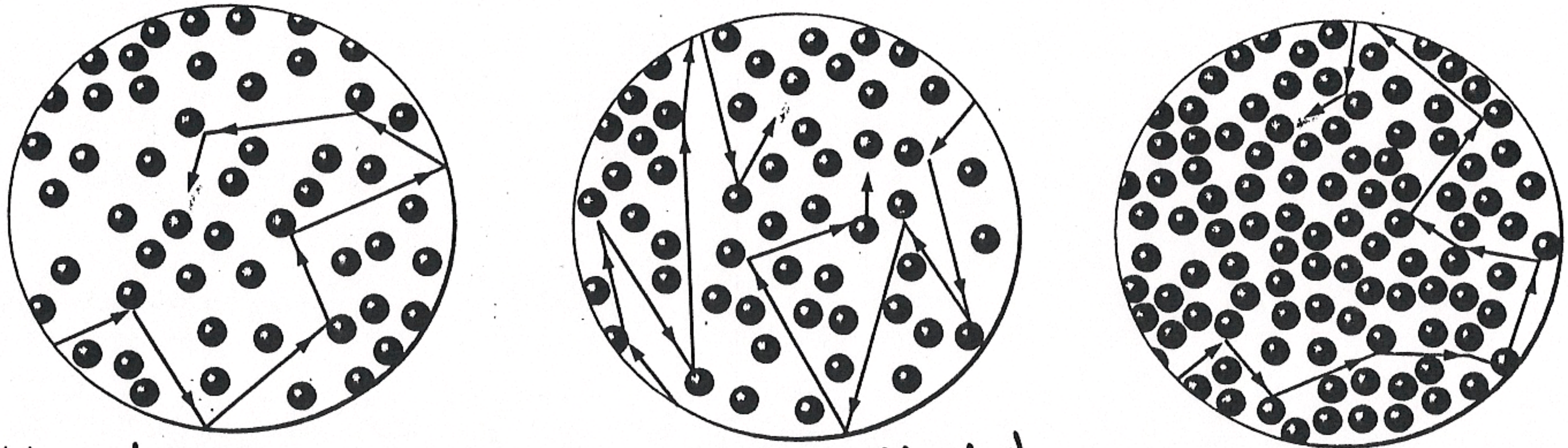
Unnumbered Figure 13.8



(a)
1 green
50 purple
5 collisions/sec

(b)
2 green (doubled)
50 purple
10 collisions/sec
(doubled)

(c)
1 green
100 purple (doubled)
10 collisions/sec
(doubled)

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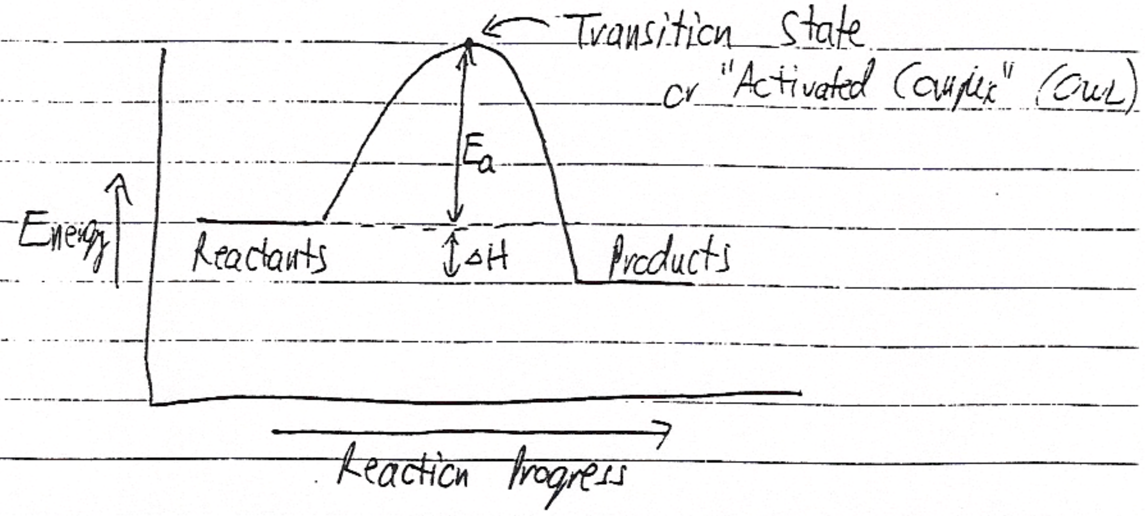
Figure 13.12

