Tro Chpt 13

Chemical Kinetics

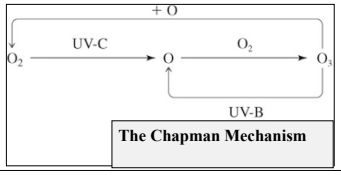
- **Rate of a chemical reaction**
- **Effect of concentration on reaction rate**
- **Integrated rate laws: How concentrations change with time**
- **Effect of temperature on rate**
- **Reaction mechanisms**

End of chapter problems Chapter 13:
25, 29, 35, 37, 38, 39, 41, 43, 49, 51, 53, 57, 59, 63, 65, 69, 71, 75, 85, 93, 97

Formation and Destruction of Stratospheric Ozone

O_3 + UV photon ($\lambda < 320$ nm) $\longrightarrow$ O_2* + O*

$O_3 + O \longrightarrow 2O_2$

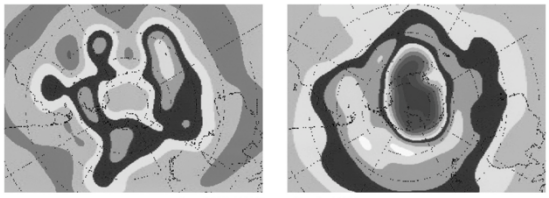


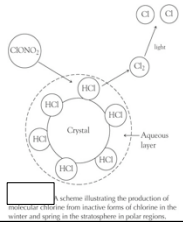
The Chapman Mechanism

So, in the stratosphere, a *steady-state* concentration of about 10 ppm is achieved

Polar Stratospheric Clouds – catalysts for O_3 destruction?

Ozone "hole" found in the Antarctic





A scheme illustrating the production of molecular chlorine from inactive forms of chlorine in the winter and spring in the stratosphere in polar regions.

Chlorine and Bromine as X catalysts

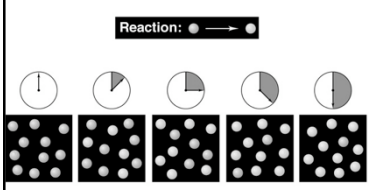
$$CH_3Cl + h\nu \xrightarrow{\text{UV-C}} Cl + CH_3$$

$$Cl + O_3 \longrightarrow ClO + O_2$$
$$ClO + O \longrightarrow Cl + O_2$$
$$\overline{O_3 + O \longrightarrow 2\ O_2 \text{ overall reaction}}$$

Tro 13.2

Rates of Chemical Reactions

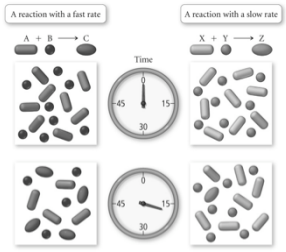
Reaction Rate



$$\text{Rate} = \frac{\Delta \text{ concentration}}{\Delta \text{ time}}$$
$$\text{Rate} = \frac{\Delta \text{ [product]}}{\Delta \text{ time}} = -\frac{\Delta \text{ [reactant]}}{\Delta \text{ time}}$$

- Rate of a chemical reaction " how much the concentration of a reactant decreases in a given period of time (or product concentration increases)
- For reactants, a negative sign is placed in front of the definition

Reaction rates continued…



at t = 0
[A] = 8
[B] = 8
[C] = 0

at t = 16
[A] = 4
[B] = 4
[C] = 4

at t = 0
[X] = 8
[Y] = 8
[Z] = 0

at t = 16
[X] = 7
[Y] = 7
[Z] = 1

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{([A]_2 - [A]_1)}{(t_2 - t_1)}$$
$$\text{Rate} = -\frac{(4-8)}{(16-0)} = 0.25$$
$$\text{Rate} = \frac{\Delta[C]}{\Delta t} = \frac{([C]_2 - [C]_1)}{(t_2 - t_1)}$$
$$\text{Rate} = \frac{(4-0)}{(16-0)} = 0.25$$

$$\text{Rate} = \frac{\Delta[Z]}{\Delta t} = \frac{([Z]_2 - [Z]_1)}{(t_2 - t_1)}$$
$$\text{Rate} = \frac{(1-0)}{(16-0)} = 0.0625$$
$$\text{Rate} = -\frac{\Delta[X]}{\Delta t} = -\frac{([X]_2 - [X]_1)}{(t_2 - t_1)}$$
$$\text{Rate} = -\frac{(7-8)}{(16-0)} = 0.0625$$

