Chapter 14

Chemical Kinetics

Deals w. rate of chem. rx., factors that influence the rate, & an explanation of the rate in terms of the reaction mechanism

Reaction Mechanism

Details of how reactants change to products, at a molecular level.

I) Four Factors that Influence Rates

a) Characteristics of reactants + products

- bond strengths
- arrangement of atoms
- surface area of solid reactant or catalyst

b) Concentration of reactants

c) Temperature

- rx's usually speed up as temp. inc.

d) Catalyst

- substance that inc. the rate w/o being consumed in overall rx.

II) Reaction Rate

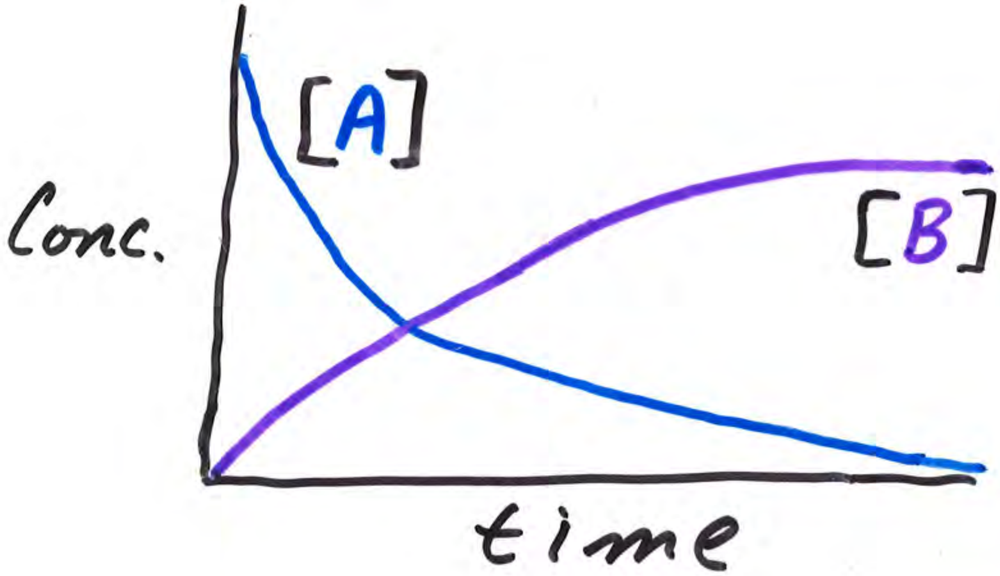
Change in conc. of reactants or products w. time

Measure conc. during course of rx.

- monitor pressure for gas rx.
- monitor intensity of color in spectrophotometer
- titration

A) Rx. Rate

$$A \longrightarrow B$$



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

rate is a positive number

([A] dec. : negative change)

Usual Units : $\frac{mol}{L \cdot s}$ or $M \cdot s^{-1}$

For this case:

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

1) General Rx

$$aA + bB \longrightarrow cC + dD$$

$$\left(\frac{1}{a}\right)\frac{-\Delta[A]}{\Delta t} = \left(\frac{1}{b}\right)\frac{-\Delta[B]}{\Delta t} = \left(\frac{1}{c}\right)\frac{\Delta[C]}{\Delta t} = \left(\frac{1}{d}\right)\frac{\Delta[D]}{\Delta t}$$

- Depends on stoichiometry

a) Ex:

$$2NO_2 \longrightarrow N_2O_4$$

$$\frac{1}{2}\left(-\frac{\Delta[NO_2]}{\Delta t}\right) = \frac{\Delta[N_2O_4]}{\Delta t}$$

$$\therefore \quad -\frac{\Delta[NO_2]}{\Delta t} = 2\,\frac{\Delta[N_2O_4]}{\Delta t}$$

b) Ex:

The rate of disappearance of B ($-\frac{\Delta[B]}{\Delta t}$) is 0.5 m/s. What is the rate of appearance of E ($\frac{\Delta[E]}{\Delta t}$)?

$$3A + 5B + 2C \longrightarrow D + 4E$$

2) Average rate

$$\text{Avg. rate} = \frac{\text{dec. in conc. of reactant}}{\text{time interval}}$$

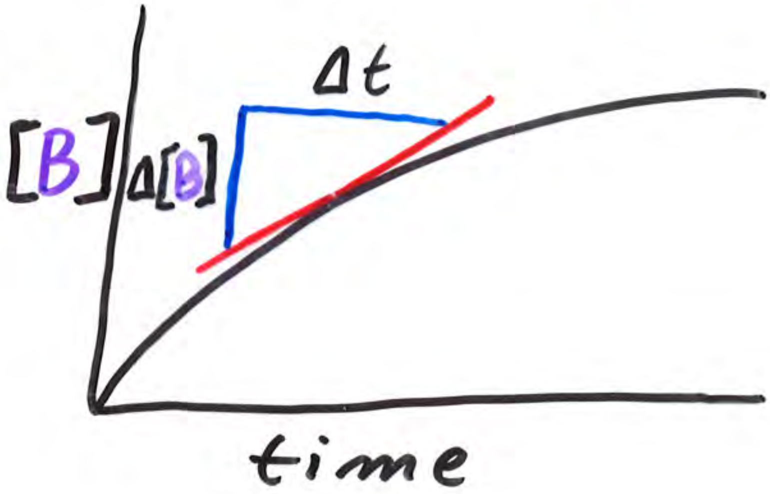
$$= \frac{-\Delta[A]}{\Delta t}$$

Time (s)	[A] (m)	Avg. rate (m/s)
0	1.000	
		9.00×10^{-3}
10	0.910	
		8.00×10^{-3}
20	0.830	
		7.00×10^{-3}
30	0.760	

$$\text{Avg. rate} = -\frac{[A]_{10s} - [A]_{0s}}{10\,s - 0\,s}$$

3) Instantaneous rate

rate at a particular time



Instant. rate = slope of tangent to curve at some time

$$= \lim_{\Delta t \to 0} \frac{\Delta [B]}{\Delta t}$$

$$= \frac{d[B]}{dt}$$

III) Dependence of Rx. Rate on Conc.