(13-16)

C. Energy Diagrams, Activation Energy, Transition State



T-state: energy max on road to products

E_a: barrier

① the higher the slower!

② T-state higher than reactants & products, but must be crossed

③ even exo reactions have barrier (because cost of breaking often precedes payoff of making)

④ higher temp ⇒ higher odds of clearing barrier. Greater Fraction Clear the barrier.

★ ⇒ k changes (increases) at diff. temp

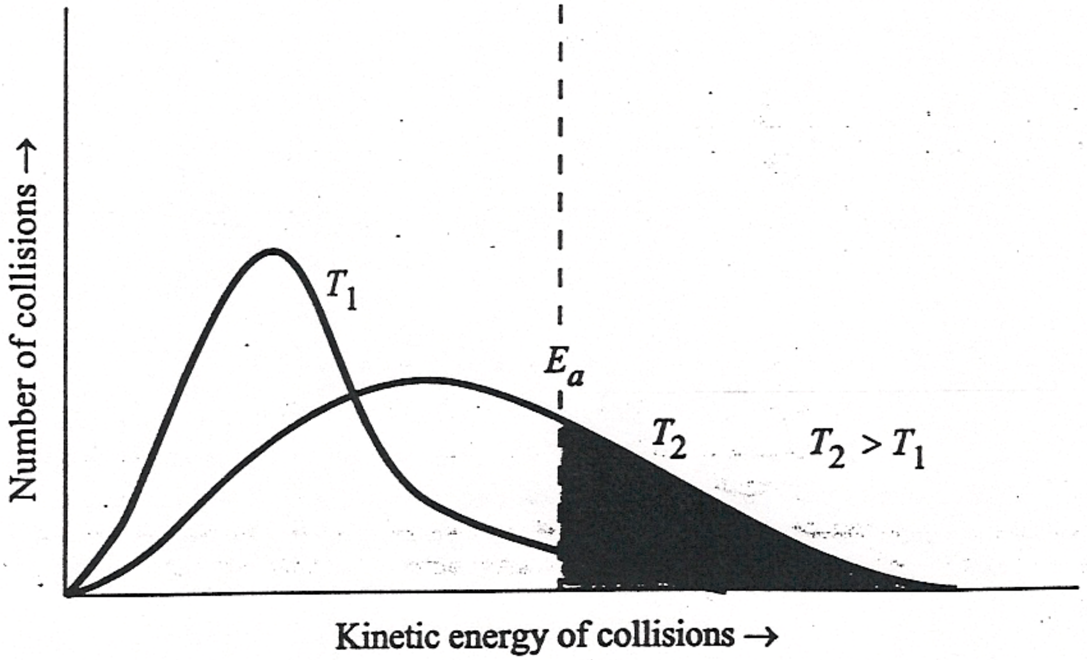
T 112, Gillespie

Fig 15.7, Gillespie

⑤ E_a unique for each reaction – no correlation with ΔH...

