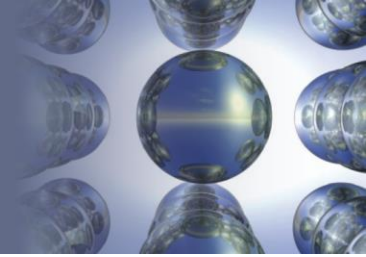


Chapter 12

Chemical Kinetics

Section 12.1

Reaction Rates



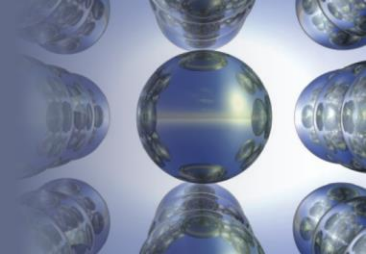
Reaction Rate

- Change in concentration of a reactant or product per unit time.

- $$Rate = \frac{[A]_{t_2} - [A]_{t_1}}{t_2 - t_1} = \frac{\Delta[A]}{\Delta t}$$

Section 12.1

Reaction Rates



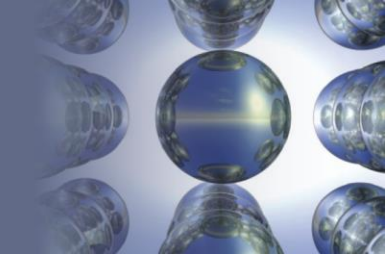
The Decomposition of Nitrogen Dioxide

Table 12.1 | Concentrations of Reactant and Products as a Function of Time for the Reaction $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$ (at 300°C)

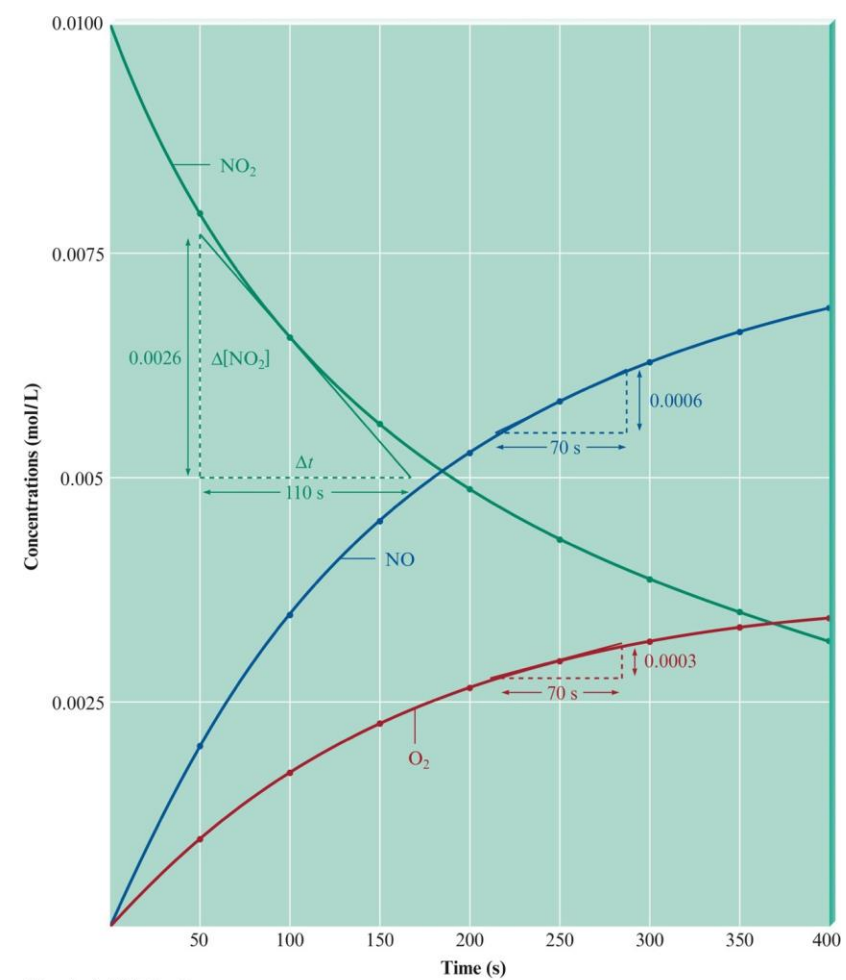
Time (± 1 s)	Concentration (mol/L)		
	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