Rate dec. as A consumed

Dependence given by,

Rate Law

$$\text{rate} \propto [A]$$

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

or

$$\frac{-d[A]}{dt} = k[A]$$

$$k \equiv \text{rate constant}$$

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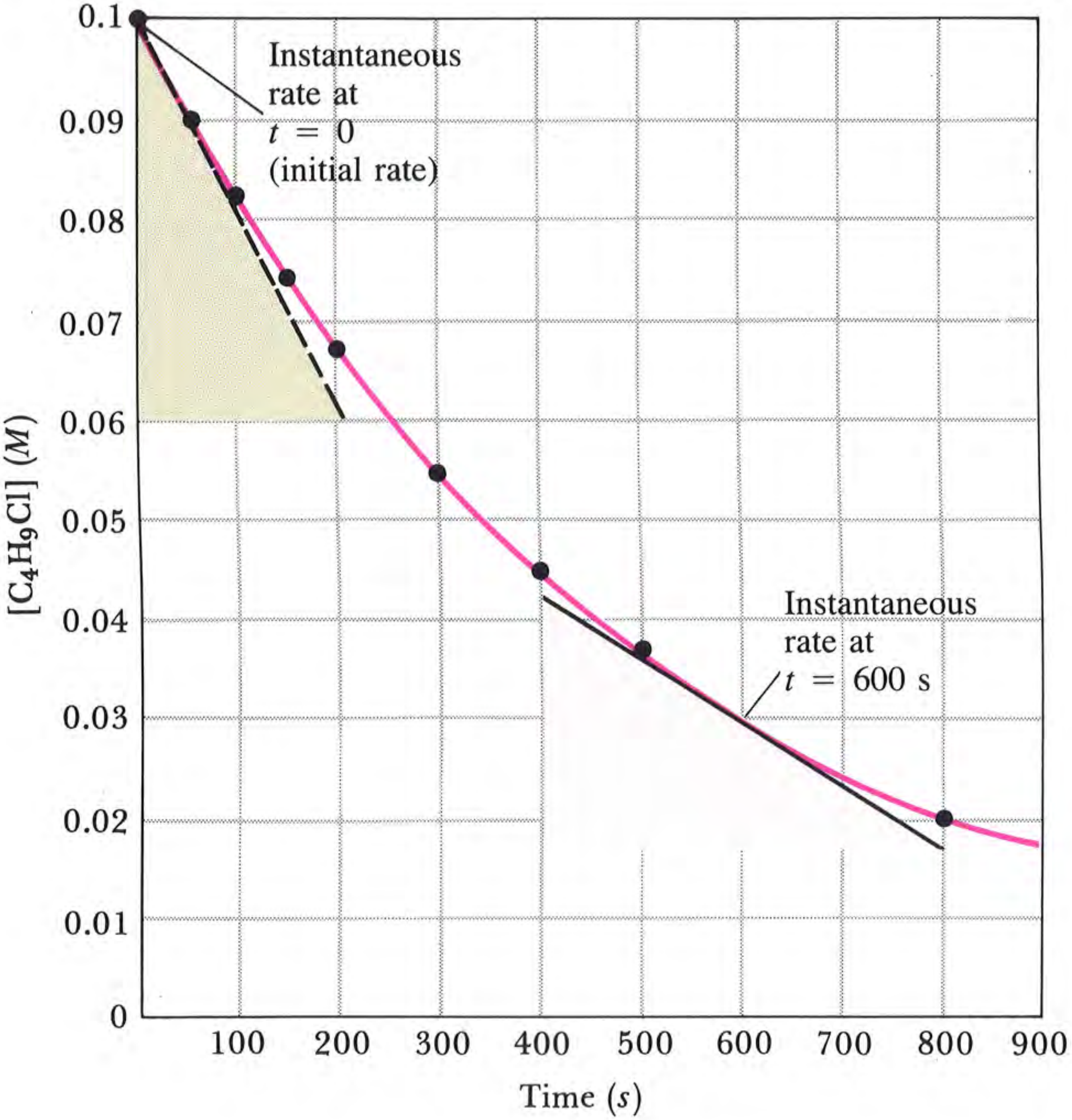
Figure 14.1 Concentration of butyl chloride as a function of time



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A) General Rx.

$A + B + C + \cdots \longrightarrow$ products

$$\text{rate} = k\,[A]^X\,[B]^Y\,[C]^Z \cdots$$

$X \equiv$ order w/rsp. A

$Y \equiv$ order w/rsp. B

$X + Y + Z + \cdots \equiv$ overall reaction order

$X, Y, Z, \ldots$ whole numbers, simple fractions, zero, negative

Generally, rate law MUST be determined EXPERIMENTALLY

2) Initial Rates

Vary initial conc. of each reactant (holding others constant) & measure rate at start of rx. -

initial rate

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

		Initial Conc. $(\times 10^3)$				Initial Rate (mm Hg/min)		
		[NO]	$[H_2]$					
		6	1	×2	×3	20	×2	×3
		6	2			40		
		6	3			60		
×3	×2	1	6			3	×4	×9
		2	6			12		
		3	6			27		

$$rate = k\,[NO]\ [H_2]$$

Ex

$$2A + B + C \longrightarrow M + N$$

Exp	[A]	[B]	[C]	rate (M/s)
1	1	1	1	X
2	2	1	1	4X
3	1	2	1	X
4	1	2	2	1.41 X
5	1	1	4	2X

$$r = k[A]^{n}[B]^{m}[C]^{P}$$

$$r_j = k[A]_j^n [B]_j^m [C]_j^p$$

$$r_i = k[A]_i^n [B]_i^m [C]_i^p$$

$$\frac{r_j}{r_i} = \frac{k[A]_j^n [B]_j^m [C]_j^p}{k[A]_i^n [B]_i^m [C]_i^p}$$

$$\frac{r_j}{r_i} = \left(\frac{[A]_j}{[A]_i}\right)^n \left(\frac{[B]_j}{[B]_i}\right)^m \left(\frac{[C]_j}{[C]_i}\right)^p$$

IV) Time Dependence of Reactant Conc.

Equations that give conc. of reactants or products as a function of time and initial conc.

A) 1st order rx.