⑥ Catalysts: change mechanism in such a way that T-state lowered

T 112 Fig. 15.8 Collision Energy Distributions



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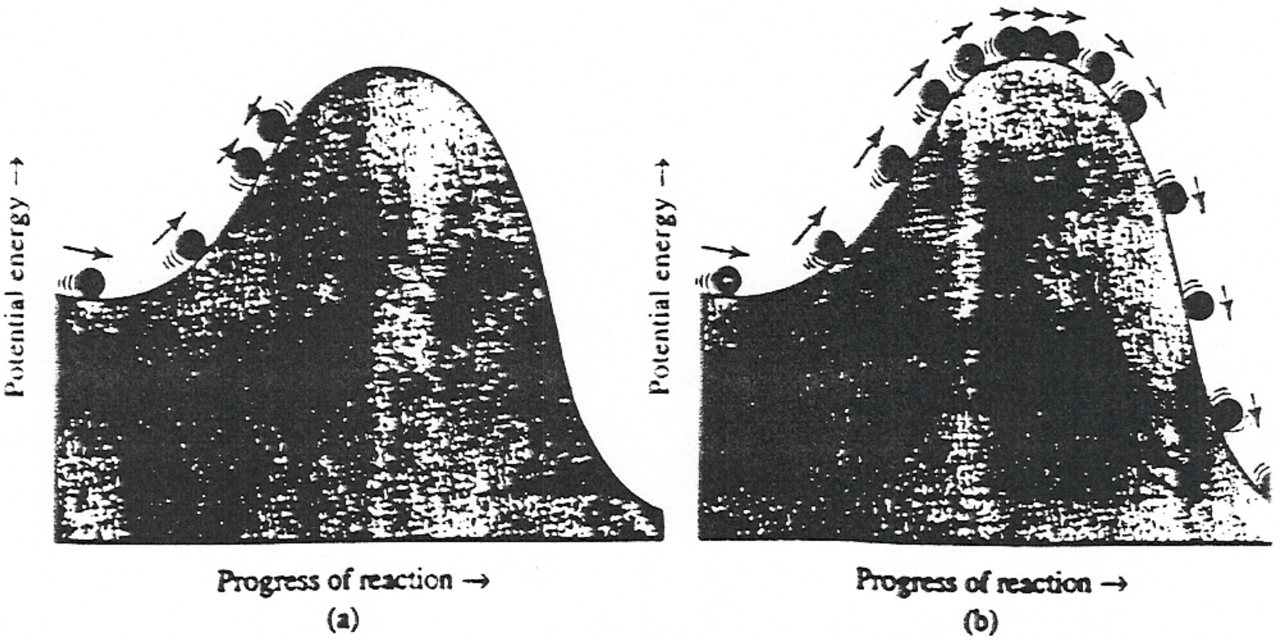

(a) (b)

IGURE 15.7 Analogy for the Activation Energy of a Chemical Reaction
Energy is required to move a ball to the top of a barrier, just as energy is required for chemical reactants to form a transition state, or activated complex. (a) Here the ball has insufficient energy to climb the potential energy barrier and rolls back down the same side of the barrier. No reaction has occurred. (b) Here the ball has sufficient energy to reach the top of the potential energy barrier and may then roll down the other side. A reaction has occurred.

D. Arrhenius Equation

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

R = constant = .00831
A = constant unique to each reaction

– complex!

☆ $\boxed{\text{Qual: ① larger } E_a \Rightarrow \text{ smaller } k \quad ② \text{ higher temp} \Rightarrow \text{ larger } k}$

Math: ln both sides

graphical solution a) $\ln k = -\frac{E_a}{.00831}\left(\frac{1}{T}\right) + \ln A$

$y = mx + b$
Graph k vs. $1/T$,
⇒ solve for E_a and A

b) 2-Point Solution

$$\boxed{\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{.00831}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

E_a: in kJ/mo
T in Kelvi

Applications
① Given k's at 2 temps, can find E_a
② Given E_a and the k at one temp, can find the k at any other
③ Given E_a and the k_1 at one temp, then can find whatever temp is needed to produce a desired k_2 (½ or 1/10th or 10 times faster...)