Section 12.1

Reaction Rates

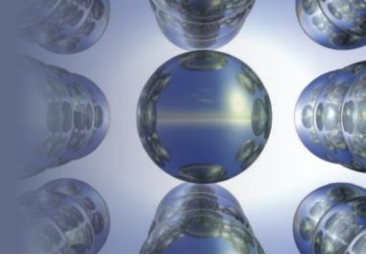


The Decomposition of Nitrogen Dioxide



Section 12.1

Reaction Rates

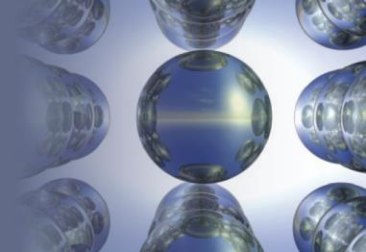


Instantaneous Rate

- Value of the rate at a particular instant of time can be obtained by computing the slope of a line tangent to the rate curve at that point.

Section 12.2

Rate Laws: An Introduction



Rate Law

- Shows how the rate depends on the concentrations of reactants.
- For the decomposition of nitrogen dioxide:



$$\text{Rate} = k[\text{NO}_2]^n:$$

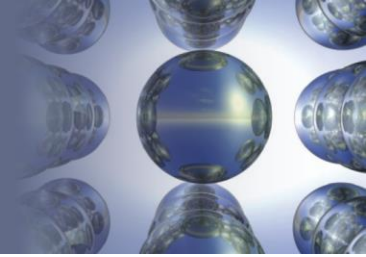
- k = rate constant ; n = order of the reactant
- The rate in terms of the concentrations of reactants and products:

$$\text{rate} = -\frac{1}{2} \frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{NO}]}{\Delta t} = \frac{\Delta[\text{O}_2]}{\Delta t}$$

$$\text{rate} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt} \quad (\textit{instantaneous rate})$$

Section 12.2

Rate Laws: An Introduction



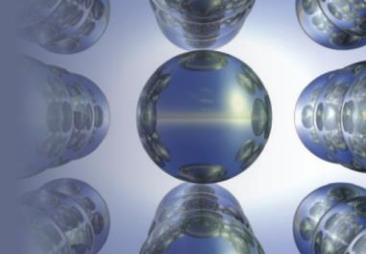
Rate Law

$$\text{Rate} = k [\text{NO}_2]^n$$

- The concentrations of the products do not appear in the rate law because the reaction rate is being studied under conditions where the reverse reaction does not contribute to the overall rate.

Section 12.2

Rate Laws: An Introduction



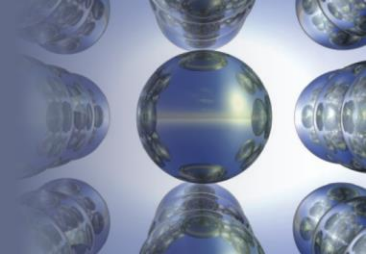
Rate Law

$$\text{Rate} = k [\text{NO}_2]^n$$

The value of the exponent n must be determined experimentally; it cannot be written from the balanced equation.

Section 12.2

Rate Laws: An Introduction

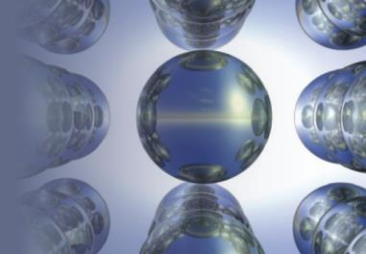


Types of Rate Laws

- Differential Rate Law (rate law) – shows how the rate of a reaction depends on concentrations.
- Integrated Rate Law – shows how the concentrations of species in the reaction depend on time.

Section 12.2

Rate Laws: An Introduction

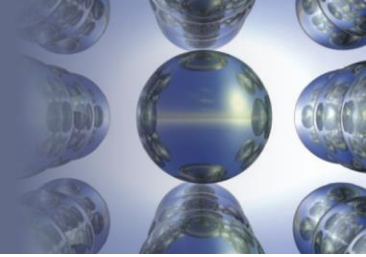


Rate Laws: A Summary

- Reaction rates are studied under conditions where the reverse reaction is unimportant. So, the concentrations of the products are not part of the rate law equation.
- The differential and integrated rate laws for a given reaction are related in a well-defined way. Therefore, the experimental determination of either of the rate laws is sufficient.