$$r = -\frac{1}{a}\frac{d[A]}{dt} = k[A]$$

$$\frac{d[A]}{[A]} = -(ak)\,dt$$

Integrate,

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = \int_0^t -(ak)\,dt$$

Gives,

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -akt$$

$$\ln[A]_t - \ln[A]_0 = -akt$$

$$\boxed{\ln[A]_t = -(ak)t + \ln[A]_0}$$

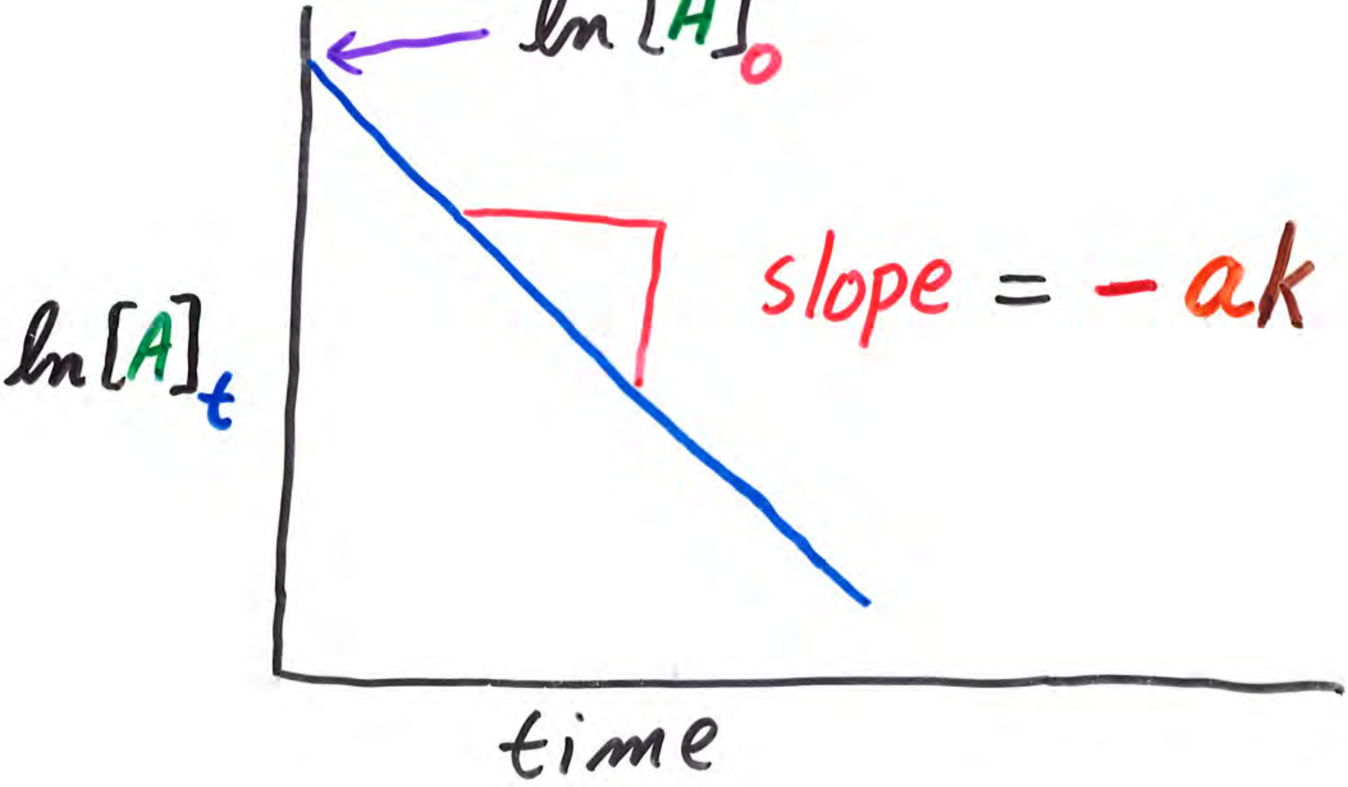

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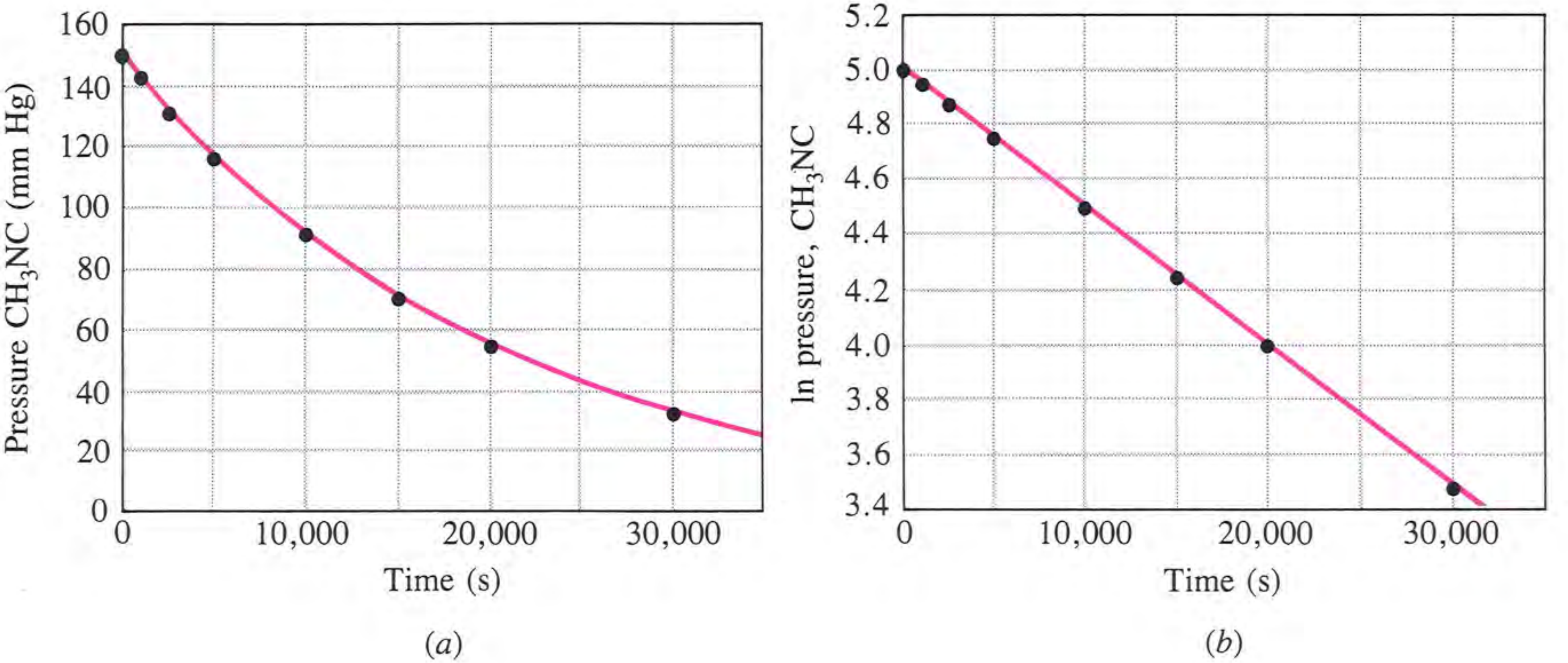
Figure 14.2 Variation in the pressure of methyl isonitrile with time



(*a*) (*b*)

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Ex: The rx.

$$N_2O_5 \rightleftharpoons 2NO_2 + \frac{1}{2}O_2$$

is 1st order, w. $k = 4.80 \times 10^{-4}\ s^{-1}$ at 45°C.

a) If the initial conc. is 1.65×10^{-2} M, what is the conc. after 825 s.

B) Half-life, $t_{1/2}$

time required for conc. of reactant to dec. to $\frac{1}{2}$ its initial value.

$$\ln \frac{[A]_t}{[A]_0} = -akt$$

$$\ln \frac{\frac{1}{2}[A]_0}{[A]_0} = -akt_{1/2}$$

$$\ln \tfrac{1}{2} = -akt_{1/2}$$

$$-0.693 = -akt_{1/2}$$

$$\boxed{t_{1/2} = \frac{0.693}{ak}}$$

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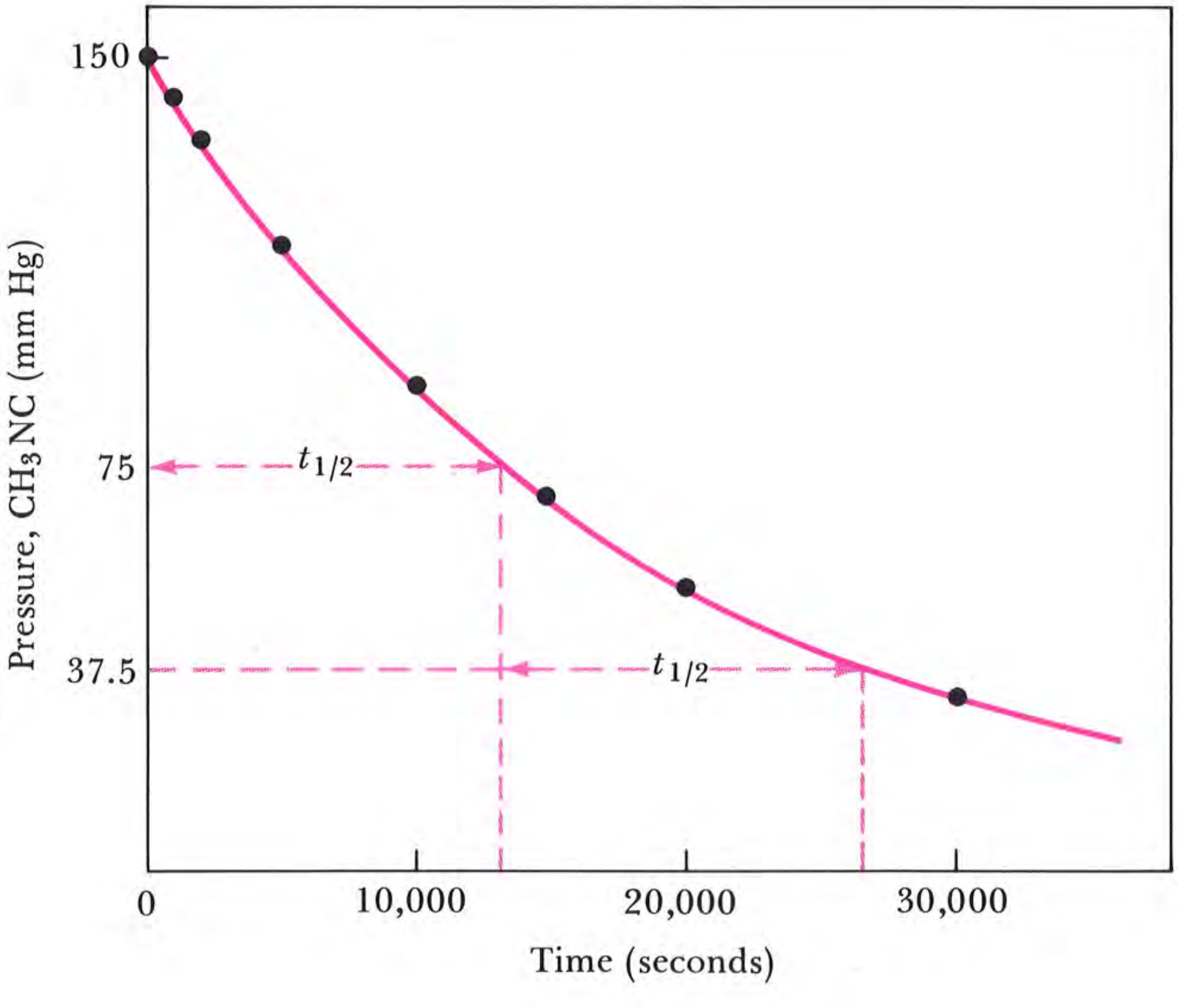
Figure 14.3 Pressure of methyl isonitrile as a function of time (half-life)



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Ex: The following rx. is 1st order w/rsp. $[Cr^{3+}]$; the rate constant is $2.0 \times 10^{-6}\ s^{-1}$

$$Cr^{3+}(aq) + SCN^{-}(aq) \longrightarrow Cr(SCN)^{2+}(aq)$$

colored soln.

If 90% rx. is req. to obtain a noticeable color from $Cr(SCN)^{2+}$, how many hours are req.?