13-18

(13.6,7) Reaction Mechanisms & Rate Laws

A. – examples

① elementary steps uni- or bimolecular

② most reactions multistep (especially catalyzed --)

③ "intermediates" – shortlived, forms in one step, destroyed in another

– since concentration normally too low to measure ⇒ * may not appear in final rate law!! (note for multiple choice)

– found on both sides, cancel out

– final rate law should only include reactants (and catalyst)

④ rate laws of elementary steps depend directly on reactants!

$A \rightarrow B \quad r = k A$

$A + A \rightarrow \quad r = k A^2$

$A + B \rightarrow \quad r = k A B$

(contrast to overall balanced --)

⇒ * given mech, can deduce rate law

⑤ elementary steps must sum to give overall balanced eqn.

– handout problems

(13-19)

For the Following, Classify Molecularity of Elementary Steps, Identify Intermediates, and Write Overall Rate Laws

① $A \rightarrow B$

② $CH_3Br + {}^{\ominus}OH \rightarrow CH_3OH + Br^{\ominus}$

③ $2A \rightarrow B + C$ slow
$B + D \rightarrow E$ fast

sum:

overall rate law r=

intermediate:

④ $A + B \rightleftharpoons C$ fast
$C + D \rightarrow E + F$ slow

⑤ $A \rightarrow B + C$ slow
$B + C + D \rightarrow E + F$ fast

sum:

intermediate(s)

overall r=

⑤ $A + A \rightleftharpoons B$ fast
$B + C \rightarrow D + E$ slow

13-19

For the Following, Classify Molecularity of Elementary Steps, Identify Intermediates, and Write Overall Rate Laws.

① $A \rightarrow B$ unimolecular $r = k[A]$
no intermediates

② $CH_3Br + {}^{\ominus}OH \rightarrow CH_3OH + Br^{\ominus}$ bimolecular
no intermediates
$r = k[A][B]$

③ $2A \rightarrow \cancel{B} + C$ slow
$\cancel{B} + D \rightarrow E$ fast

sum: $2A + D \rightarrow C + E$

overall rate law $r = k[A]^2$

intermediate: B

④ $A + B \rightleftharpoons \cancel{C}$ fast
$\cancel{C} + D \rightarrow E + F$ slow

sum: $A + B + D \rightarrow E + F$

intermediate(s) C

overall $r = k[A][B][D]$

⑤ $A \rightarrow \cancel{B} + C$ slow
$\cancel{B} + C + D \rightarrow E + F$ fast

$A + D \rightarrow E + F$

$\boxed{\text{rate} = k[A]}$

⑤ $A + A \rightleftharpoons \cancel{B}$ fast
$\cancel{B} + C \rightarrow D + E$ slow

$2A + C \rightarrow D + E$

$\boxed{r = k[A]^2[C]}$

B. Deducing Rate Laws from Multistep Mech: Determined by Slowest Step ≡ RATE DETERMINING STEP

- bottleneck

  (I-94 Chicago; pizzas in one oven kitchen; Hornbacher...)

- any step _after_ slow step has no impact on rate
- any _reactant_ after slow step does not appear in rate law
- All _reactants_ in or before slow step appear in rate law (overall)
- (NO _Intermediates_ allowed!!)

Practice Problems

Skills: ① Given mech ⇒ write rate law
② Given rate law ⇒ distinguish plausible from implausible mechanisms

13-21

Chem 160-Jasperse

Mechanisms and Rate Laws

Distinguishing among possible mechanisms, given a rate law:

1. Which mechanism is plausible for the reaction shown, given the rate law:

$$A + 2B \rightarrow C \qquad \text{rate} = k[A]$$

a. $A + B \rightarrow D$ (slow)
$D + B \rightarrow C$ (fast)

b. $B + B \rightarrow E$ (slow)
$A + E \rightarrow C$ (fast)

c. $A \rightarrow F$ (slow)
$F + B \rightarrow G$ (fast)
$G + B \rightarrow C$ (fast)

d. $B + B \rightarrow H$ (fast)
$A + H \rightarrow C$ (slow)