Reaction rates continued…

at t = 16
[A] = 4
[B] = 4
[C] = 4

at t = 16
[X] = 7
[Y] = 7
[Z] = 1

at t = 32
[A] = 2
[B] = 2
[C] = 6

at t = 32
[X] = 6
[Y] = 6
[Z] = 2

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{([A]_2 - [A]_1)}{(t_2 - t_1)}$$
$$\text{Rate} = -\frac{(2-4)}{(16-0)} = 0.125$$
$$\text{Rate} = \frac{\Delta[C]}{\Delta t} = \frac{([C]_2 - [C]_1)}{(t_2 - t_1)}$$
$$\text{Rate} = \frac{(6-4)}{(16-0)} = 0.125$$

$$\text{Rate} = -\frac{\Delta[X]}{\Delta t} = -\frac{([X]_2 - [X]_1)}{(t_2 - t_1)}$$
$$\text{Rate} = -\frac{(6-7)}{(16-0)} = 0.0625$$
$$\text{Rate} = \frac{\Delta[Z]}{\Delta t} = \frac{([Z]_2 - [Z]_1)}{(t_2 - t_1)}$$
$$\text{Rate} = \frac{(2-1)}{(16-0)} = 0.0625$$

Reaction rates continued…

at t = 32
[A] = 2
[B] = 2
[C] = 6

at t = 32
[X] = 6
[Y] = 6
[Z] = 2

at t = 48
[A] = 0
[B] = 0
[C] = 8

at t = 48
[X] = 5
[Y] = 5
[Z] = 3

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{([A]_2 - [A]_1)}{(t_2 - t_1)}$$

$$\text{Rate} = -\frac{(0-2)}{(16-0)} = 0.125$$

$$\text{Rate} = -\frac{\Delta[X]}{\Delta t} = -\frac{([X]_2 - [X]_1)}{(t_2 - t_1)}$$

$$\text{Rate} = -\frac{(5-6)}{(16-0)} = 0.0625$$

$$\text{Rate} = \frac{\Delta[C]}{\Delta t} = \frac{([C]_2 - [C]_1)}{(t_2 - t_1)}$$

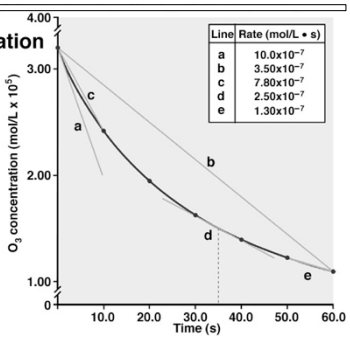
$$\text{Rate} = \frac{(8-6)}{(16-0)} = 0.125$$

$$\text{Rate} = \frac{\Delta[Z]}{\Delta t} = \frac{([Z]_2 - [Z]_1)}{(t_2 - t_1)}$$

$$\text{Rate} = \frac{(3-2)}{(16-0)} = 0.0625$$

Instantaneous vs. Average Rates

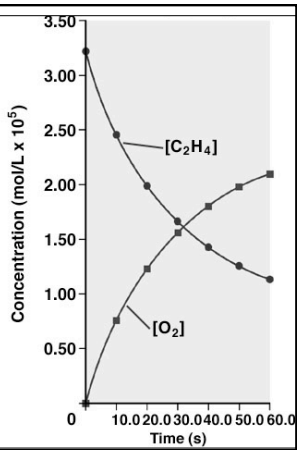
Plot of Concentration of O_3 vs. Time



$$C_2H_4 + O_3 \longrightarrow C_2H_4O + O_2$$

Plots of $[C_2H_4]$ and $[O_2]$ vs. Time

$$C_2H_4 + O_3 \longrightarrow C_2H_4O + O_2$$



Defining reaction rates - reaction stoichiometry

$$C_2H_4 + O_3 \longrightarrow C_2H_4O + O_2$$

$$\text{rate} = -\frac{\Delta[C_2H_4]}{\Delta t} = -\frac{\Delta[O_3]}{\Delta t} = +\frac{\Delta[C_2H_4O]}{\Delta t} = +\frac{\Delta[O_2]}{\Delta t}$$

$$H_2 + I_2 \longrightarrow 2HI$$

$$\text{rate} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

or

$$\text{rate} = -2\frac{\Delta[H_2]}{\Delta t} = -2\frac{\Delta[I_2]}{\Delta t} = +\frac{\Delta[HI]}{\Delta t}$$