__Ex__ : What is the half-life for the previous ex., in hours.

$k = 2.0 \times 10^{-6}\ s^{-1}$

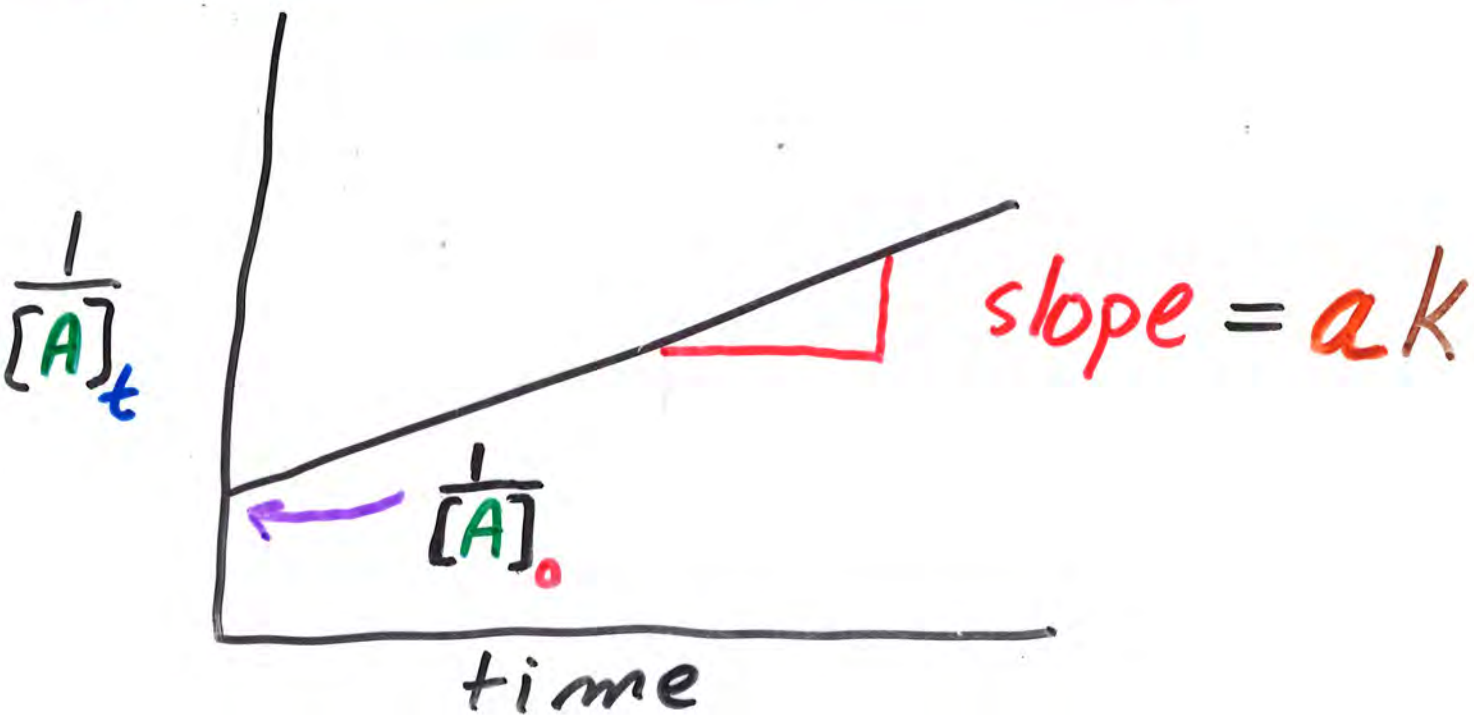
B) 2nd order rx.

$$r = -\frac{1}{a}\frac{d[A]}{dt} = k\,[A]^2$$

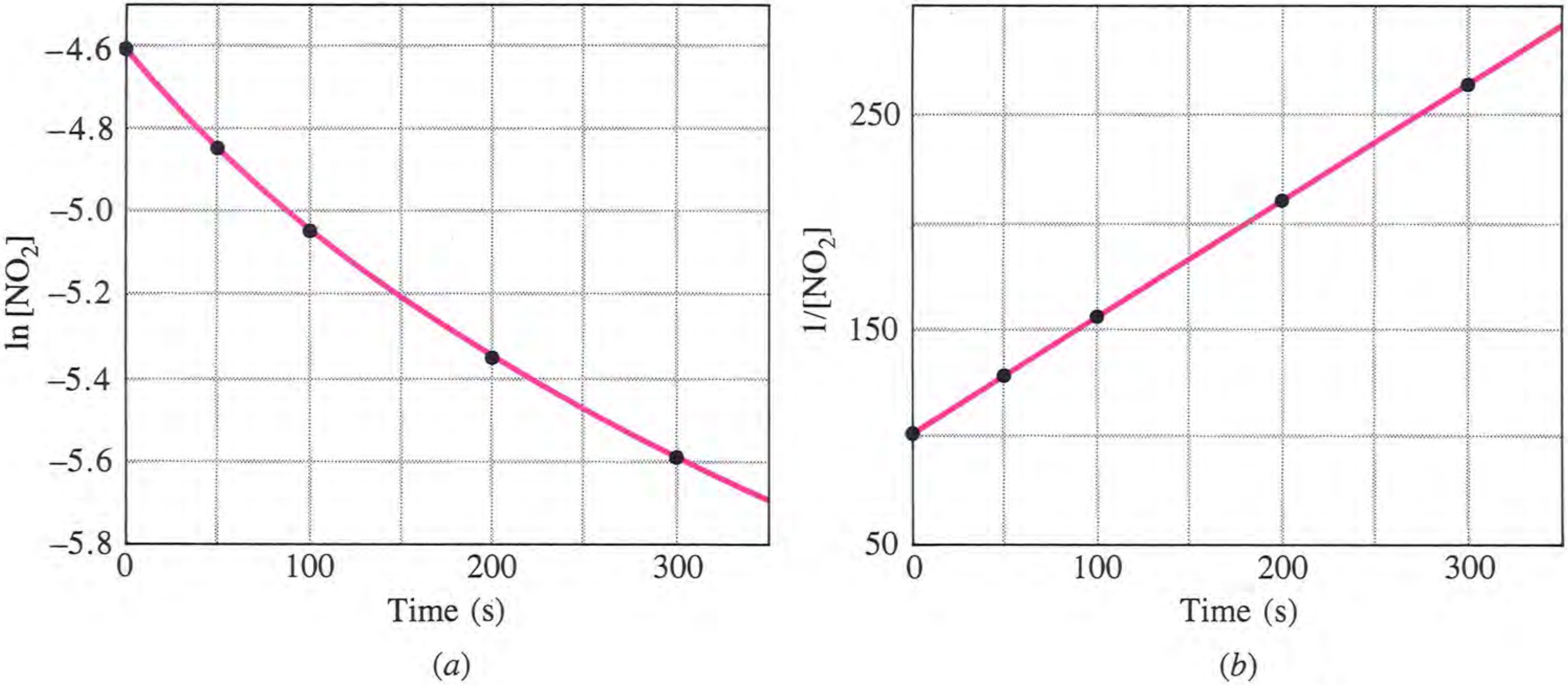
$$-\frac{d[A]}{[A]^2} = (ak)\,dt$$

$\Downarrow$ integrate + rearrange

$$\boxed{\frac{1}{[A]_t} = (ak)t + \frac{1}{[A]_0}}$$



Transparency 102 **Figure 14.4** **Plots of the kinetic data for the reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$**



(*a*) (*b*)