Identifying a Rate Law, given the Mechanism:

2. Given the mechanism shown, what is a reasonable rate law?

$$2A + 2B \rightarrow C$$

Mechanism: $A + B \rightarrow D$ (slow)
$D + B \rightarrow E$ (fast)
$A + E \rightarrow C$ (fast)

a. $r = k[A][B]$

b. $r = k[A][E]$

c. $r = k[A]^2[B]^2$

d. $r = k[A]^2[B]^2[D][E]$

13-21

Chem 160-Jasperse

Mechanisms and Rate Laws

Distinguishing among possible mechanisms, given a rate law:

1. Which mechanism is plausible for the reaction shown, given the rate law:

$A + 2B \rightarrow C$ rate = k[A]

a. $A + B \rightarrow D$ (slow)
$D + B \rightarrow C$ (fast)
$r = k\ A\ B$

b. $B + B \rightarrow E$ (slow)
$A + E \rightarrow C$ (fast)
$r = k\ B^2$

✓ [✓ c.] $A \rightarrow F$ (slow)
$F + B \rightarrow G$ (fast)
$G + B \rightarrow C$ (fast)
$r = kA$

d. $B + B \rightarrow H$ (fast)
$A + H \rightarrow C$ (slow)
$r = k\ A\ B^2$

Identifying a Rate Law, given the Mechanism:

2. Given the mechanism shown, what is a reasonable rate law?

$2A + 2B \rightarrow C$

Mechanism: $A + B \rightarrow D$ (slow)
$D + B \rightarrow E$ (fast)
$A + E \rightarrow C$ (fast)
$r = k\ A\ B$

[✓ a. $r = k[A][B]$]

b. $r = k[A][E]$

c. $r = k[A]^2[B]^2$

d. $r = k[A]^2[B]^2[D][E]$

Derivation of Rate Law When 1st Step Isn't Slow

$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C$ fast, but reversible

$C + D \xrightarrow{k_2} E + F$ slow

$A + B + D \rightarrow E + F$ $r = k[A][B][C]$

① Intermediates (C) don't build up. They reach a steady state, (usually very low concentration) in which formation = destruction

rate formation = rate destruction

$$k_1[A][B] = K_1[C] + k_2[C][D]$$

since step 2 is slow, it probably makes a small contribution to the rate of destruction and can be dropped.

Thus $k_1[A][B] = k_1[C]$

Rearranged: $[C] = \frac{k_1}{k_{-1}}[A][B]$

② Overall rate given by slow step: $r = k_2[C][D]$

substituting for [C] $r = \frac{k_2 k_1}{(k_{-1}}[A][B])[D]$

since $\frac{k_2 k_1}{k_1}$ is itself constant, overall $\boxed{r = k'[A][B][D]}$

13.8 Catalysts

① Increase rates

② Are themselves recycled ("catalytic converter")
- not used up, final quantity of catalyst equals initial
- used early, regenerated late in mech ("anti-intermediate")

(Fig 13.13–15)

③ Recognition: do not appear in balanced eqn
$\boxed{\text{do}}$ appear in rate law

④ Speed up by providing new mech with lower T-state
(Fig 13.14, 13.17)

- new mech always more complex
- "tunnel" through energy barrier

⑤ While Ea reduced, overall ΔH is unchanged!! (metabolism)

⑥ Tiny quantities suffice (because recycled)

⑦ Can reduce temp/heat requirements (metabolism)

⑧ attraction: cost, small amounts benefits of temp, no waste ---
- industry loves them! (13.10)

⑨ Enzymes: Big Proteins that Catalyze Biology (13.9)
- >100,000 enzymes
- can increase rates by millions a billions!
- remarkable specificity
- most diseases involve enzyme malfunction, medical research addresses (on/off)