$O_2 + 2NO \longrightarrow 2NO_2$

Initial Rates for a Series of Experiments in the Reaction Between O_2 and NO

Experiment	Initial Reactant Concentrations (mol/L) O_2	NO	Initial Rate (mol/L • s)
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}
5	1.10×10^{-2}	3.90×10^{-2}	28.8×10^{-3}

The Rate Law - *experimentally determined*!

Rate = k[concentration] **(first order reaction)**

Rate = k[concentration]^2 **(second order reaction)**

$NO + O_3 \longrightarrow NO_2 + O_2$ rate = $k[NO][O_3]$

$2NO + H_2 \longrightarrow N_2 + 2H_2O$ rate = $k[NO]^2[H_2]$

$(CH_3)_3C\text{-}Br + H_2O \longrightarrow (CH_3)_3\text{-}OH + H^+ + Br^-$ rate = $k[(CH_3)_3C\text{-}Br]$

$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$ rate = $k[CHCl_3][Cl_2]^{1/2}$

$2O_3 \longrightarrow 3O_2$ rate = $k[O_3]^2[O_2]^{-1}$

Using data to determine a rate law

$O_2 + 2NO \longrightarrow 2NO_2$

Experiment	Initial Reactant Concentrations (mol/L) O_2	NO	Initial Rate (mol/L • s)
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}
4	3.30×10^{-2}	1.30×10^{-2}	9.60×10^{-3}
5	1.10×10^{-2}	3.90×10^{-2}	28.8×10^{-3}

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[O_2]_2^m[NO]_2^n}{k[O_2]_1^m[NO]_1^n}$$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k[O_2]_2^m}{k[O_2]_1^m} = \left(\frac{[O_2]_2}{[O_2]_1}\right)^m$$

$$\frac{6.4\times10^{-3}\ \text{molL}^{-1}\text{S}^{-1}}{3.21\times10^{-3}\ \text{molL}^{-1}\text{S}^{-1}} = \left(\frac{[2.20\times10^{-2}\ \text{molL}^{-1}\text{S}^{-1}]}{[1.1\times10^{-2}\ \text{molL}^{-1}\text{S}^{-1}]}\right)^m$$

$1.99 = (2.00)^m$

$m = 1$

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \left(\frac{[NO]_3}{[NO]_1}\right)^n$$

$$\frac{12.8\times10^{-3}\ \text{molL}^{-1}\text{S}^{-1}}{3.21\times10^{-3}\ \text{molL}^{-1}\text{S}^{-1}} = \left(\frac{[2.60\times10^{-2}\ \text{molL}^{-1}\text{S}^{-1}]}{[1.3\times10^{-2}\ \text{molL}^{-1}\text{S}^{-1}]}\right)^m$$

$3.99 = (2.00)n$

$n = 2$

Rate = k $[O_2][NO]^2$

Relationship between time elapsed and reactant (or product) concentration: Integrated Rate Laws

Rate = $-\Delta[A]/\Delta t = k[A]$ (a *first order reaction)*

Integrate this differential rate law…

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

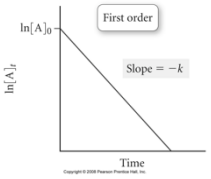
$$\ln[A]_0 - \ln[A]_t = kt$$

Rate = $-\Delta[x]/\Delta t = k[x]^2$ (a *second order reaction)*

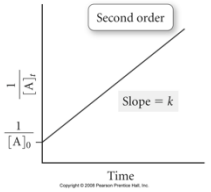
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Using data to determine the reaction order