Section 12.3

Determining the Form of the Rate Law

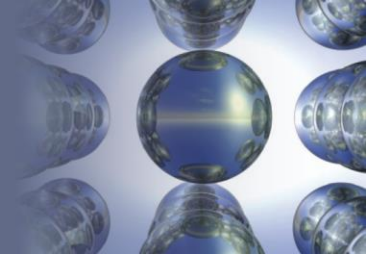


Method of Initial Rates

- Several experiments are carried out using different initial concentrations of each of the reactants where the initial rate is determined for each run.
- The results are then compared to see how the initial rate depends on the initial concentrations of each of the reactants.

Section 12.3

Determining the Form of the Rate Law



Overall Reaction Order

- The sum of the exponents in the reaction rate equation.

$$\text{Rate} = k [A]^n [B]^m$$

$$\text{Overall reaction order} = (n + m)$$

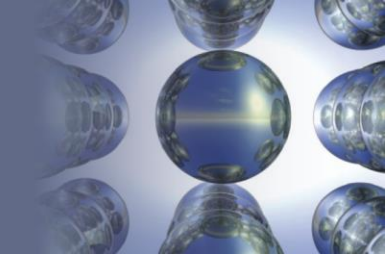
k = rate constant

[A] = concentration of reactant A

[B] = concentration of reactant B

Section 12.4

The Integrated Rate Law



First-Order:

- Consider the reaction: $A \rightarrow \text{products}$

- $Rate = k[A]_i = \frac{d[A]}{dt}$ (*"A" is a reactant, the power of [A] is one*)

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

- Integrate: *[A]₀ to [A]_t and time t=0 to time t,*

$$\ln[A] = -kt + \ln[A]_0 \quad (\textit{this is linear form of the rate law equation})$$

Plot of $\ln[A]$ against t give a straight line with negative slope of $-k$ and intercept of $\ln[A]_0$.

$[A]$ = concentration of A at time t

k = rate constant

t = time

$[A]_0$ = initial concentration of A

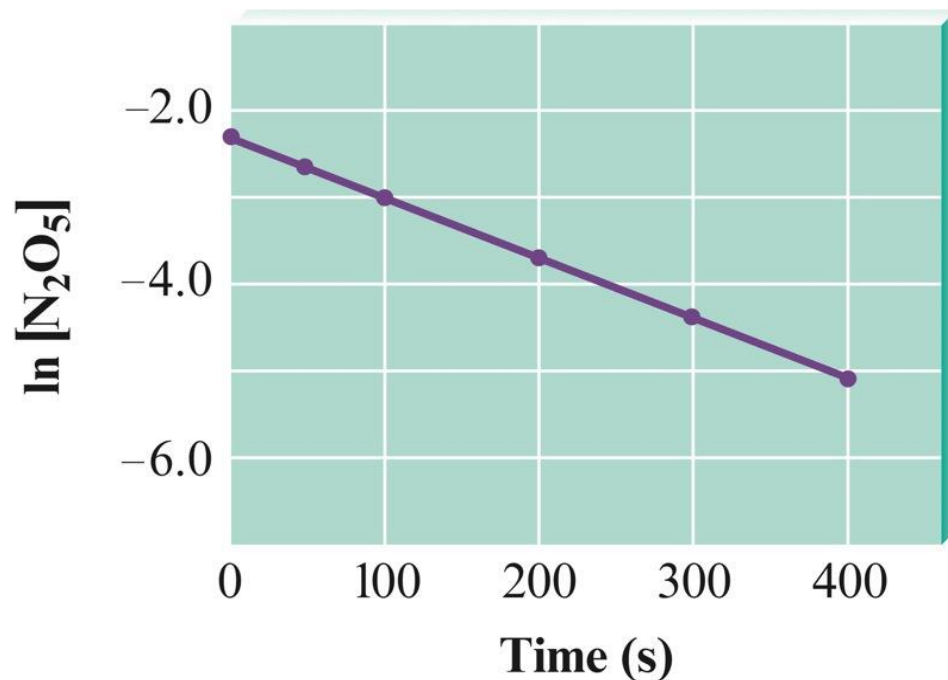
Section 12.4

The Integrated Rate Law

Plot of $\ln[\text{N}_2\text{O}_5]$ vs Time

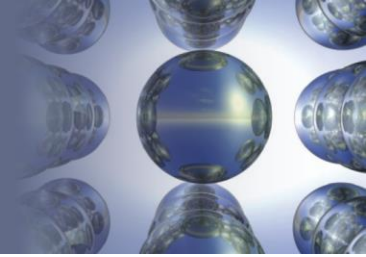
$$\text{slope} = -k = \frac{[-5 - (-3)]}{400 - 100} = -0.0133, \text{ so, } k = 0.0133$$