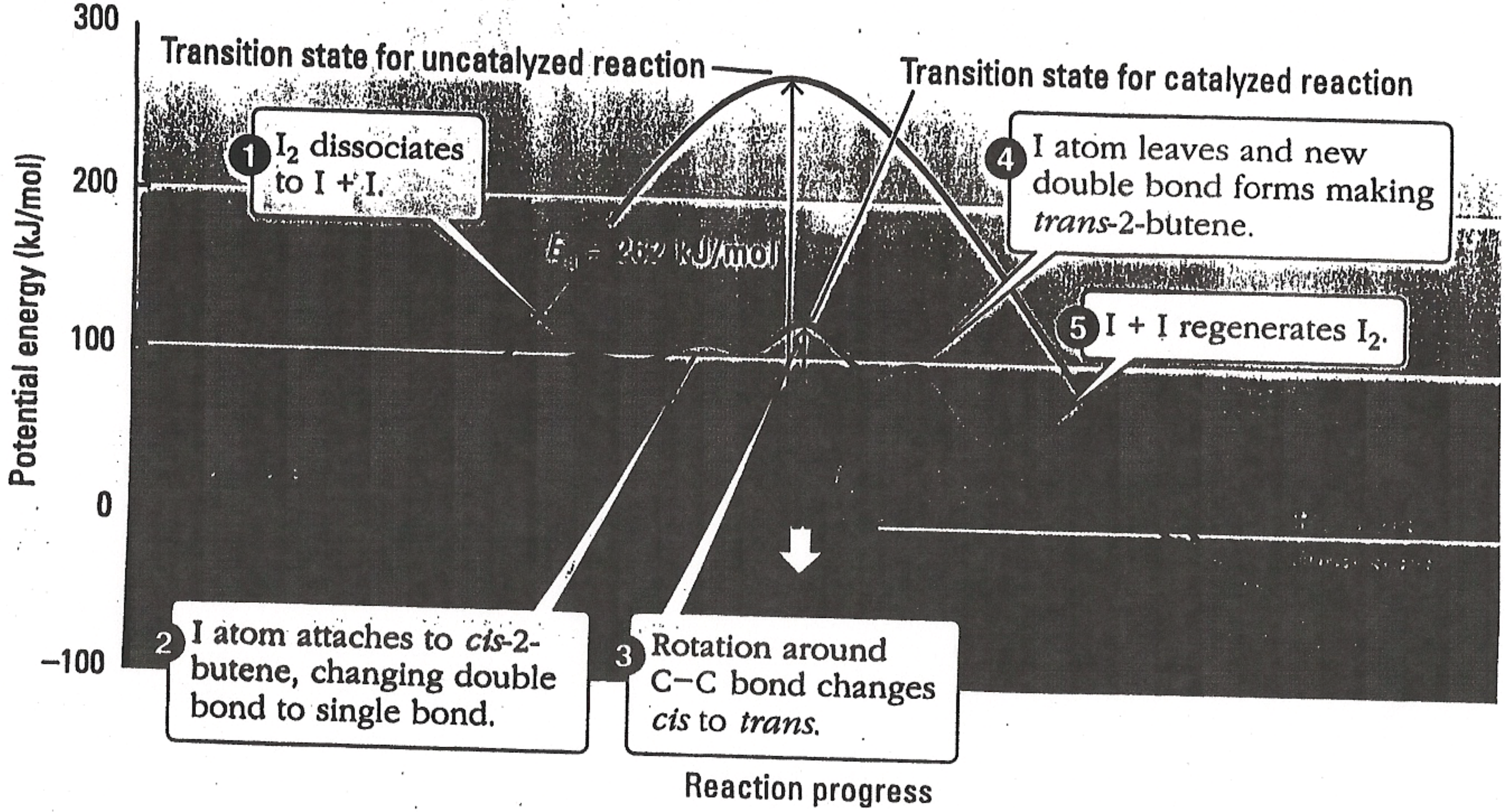

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