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



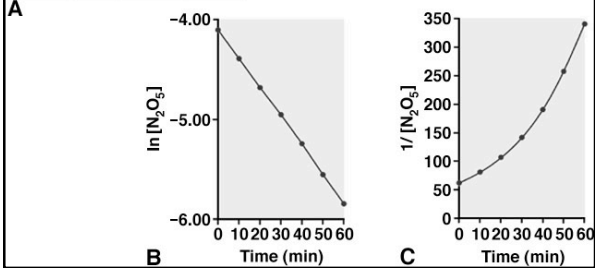
$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$



Time (min)	$[N_2O_5]$	ln $[N_2O_5]$	$1/[N_2O_5]$
0	0.0165	−4.104	60.6
10	0.0124	−4.390	80.6
20	0.0093	−4.68	1.1×10^2
30	0.0071	−4.95	1.4×10^2
40	0.0053	−5.24	1.9×10^2
50	0.0039	−5.55	2.6×10^2
60	0.0029	−5.84	3.4×10^2

Reaction Order for the Decomposition of N_2O_5

$2N_2O_5 \longrightarrow 4NO_2 + O_2$



Sample problem using the integrated rate law…

2HI $\longrightarrow$ $H_2 + I_2$

Rate = $k[HI]^2$ and $k = 2.4 \times 10^{-21}$ $Lmol^{-1}s^{-1}$

Suppose 0.0100 mol of HI is placed in a 1 liter flask; how long before [HI] = 0.009 M?

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[0.009]_t} - \frac{1}{[0.010]} = (2.4\times10^{-21}\,Lmol^{-1}s^{-1})t$$

Back to first order reactions…

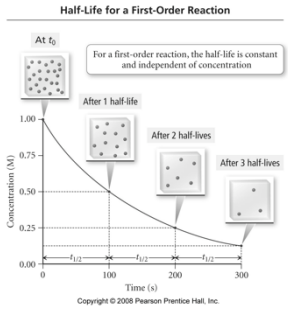
$$[A]_t = [A]_0 e^{-kt}$$

$$\frac{[A]_t}{[A]_0} = e^{-kt}$$

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

$$\ln\frac{0.5[A]_0}{[A]_0} = -kt_{1/2}$$

$$0.693 = kt_{1/2}$$

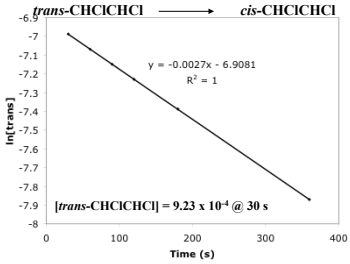


What's the half life for the conversion of cyclobutane to ethylene if $k = 0.0277$ min^{-1}?

Review problems - integrated rate laws

" Given the data for the change in [reactant]/ΔT, determine the half life and the initial concentration of the reactant for

trans-CHClCHCl ⟶ *cis*-CHClCHCl



$t_{1/2}$=0.693/*k*

$t_{1/2}$ = *0.693/.0027 = 256 s*

$$\ln\frac{[9.23\times10^{-4}]_t}{[A]_0} = -(0.0027 s^{-1}) * (30s)$$

$[A]_0$ = 1.00 x 10^{-3} M

Review problems - integrated rate laws cont'd

"The decomposition of N_2O_5 is first order with a rate constant of 2.5 x 10^{-4} s^{-1}.

a) What is the half life for the decomposition of N_2O_5?

$t_{1/2}$ = 0.693/*k* = 2772 s^{-1}

b) How long does it take for the concentration of N_2O_5 to drop to 1/32 of its original value?

$$\ln\frac{[1]_t}{[32]_0} = -(2.5\times10^{-4} s^{-1}) * (t)$$

t = 13862 s

c) How long does it take for the concentration of N_2O_5 to drop from 3.4 x 10^{-3}M to 2.3 x 10^{-5} M?