$\ln[\text{N}_2\text{O}_5]$	Time (s)
-2.303	0
-2.649	50
-2.996	100
-3.689	200
-4.382	300
-5.075	400



Section 12.4

The Integrated Rate Law



First-Order

- Time required for a reactant to reach half its original concentration

$$\ln[A] = -kt + \ln[A]_o$$

- $\ln(1/2[A]_o) = -k t_{1/2} + \ln[A]_o$

- Half-Life:

$$t_{1/2} = \frac{0.693}{k}$$

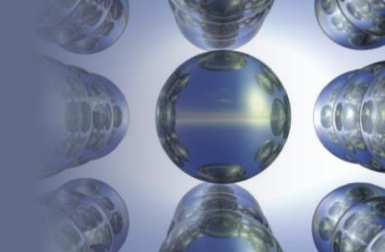
k = rate constant

- Half-life does not depend on the concentration of reactants.

- $t_{1/2} = \frac{0.693}{0.0133} = 52.1 \text{ s}$

Section 12.4

The Integrated Rate Law



- A first order reaction is **35%** complete at the end of **55** minutes. What is the value of k ?

$$\ln[A] = -kt + \ln[A]_o \quad (\text{first-order reaction})$$

$$\ln(0.65[A]_o) = -k(55 \text{ min.}) + \ln[A]_o$$

$$\ln \frac{0.65[A]_o}{[A]_o} = -kt$$

$$k = -\frac{\ln(0.65)}{55 \text{ min}} = -\frac{-0.431}{55 \text{ min}} = 7.8 \times 10^{-3} \text{ min}^{-1}$$

Section 12.4

The Integrated Rate Law

Second-Order

- Consider the reaction $A \rightarrow \text{products}$

- $\text{Rate} = \frac{d[A]}{dt} = k[A]^2$

- $\frac{d[A]}{[A]^2} = k dt$

- Integrated:
$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

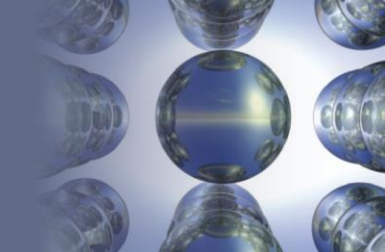
$[A]$ = concentration of A at time t ; k = rate constant ; t = time

$[A]_0$ = initial concentration of A

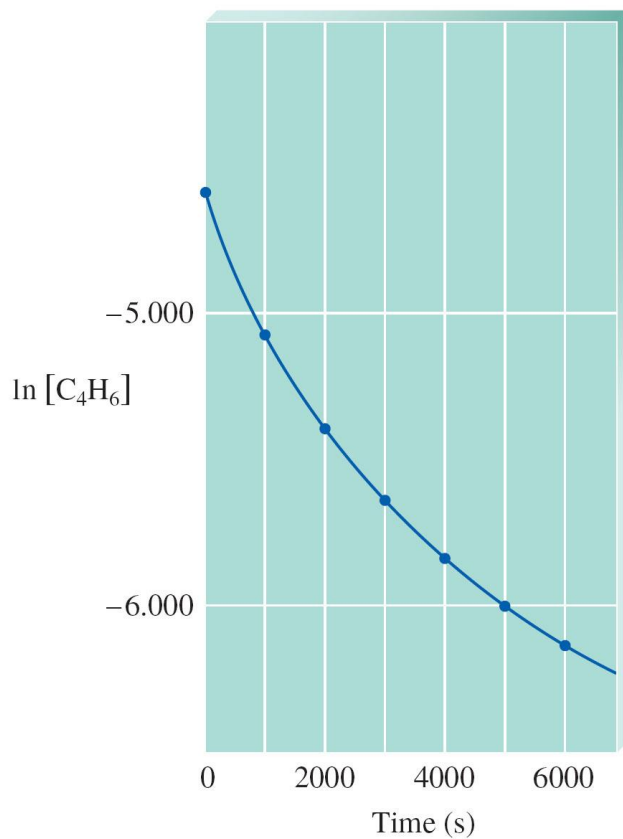
plot of $\frac{1}{[A]}$ against t produces straight line with slope k and intercept of $1/[A]_0$.