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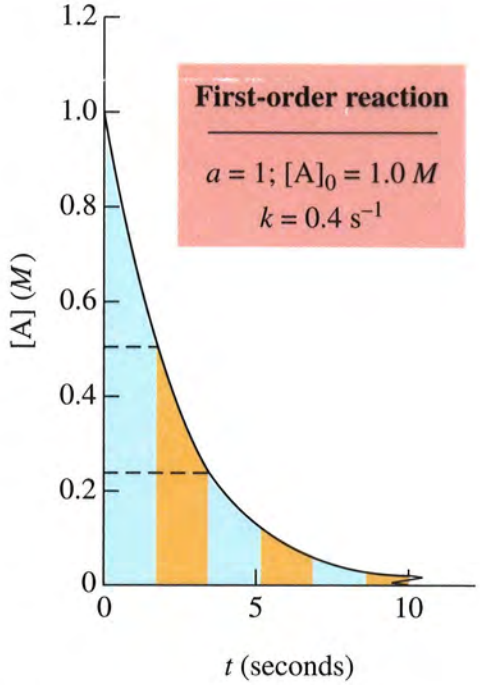
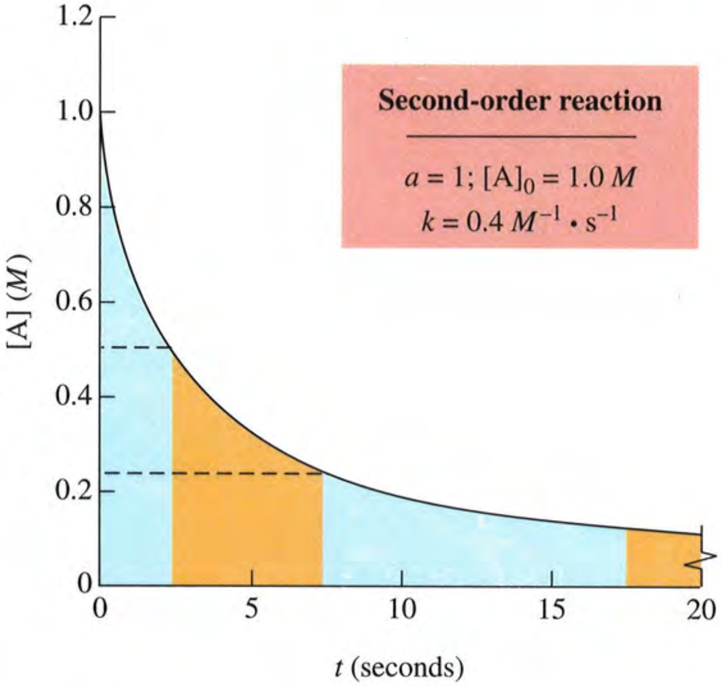


(a)



(b)

Whitten/Davis/Peck, *General Chemistry and*
General Chemistry with Qualitative Analysis, 5/e

Saunders College Publishing

1) Half-life for 2nd order

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = akt_{1/2}$$

$$\frac{1}{[A]_0} = akt_{1/2}$$

$$\boxed{t_{1/2} = \frac{1}{ak[A]_0}}$$

Depends on initial conc.

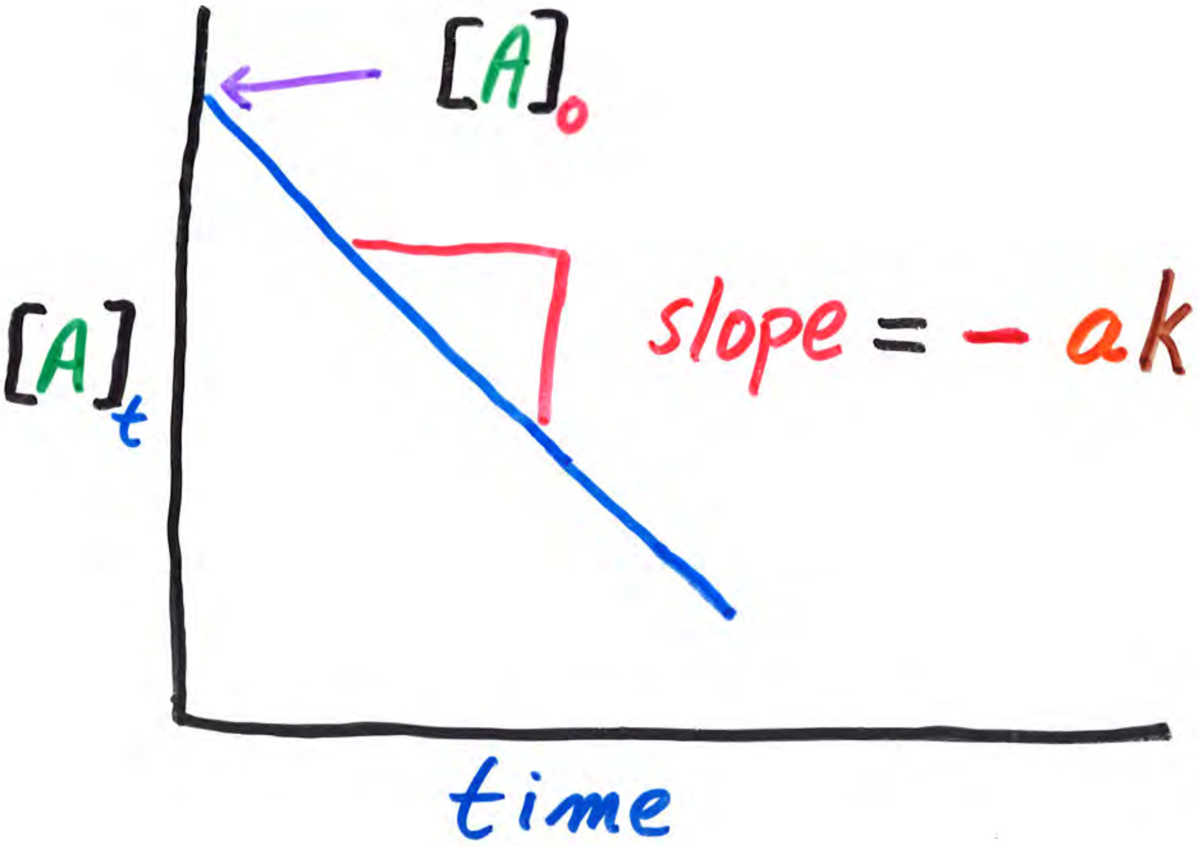
$[A]_0$ dec. , $t_{1/2}$ inc.

C) Zero Order Rx

$$r = -\frac{1}{a}\frac{d[A]}{dt} = k$$

Integrated rate eqn.:

$$\boxed{[A]_t = -(ak)t + [A]_0}$$



1) Half-life for Zero Order

$$\frac{1}{2}[A]_0 - [A]_0 = -akt_{1/2}$$

$$-\frac{1}{2}[A]_0 = -akt_{1/2}$$

$$\boxed{t_{1/2} = \frac{[A]_0}{2ak}}$$

Depends on initial conc.

$[A]_0$ dec. , $t_{1/2}$ dec.

Order	0^{th}	1^{st}	2^{nd}
rate law	$r = k$	$r = k[A]$	$r = k[A]^2$
units for k **ex.:**	$\frac{conc}{time}$ $\frac{M}{\text{sec}}$ $M \cdot s^{-1}$	$\frac{1}{time}$ $\frac{1}{min}$ min^{-1}	$\frac{1}{conc \cdot time}$ $\frac{1}{M \cdot sec}$ $M^{-1} \cdot s^{-1}$
integrated rate expression	$[A]_t = -kt + [A]_0$	$\ln[A]_t = -kt + \ln[A]_0$ or $\ln\frac{[A]_t}{[A]_0} = -kt$ or $[A]_t = [A]_0 e^{-kt}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$
plot as y	$[A]$	$\ln [A]$	$\frac{1}{[A]}$
plot as x	t	t	t
slope	$-k$ (neg. slope)	$-k$ (neg. slope)	k (pos. slope)
y-intercept	$[A]_0$	$\ln[A]_0$	$\frac{1}{[A]_0}$
$t_{1/2}$	$\frac{[A]_0}{2k}$	$\frac{0.693}{k}$	$\frac{1}{k[A]_0}$

VI) How Chemical Rx's Occur

(Temp. Dependence of Rx. Rates)

Two generally accepted theories that can explain relationship between rate and conc. & temp.

Collision Theory

Transition State Theory

A) Collision Theory

Molecules must collide for a rx. to occur

$$\text{rate} \propto \frac{\text{no. collisions/vol.}}{\text{sec.}}$$

Can use KMT to calc. collision frequency for gases. Results predict coll. freq on order of $10^{10} - 10^{20}$ greater than exp. rx. rates.

- Simple collision is not enough to cause rx.

In order for collision to be effective the molecules must:

(1) possess some min. energy
(2) have a particular orientation

Rate constant reflects these requirements,

$$k = Z \cdot f \cdot P$$

$Z \equiv$ collision freq.