$$\ln\frac{[2.3\times10^{-5}]_t}{[3.4\times10^{-3}]_0} = -(2.5\times10^{-4} s^{-1}) * (t)$$

t = 19984 s

TABLE 13.2 Rate Law Summary Table

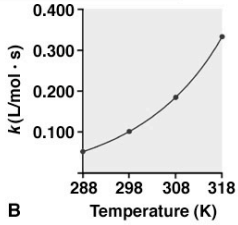
Order	Rate Law	Units of *k*	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M s^{-1}$	$[A]_t = -kt + [A]_0$	*y*-intercept = $[A]_0$; Slope = $-k$; Time *t*	$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k}\frac{[A]_0}{2}$
1	Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$; $\ln\frac{[A]_t}{[A]_0} = -kt$	*y*-intercept = $\ln[A]_0$; Slope = $-k$; Time *t*	$t_{1/2} = \frac{0.693}{k} = \frac{1}{k}(0.693)$
2	Rate = $k[A]^2$	$M^{-1}s^{-1}$	$\frac{1}{[A]_0} = kt + \frac{1}{[A]_0}$	Slope = k; *y*-intercept = $1/[A]_0$; Time *t*	$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k}\frac{1}{[A]_0}$

Tro 13.5

The Effect of Temperature on Reaction Rate

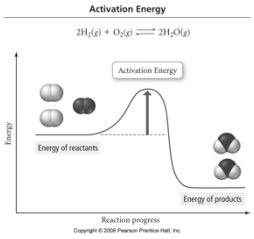
Expt	[Ester]	[H_2O]	*T*(K)	Rate (mol/L · s)	*k* (L/mol · s)
1	0.100	0.200	288	1.04×10^{-3}	0.0521
2	0.100	0.200	298	2.02×10^{-3}	0.101
3	0.100	0.200	308	3.68×10^{-3}	0.184
4	0.100	0.200	318	6.64×10^{-3}	0.332

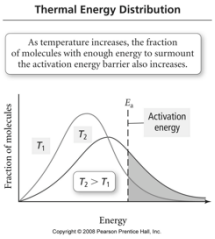
A



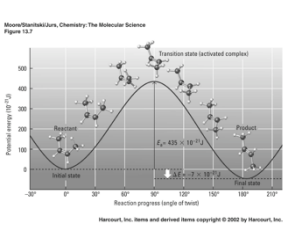
B

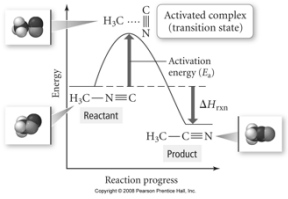
Effect of Temperature on Rates of Chemical Reactions cont'd





Energy Diagrams





***cis*-2-butene** ***trans*-2-butene**

Rate constant *k* increases rapidly with temperature

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

$$\ln(k) = \ln(A) + (-E_a/RT)$$

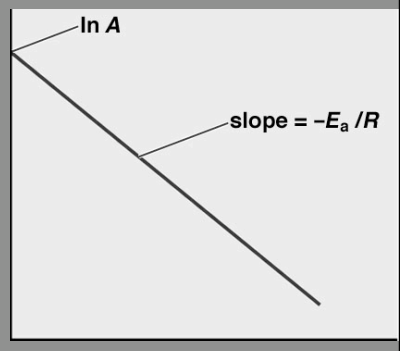
Where *A* is the frequency factor, E_a is the activation energy, R is the gas constant (8.314 $Jmol^{-1}K^{-1}$) and T is temperature in Kelvin

Arrhenius Plots: Experimental Measurements of E_a

$$y = mx + b$$

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

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



Using the Arrhenius Equation- calculating E_a

$$2HI \longrightarrow H_2 + I_2$$

At 500 K, $k = 9.51 \times 10^{-9}$ Lmol^{-1}s^{-1}

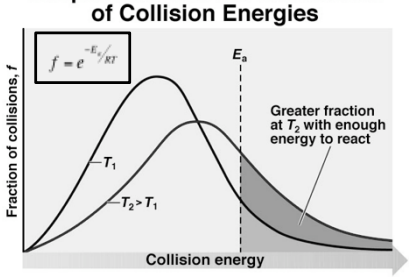
At 600 K, $k = 1.10 \times 10^{-5}$ Lmol^{-1}s^{-1}