Section 12.4

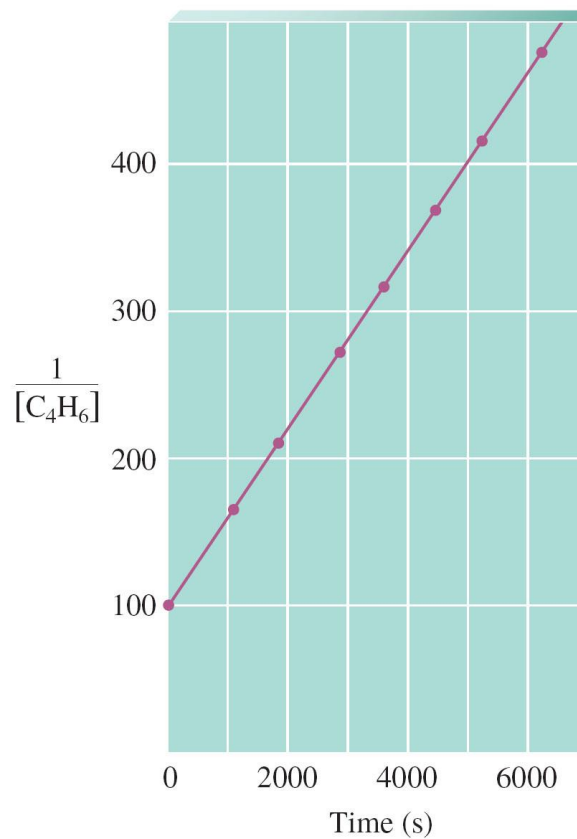
The Integrated Rate Law



Plot of $\ln[\text{C}_4\text{H}_6]$ vs Time and Plot of $1/[\text{C}_4\text{H}_6]$ vs Time



(a)



(b)

Section 12.4

The Integrated Rate Law

Second-Order

Use the data (slide 18) to calculate the half-life?

- For second-order reaction, $K = \text{slope of the line}$

- $\text{slope} = k = \frac{400 - 100}{5000 - 0} = 0.06 \frac{L}{\text{mol}\cdot\text{s}}$

- From the plot $[A]_0 = 100 \text{ M}$

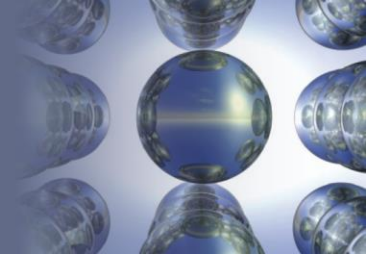
- $t\left(\frac{1}{2}\right) = \frac{1}{k[A]_0} = \frac{1}{(0.06)(100)} = 0.167 \text{ s.}$

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

- Half-life gets longer as the reaction progresses and the concentration of reactants decrease.
- Each successive half-life is double the preceding one.

Section 12.4

The Integrated Rate Law



Zero-Order

- Consider the reaction: $A \rightarrow \text{Products}$
- $\text{Rate} = \frac{d[A]}{dt} = k [A]^0 = k$ rearrange,
- $d[A] = k dt$, integrate,
 $[A] = -kt + [A]_0$

Plot of $[A]$ against t gives straight line of slope $-k$ and intercept $[A]_0$.