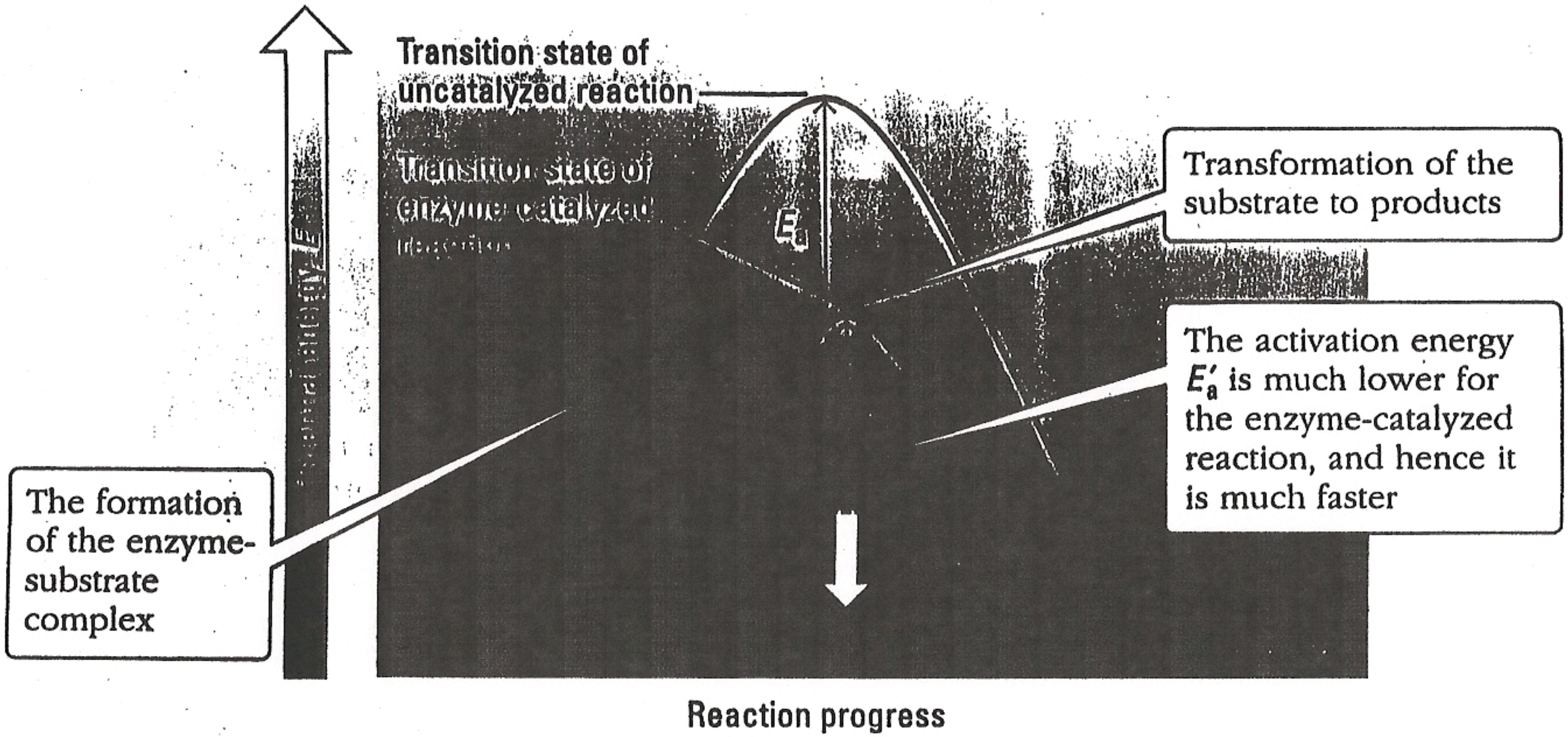
Figure 13.14



Moore/Sta[illegible]ski/Jurs, Chemistry: The Molecular Science
Figure 13.17