Calculate E_a

$$\ln\left(\frac{1.1\times10^{-5}}{9.51\times10^{-9}}\right) = -\left(\frac{E_a}{8.314}\right)\left(\frac{1}{600} - \frac{1}{500}\right)$$

$E_a = 1.76 \times 10^2$ kJmol^{-1}

Temperature and the Distribution of Collision Energies



Effect of E_a and T on "f"

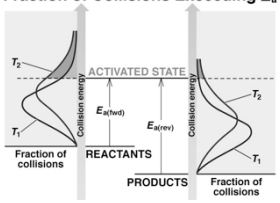
$$f = e^{-E_a/RT}$$

Activation Energy

The Effect of E_a and T on the Fraction (f) of Collisions with Sufficient Energy to Allow Reaction

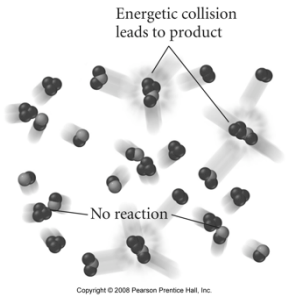
E_a (kJ/mol)	f (at T = 298 K)
50	1.70×10^{-9}
75	7.03×10^{-14}
100	2.90×10^{-18}
T	f (at E_a = 50 kJ/mol)
25°C (298 K)	1.70×10^{-9}
35°C (308 K)	3.29×10^{-9}
45°C (318 K)	6.12×10^{-9}

Fraction of Collisions Exceeding E_a

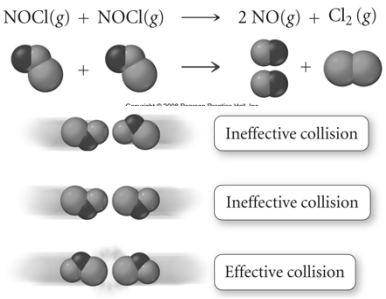


Effective Collisions
Kinetic Energy Factor

for a collision to lead to overcoming the energy barrier, the reacting molecules must have sufficient kinetic energy so that when they collide it can form the activated complex



Effective Collisions
Orientation Effect

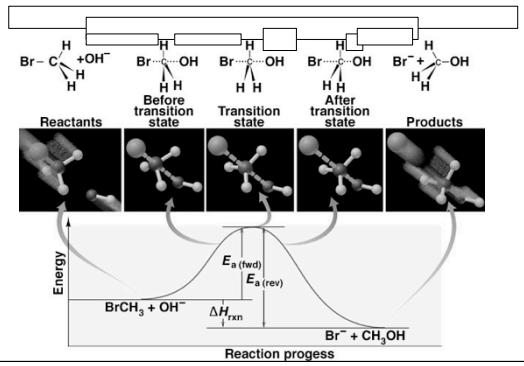


Collision Theory and the Arrhenius Equation

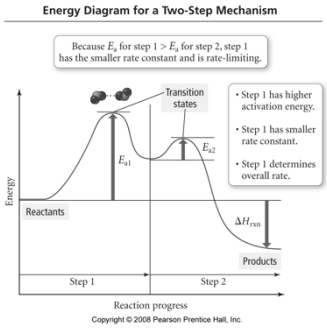
- *A* is the factor called the **frequency factor** and is the number of molecules that can approach overcoming the energy barrier
- there are two factors that make up the frequency factor – the **orientation factor (*p*)** and the **collision frequency factor (*z*)**

$$k = A\left(e^{\frac{-E_a}{RT}}\right) = pze^{\frac{-E_a}{RT}}$$

Tro 13.6



Tro 13.6-13.7



Reaction Mechanisms: Steps in the overall reaction

2A + B ⟶ E + F

(1) A + B ⟶ C

(2) C + A ⟶ D

(3) D ⟶ E + F

Elementary steps and molecularity

Net: 2A + B ⟶ E + F

"The exponents in the rate law of an elementary step are identical to the coefficients in the equation for the step"

Rate Laws of Elementary Steps

TABLE 13.3 Rate Laws for Elementary Step

Elementary Step	Molecularity	Rate Law
A ⟶ products	1	Rate = k[A]
A + A ⟶ products	2	Rate = k[A]^2
A + B ⟶ products	2	Rate = k[A][B]
A + A + A ⟶ products	3 (rare)	Rate = k[A]^3
A + A + B ⟶ products	3 (rare)	Rate = k[A]^2[B]
A + B + C ⟶ products	3 (rare)	Rate = k[A][B][C]