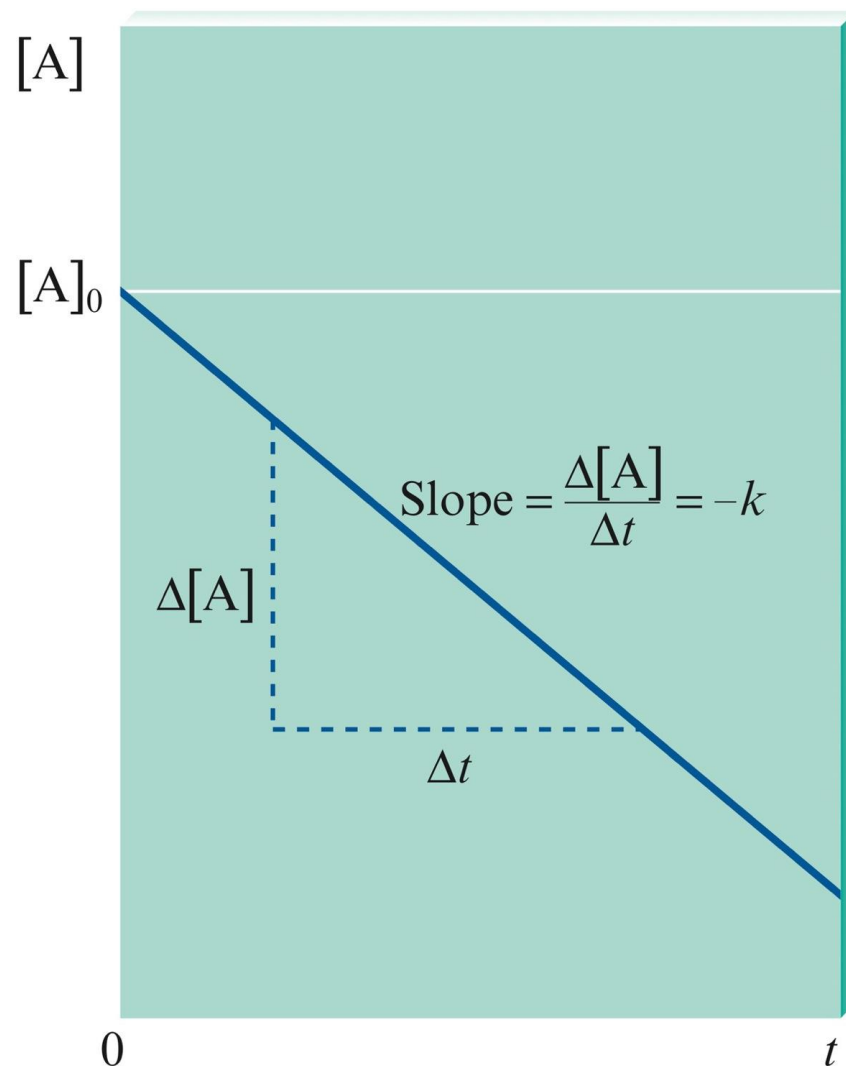
$[A]$ = concentration of A at time t

k = rate constant ; t = time ; $[A]_0$ = initial concentration of A

Section 12.4

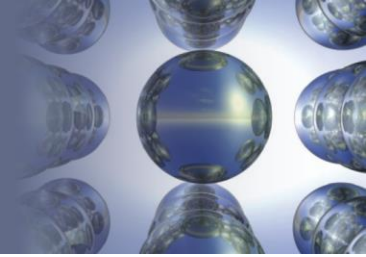
The Integrated Rate Law

Plot of [A] vs Time



Section 12.4

The Integrated Rate Law



Zero-Order

- Half-Life:

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

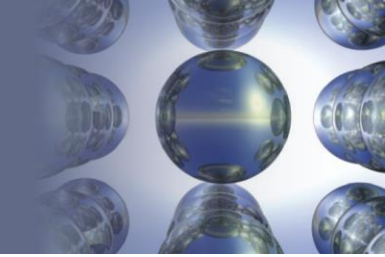
k = rate constant (s/M) ; l/M = L/mol.

$[A]_0$ = initial concentration of A

- Half-life gets shorter as the reaction progresses and the concentration of reactants decrease.

Section 12.4

The Integrated Rate Law



CONCEPT CHECK!

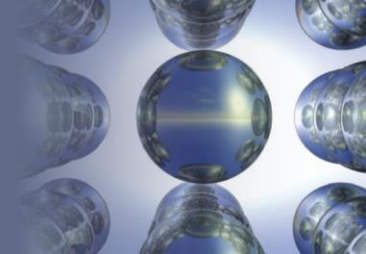
How can you tell the difference among 0th, 1st, and 2nd order rate laws from their graphs?

How can you tell the difference among 0th, 1st, and 2nd order rate laws from the units of their rate constant?

How can you tell the difference among 0th, 1st, and 2nd order rate laws from the dependence of the half-life on the initial concentration?

Section 12.4

The Integrated Rate Law



Summary of the Rate Laws

Table 12.6 | Summary of the Kinetics for Reactions of the Type $aA \rightarrow \text{Products}$ That Are Zero, First, or Second Order in $[A]$

	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-Life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Section 12.4

The Integrated Rate Law

EXERCISE!

Consider the reaction $aA \rightarrow \text{Products}$.

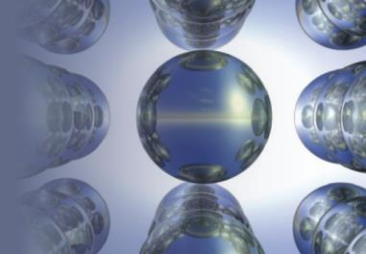
$[A]_0 = 5.0 \text{ M}$ and $k = 1.0 \times 10^{-2}$ (assume the units are appropriate for each case). Calculate $[A]$ after 30.0 seconds of the reaction, assuming the reaction is:

- a) Zero order **4.7 M**
- b) First order **3.7 M**
- c) Second order **2.0 M**

End of CH 12 for Chemistry 108

Section 12.4

The Integrated Rate Law



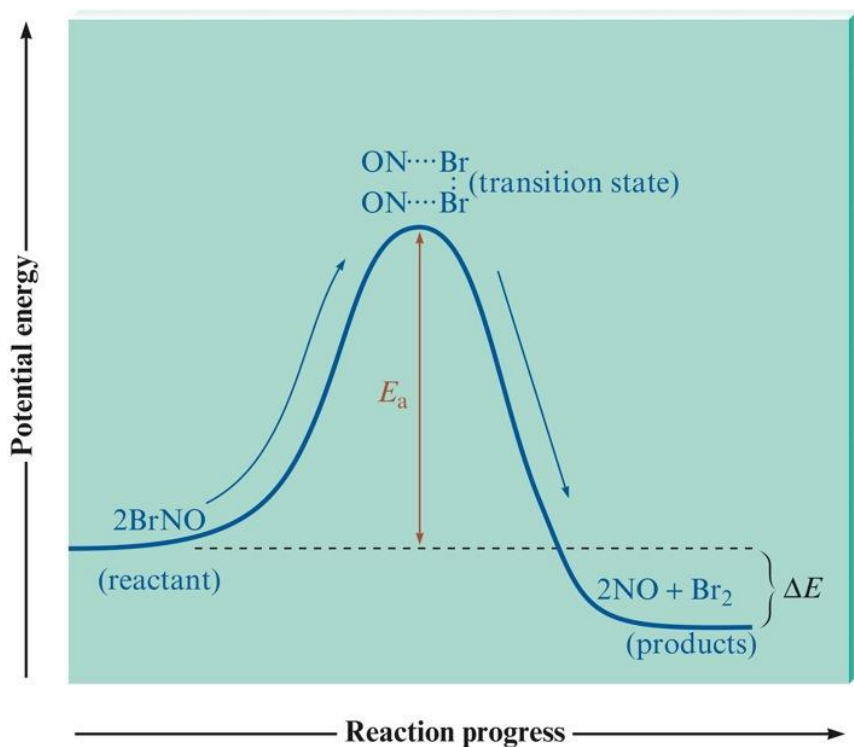
Activation Energy, E_a

- Energy that must be overcome to produce a chemical reaction.

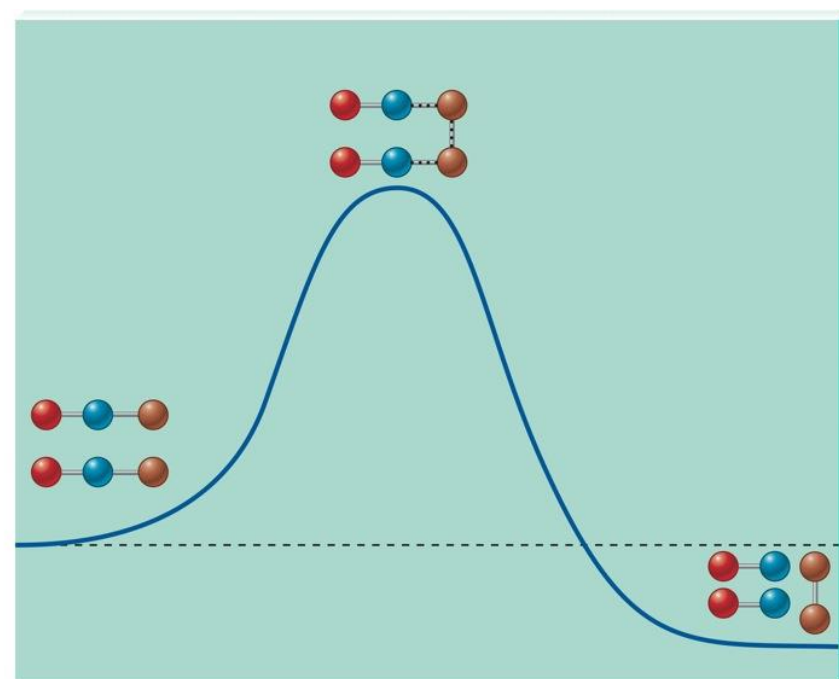
Section 12.4

The Integrated Rate Law

Change in Potential Energy



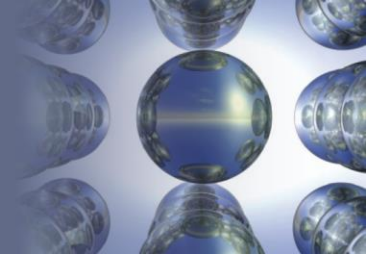
a



b

Section 12.4

The Integrated Rate Law



Arrhenius Equation

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

A = frequency factor

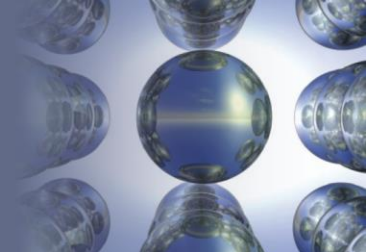
E_a = activation energy

R = gas constant (8.3145 J/K·mol)