$f \equiv$ fraction of coll. w. some min. energy, E_a
- related to $e^{-(E_a/RT)}$

$P \equiv$ probability that molecules have required orientation.

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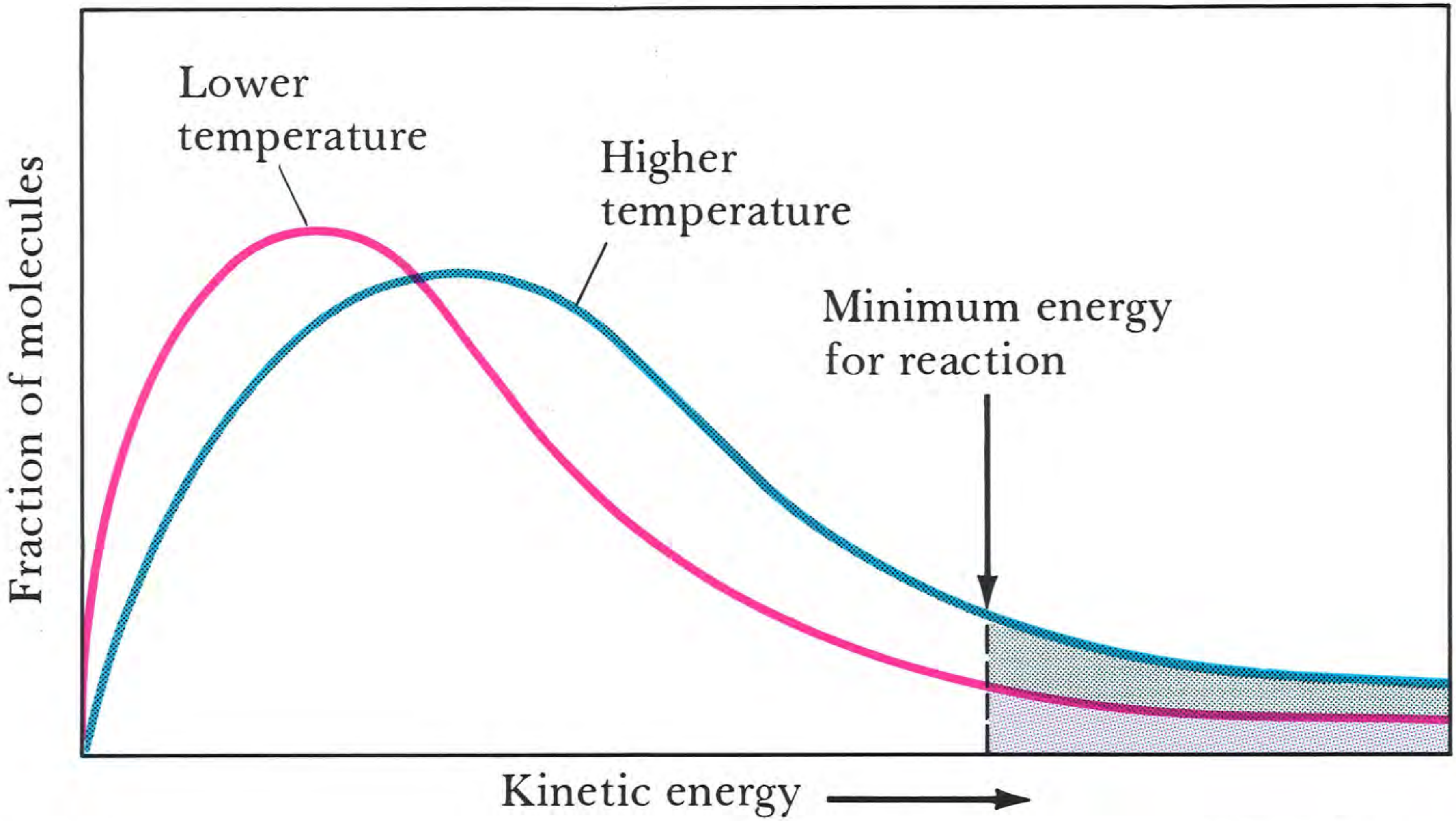
Figure 14.9 Distribution of kinetic energies at two temperatures



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B) Transition State Theory

Need two factors as modifications on coll. freq. in coll. theory.

- Energy + Geom. of reactants upon collision

Consider gas phase rx:

$$A_2 + B_2 \rightarrow 2AB$$

1) Energy of molec. is too low

- cannot overcome repulsion

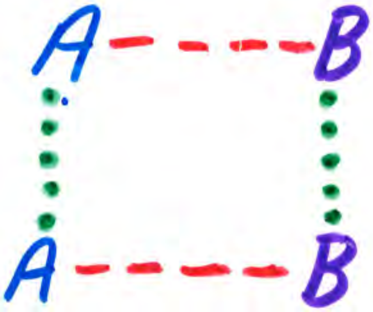
Bounce off each other

2) High energy molec. formed

Activated Complex

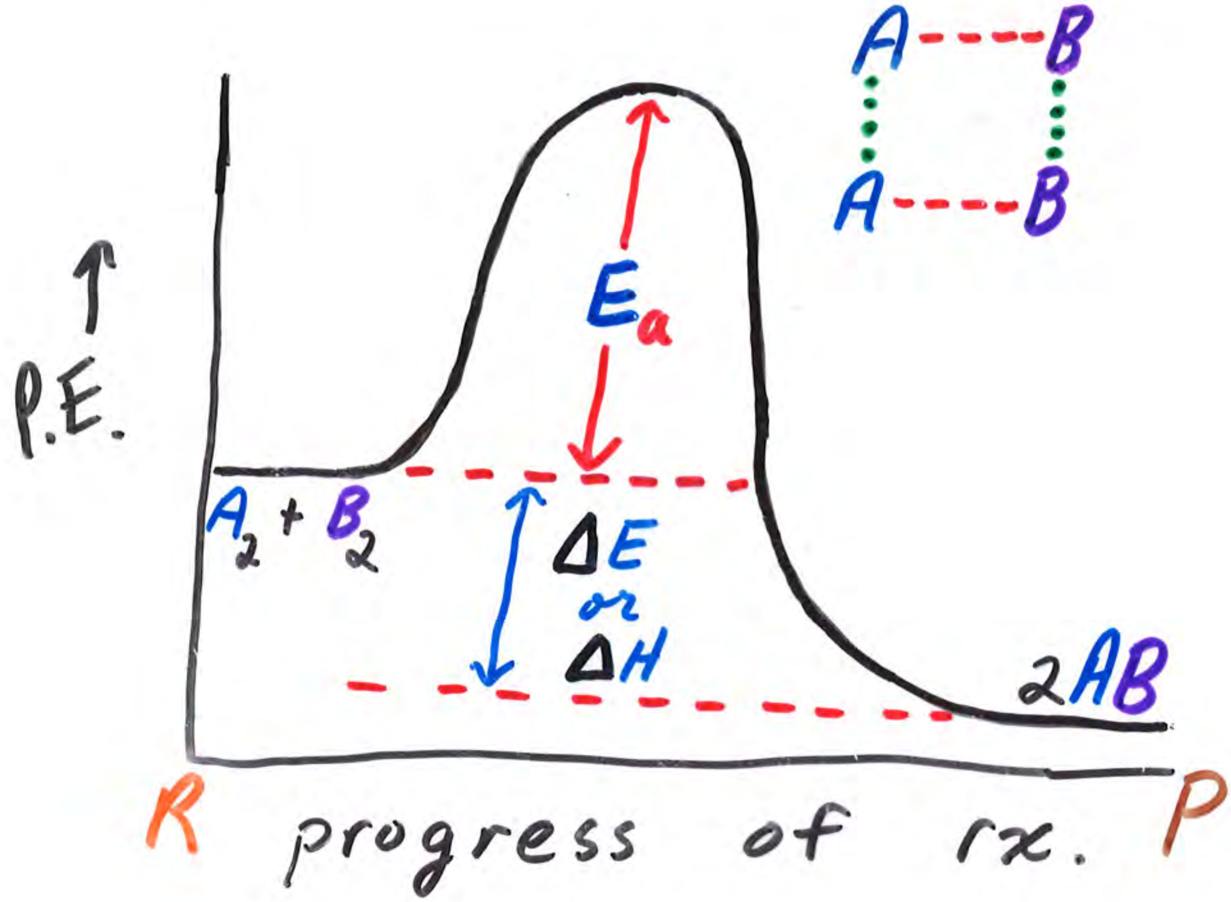
or

Transition State



Particular configuration w. only a transient existance

- inherently unstable

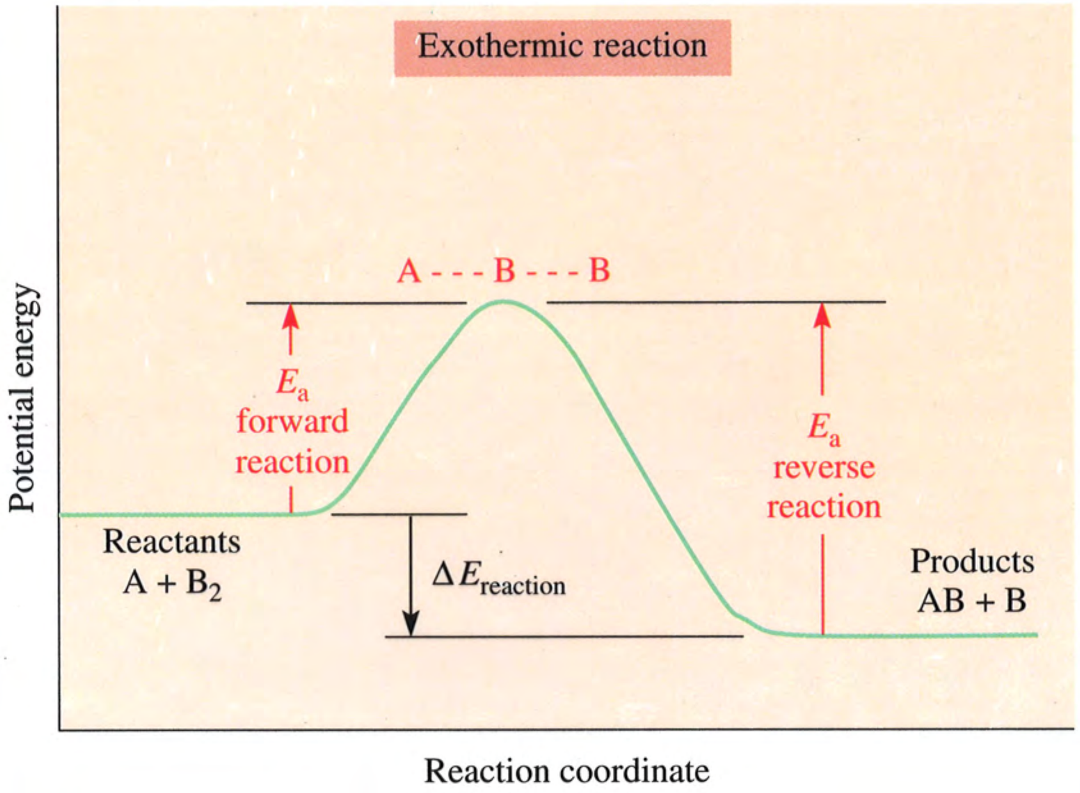


Rate of rx. is given by the rate of passage through transition state.

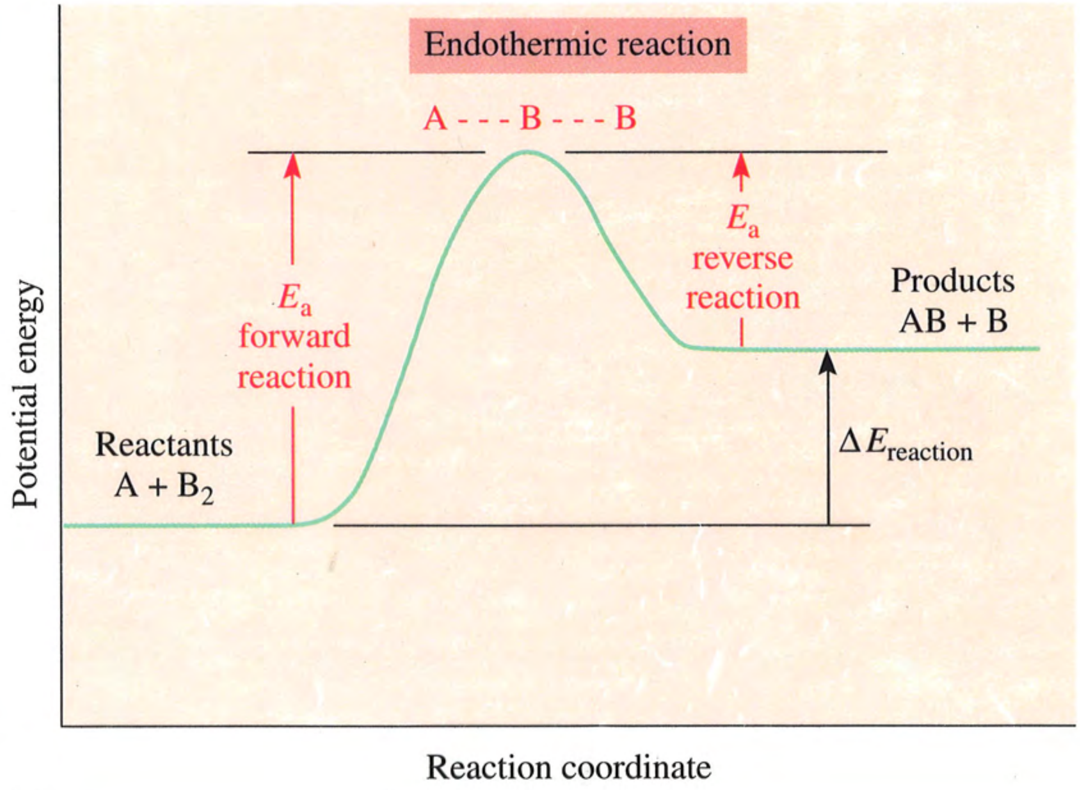
E_a - <u>Activation Energy</u>

min. energy necessary to cause rx.

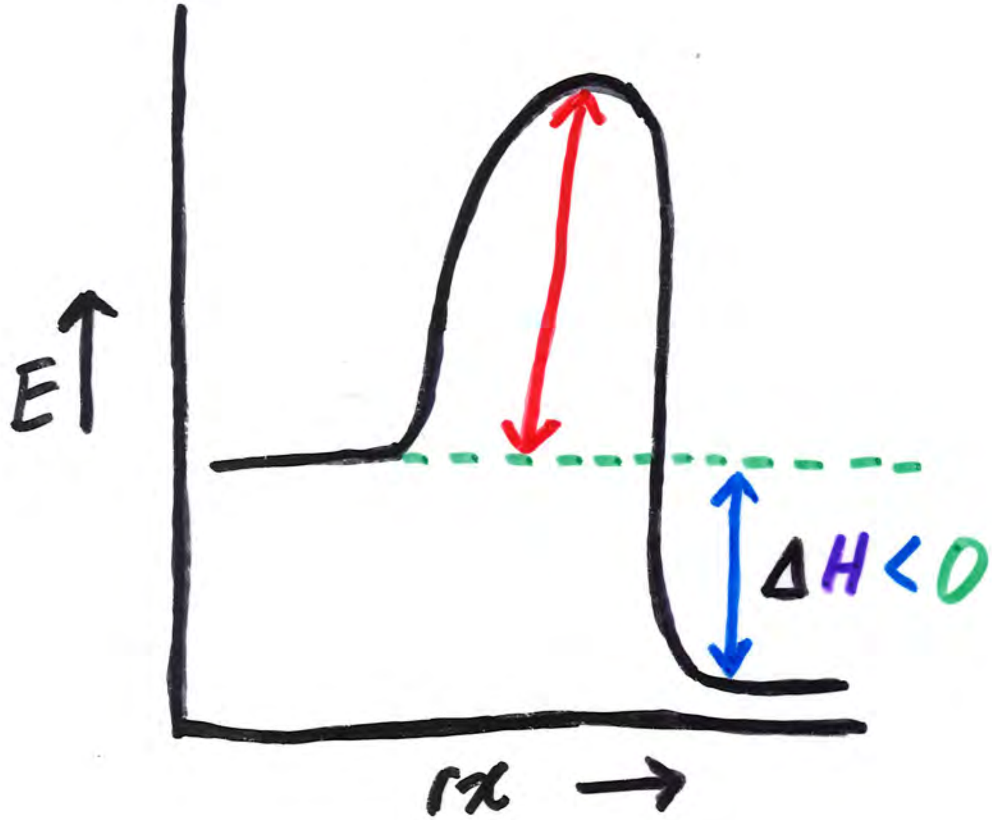
— form T.S.