Devising the reaction mechanism

Step 1: $H_2O_2 + I^- \longrightarrow H_2O + O_2 + IO^-$ **slow**

Step 2: $H_2O_2 + IO^- \longrightarrow H_2O + O_2 + I^-$ **fast**

Overall: $2H_2O_2 \longrightarrow 2H_2O + 2\,O_2$

Rate = k $[H_2O_2][I^-]$

http://www.scielo.br/scielo.php?pid=S0103-50532008000600008&script=sci_arttext

Devising the reaction mechanism when the first step is NOT the slow step

$2O_3 \longrightarrow 3O_2$ $\text{rate} = k\dfrac{[O_3]^2}{[O_2]}$ **Observed rate law**

Step 1: $O_3 + M \rightleftharpoons O_2 + O + M$ **fast**

Step 2: $O + O_3 \longrightarrow 2O_2$ **slow**

Overall: $2O_3 \longrightarrow 3O_2$

BUT! rate = k_3[O][O_3] is *not* observed!

$2O_3 \longrightarrow 3O_2$ $\text{rate} = k\frac{[O_3]^2}{[O_2]}$ **Observed rate law**

Step 1: $O_3 + M \rightleftharpoons O_2 + O + M$		**fast**
Step 2: $O + O_3 \longrightarrow 2O_2$		**slow**

Steady-state approximation: i.e. "O" as an intermediate

Rate=$k_1[O_3][M]$ is the rate of formation of "O"

Rate = $k_{-1}[O_2][O][M]$ is the rate of consumption of "O"

$k_1[O_3][M] = k_{-1}[O_2][O][M]$

$$\frac{k_1[O_3]}{k_{-1}[O_2]} = [O]$$

$$\text{rate} = k_2\frac{k_1[O_3]}{k_{-1}[O_2]}[O_3] = k\frac{[O_3]^2}{[O_2]}$$

Mechanism Problem

$2NO + Cl_2 \longrightarrow 2NOCl$

$NO + Cl_2 \rightleftharpoons NOCl_2$		**fast**
$NOCl_2 + NO \longrightarrow 2NOCl$		**slow**

What is the rate law for this mechanism?

15. Consider the gas-phase reaction between nitrogen monoxide and bromine:

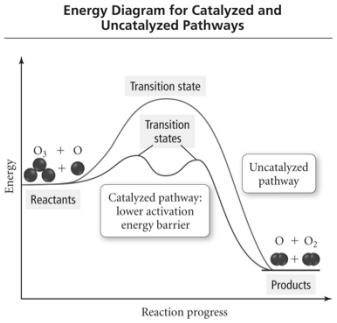
$2NO\ (g) + Br_2\ (g) \longrightarrow 2NOBr\ (g)$

Could the following mechanism be valid if the observed rate law is: rate = $k[NO]^2[br_2]$? **EXPLAIN** (note: N_2O_2 is an intermediate!) **by deriving the rate law from the mechanism!**

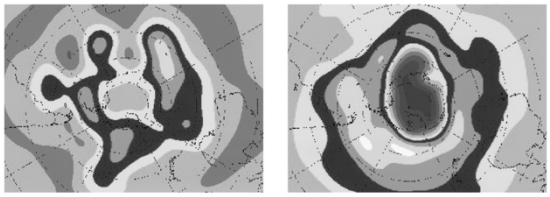
(1) $NO\ (g) + NO\ (g) \rightleftharpoons N_2O_2\ (g)$		fast
(2) $N_2O_2\ (g) + Br_2\ (g) \longrightarrow 2NOBr\ (g)$		slow

Catalysis

polar stratospheric clouds contain ice crystals that catalyze reactions that release Cl from atmospheric chemicals