T = temperature (in K)

Section 12.4

The Integrated Rate Law



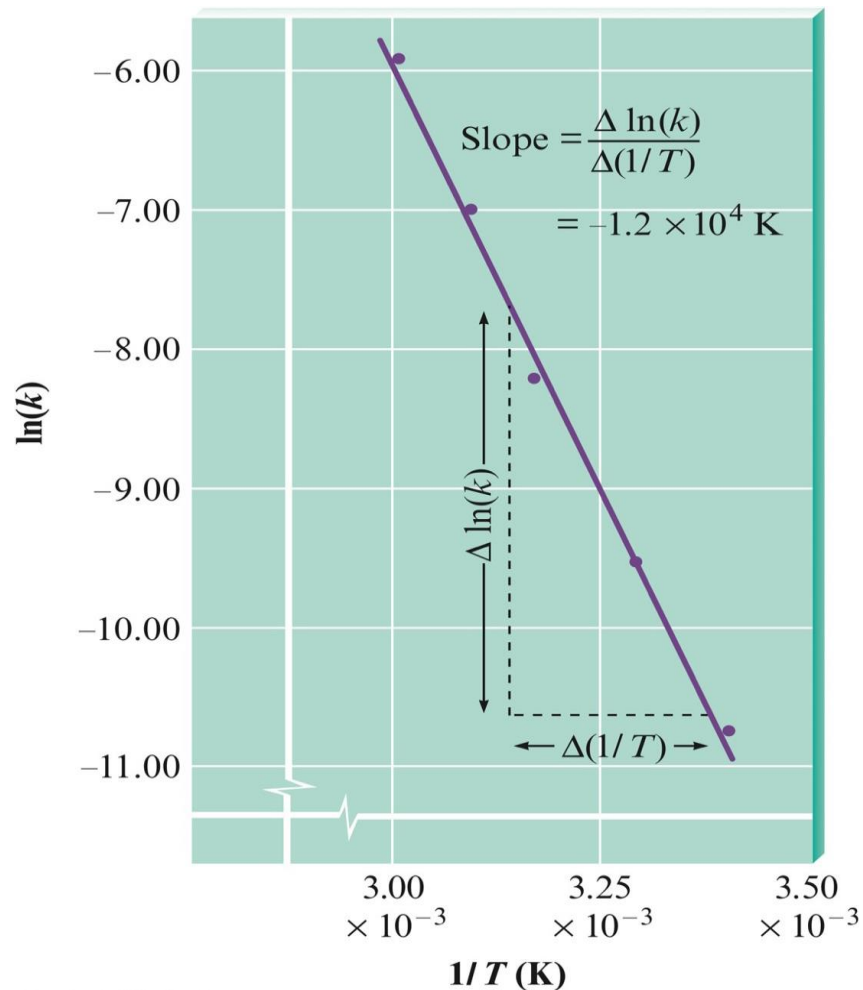
Linear Form of Arrhenius Equation

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

Section 12.4

The Integrated Rate Law

Linear Form of Arrhenius Equation



Section 12.4

The Integrated Rate Law

EXERCISE!

- Chemists commonly use a rule of thumb that an increase of 10 K in temperature doubles the rate of a reaction. What must the **activation energy** be for this statement to be true for a temperature increase from 25° C to 35° C?

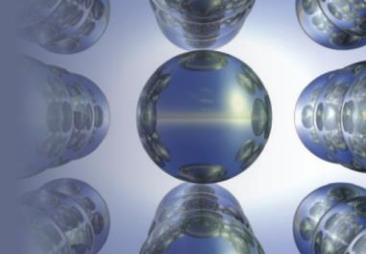
$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$k_2 = 2k_1 \quad \text{and} \quad T_1 = 298\text{k} \quad , \quad T_2 = 308\text{k}$$

Answer: $E_a = 53 \text{ kJ}$

Section 12.4

The Integrated Rate Law



Catalyst

- A substance that speeds up a reaction without being consumed itself.
- Provides a new pathway for the reaction with a lower activation energy.

Section 12.4

The Integrated Rate Law

Energy Plots for a Catalyzed and an Uncatalyzed Pathway for a Given Reaction