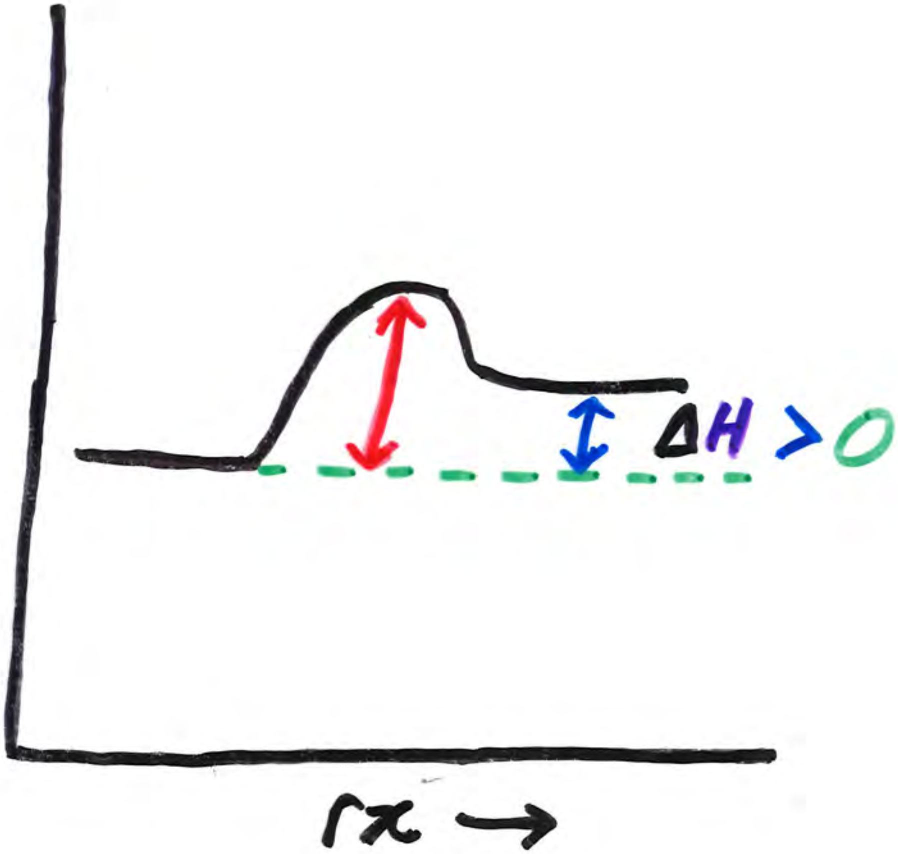

Exothermic reaction
A - - - B - - - B
E_a forward reaction
E_a reverse reaction
Reactants $A + B_2$
$\Delta E_{reaction}$
Products $AB + B$
Potential energy
Reaction coordinate

(a)


Endothermic reaction
A - - - B - - - B
E_a forward reaction
E_a reverse reaction
Products $AB + B$
Reactants $A + B_2$
$\Delta E_{reaction}$
Potential energy
Reaction coordinate

(b)


E
ΔH < 0
rx →


ΔH > 0
rx →

c) Effect of Temperature

Arrhenius Eqn.

$$\boxed{k = A\, e^{-(E_a/RT)}}$$

$A \equiv$ constant, characteristic of the rx. - frequency factor

$E_a \equiv$ Activation Energy

$R \equiv$ gas constant (8.314 J/mol-K)

$T \equiv$ Temp. (Kelvin)

$e^{-(E_a/RT)} \Rightarrow$ related to fraction of molec. that have $E \geq E_a$

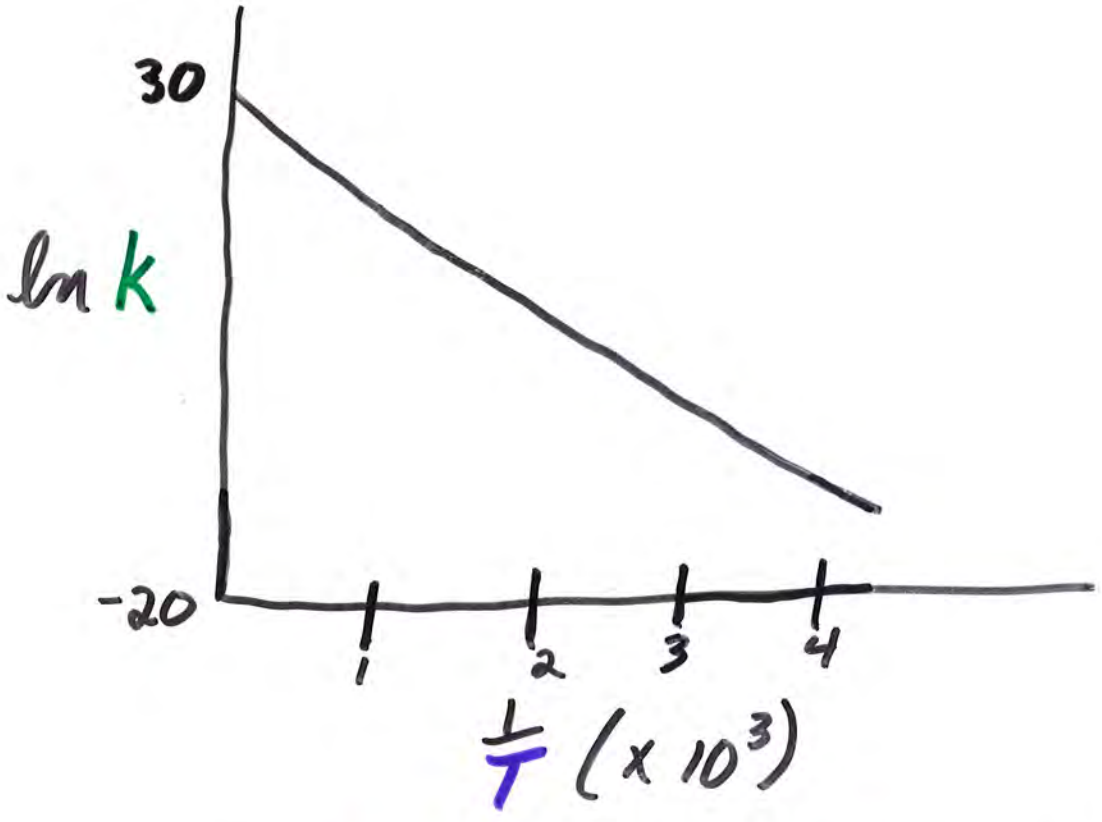
As, E_a inc., k dec., rate dec.

T inc., k inc., rate inc.

1) Straight-line Form

$$\boxed{\ln k = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln A}$$

$2\,NOCl \longrightarrow 2NO + Cl_2$



$\ln A = 30$, $A = 1.1 \times 10^{13}\ M^{-1}s^{-1}$

slope $= -1.216 \times 10^{4}\,K$, $E_a = 101\ kJ/mol$

2) Two-Point Form

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

3) Ex: What is E_a & A

$$2\,NOCl \longrightarrow 2\,NO + Cl_2$$

$k_1 = 2.8 \times 10^{-5}\ M^{-1}s^{-1}$ at 300 K

$k_2 = 7.0 \times 10^{-1}\ M^{-1}s^{-1}$ at 400 K

$$\ln\left(\frac{7.0 \times 10^{-1}}{2.8 \times 10^{-5}}\right) = \frac{E_a}{8.314 \times 10^{-3}\,kJ/mol\text{-}K}\left(\frac{1}{300\,K} - \frac{1}{400\,K}\right)$$

$$E_a = 101\ kJ/mol$$