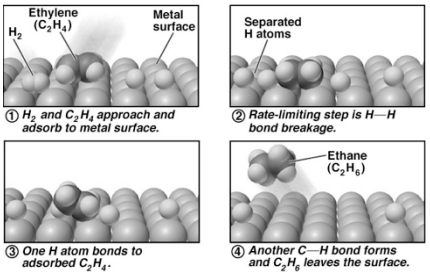


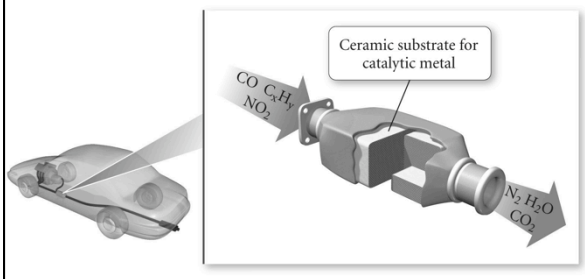
Ozone Depletion over the Antarctic



Heterogeneous Catalysis

Metal-Catalyzed Hydrogenation

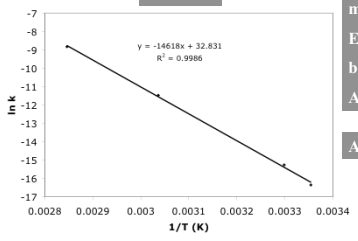




Additional Review problems from Chapter 13

Temperature (°C)	$k(s^{-1})$	1/T (K)	ln(k)
25	7.95E-08	0.0034	-16.3
30	2.37E-07	0.0033	-15.3
56.2	1.04E-05	0.003	-11.5
78.2	1.45E-04	0.0028	-8.84

- Calculate E_a
- Calculate A
- Calculate k @ 100 °C



m = $-E_a/R$

E_a = 121 kJmol^{-1}

b = ln(A) = 32.831

A = 1.8x 10^{14}

At 100°C, k = 1.7 x 10^{-3} s^{-1}

Review of sample problems from Chapter 13

For the gas phase reaction

$CH_3CH_2I \longrightarrow CH_2CH_2 + HI$

The activation energy is 221 kJmol^{-1} and the frequency factor *A* is 1.2 x 10^{14} s^{-1}. If the concentration of CH_3CH_2I is 0.012 mol L^{-1}, what is the rate of the reaction at 400 ˚C?

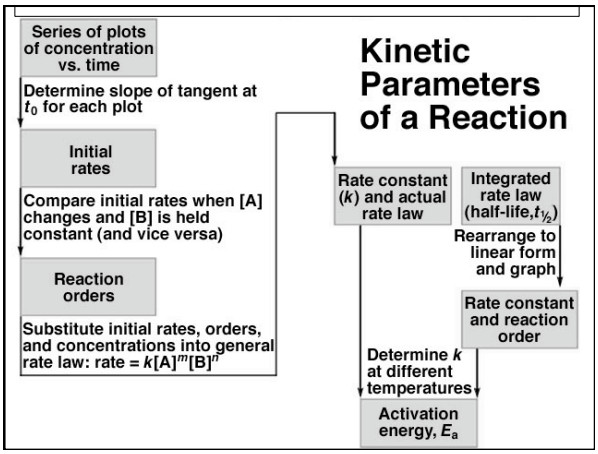


TABLE 13.2 Rate Law Summary Table

Order	Rate Law	Units of k	Integrated Rate Law	Straight-Line Plot	Half-Life Expression
0	Rate = $k[A]^0$	$M s^{-1}$	$[A]_t = -kt + [A]_0$	y-intercept = $[A]_0$; Slope = $-k$; $[A]$ vs. Time t	$t_{1/2} = \frac{[A]_0}{2k} = \frac{1}{k}\frac{[A]_0}{2}$
1	Rate = $k[A]^1$	s^{-1}	$\ln[A]_t = -kt + \ln[A]_0$; $\ln\frac{[A]_t}{[A]_0} = -kt$	y-intercept = $\ln[A]_0$; Slope = $-k$; $\ln[A]$ vs. Time t	$t_{1/2} = \frac{0.693}{k} = \frac{1}{k}(0.693)$
2	Rate = $k[A]^2$	$M^{-1} s^{-1}$	$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$	Slope = k; y-intercept = $1/[A]_0$; $1/[A]$ vs. Time t	$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{k}\frac{1}{[A]_0}$