# **Chapter 14. Chemical Kinetics**

# 14.1 Factors that Affect Reaction Rates

- **Chemical kinetics** = the study of how fast chemical reactions occur.
  - Factors which affect rates of reactions:
    - Physical state of the reactants.
    - Concentration of the reactants.
    - Temperature of the reaction.
    - Presence or absence of a catalyst.
- Goal: to understand chemical reactions at the molecular level.

# 14.2 Reaction Rates

- The speed of a reaction is defined as the change that occurs per unit time.
  - It is often determined by measuring the change in concentration of a reactant or product with time.
  - The speed of the chemical reaction is its reaction rate.
- For a reaction  $A \rightarrow B$

Average rate with respect to  $B = \frac{\text{Change in the concentration of } B}{\text{Change in time}}$ 

• Here the change in the concentration of B is defined as:  $\Delta [B] = [B]$  at final time - [B] at initial time



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0.30 mol A 0.70 mol B (c)

# $\begin{array}{l} \mbox{Progress of a hypothetical} \\ \mbox{reaction } A \rightarrow B. \end{array}$

Each red sphere represents 0.01 mol A, each blue sphere represents 0.01 mol B, and the vessel has a volume of 1.00 L. (a) At time zero the vessel contains 1.00 mol A (100 red spheres) and 0 mol B (no blue spheres).

(b) After 20 s the vessel contains 0.54 mol A and 0.46 mol B.

(c) After 40 s the vessel contains 0.30 mol A and 0.70 mol B.

- Illustrate this with an example:
  - Suppose A reacts to form B. Let us begin with 1.00 M A.
  - At t = 0 (time zero) there is 1.00 M A and no B present.
  - At t = 20 sec, there is 0.54 *M* A and 0.46 *M* B.
  - At t = 40 sec, there is 0.30 *M* A and 0.70 *M* B.

• We can use this information to find the average rate with respect to B:

$$Avg Rate = \frac{0.46M - 0.00 M}{20 s - 0 s} = 0.023 \frac{M}{s}$$
$$Avg Rate = \frac{\Delta (Conc B)}{\Delta t} = \frac{(Conc of B at t = 20s) - (Conc of B at t = 0 s)}{20s - 0 min}$$

- For the reaction  $A \rightarrow B$  there are two ways of measuring rate:
  - The rate of appearance of product B (i.e., change in moles of B per unit time) as in the preceding example.
  - The rate of disappearance of reactant A (i.e., the change in moles of A per unit time).

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

- Note the negative sign! This reminds us that rate is being expressed in terms of the *disappearance* of a reactant.
- A plot of number of moles versus time shows that as the reactants (A) disappear, the products (B) appear.

# Sample Exercise 14.1 (p. 578)

For the reaction pictured at the bottom of the previous page, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.

 $(1.2 \text{ x } 10^{-2} \text{ M/s})$ 

# Practice Exercise 1 (14.1)

If the experiment on the previous page is run for 60 s, 0.16 mol A remain. Which of the following statement is or is not true?

- (i) After 60 s there are 0.84 mol B in the flask.
- (ii) The decrease in the number of moles of A from  $t_1 = 0$  s to  $t_2 = 20$  s is greater than that from  $t_1 = 40$  s to  $t_2 = 60$  s.
- (iii) The average rate for the reaction from  $t_1 = 40$  s to  $t_2 = 60$  s is 7.0 x 10<sup>-3</sup> M/s.
- (a) Only one of the statements is true.
- (b) Statements (i) and (ii) are true.
- (c) Statements (i) and (iii) are true.
- (d) Statements (ii) and (iii) are true.
- (e) All three statements are true.

# Practice Exercise 2 (14.1)

From the reaction pictured, calculate the average rate of appearance of B over the time interval from 0 to 40 s.

(1.8 x 10<sup>-2</sup> M/s)

## Change of Rate with Time

- In most chemical reactions we will determine the reaction rate by monitoring a change in concentration (of a reactant or product).
  - The most useful unit to use for rate is molarity.
    - Since volume is constant, molarity and moles are directly proportional.
  - Consider the following reaction:

$$C_4H_9Cl_{(aq)} + H_2O_{(l)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)}$$

- We can calculate the average rate in terms of the disappearance of  $C_4H_9Cl$ .
- The units for average rate are mol/L's or *M*/*s*.
- The average rate decreases with time.

# **Instantaneous Rate**

- We can plot  $[C_4H_9Cl]$  versus time.
  - The rate at any instant in time is called the instantaneous rate.
  - It is the slope of the straight line tangent to the curve at that instant.
  - Instantaneous rate is different from average rate.
  - It is the rate at that particular instant in time.
    - For our discussion we will call the "instantaneous rate" the rate, unless otherwise indicated.



TABLE 14.1	Rate Data for Reaction	on of C <sub>4</sub> H <sub>9</sub> Cl with Water
Time, t 60	[C <sub>4</sub> H <sub>6</sub> CI] (M)	Average Rate (M/s)
0.0 50.0 100.0 150.0 200.0 300.0 400.0 500.0 800.0 10.000	0.1000 0.0905 0.0820 0.0741 0.0549 0.0448 0.0448 0.0468 0.0200 0	$ \begin{array}{l} & 1.9 \\ & > 1.7 \\ & > 1.7 \\ & > 1.6 \\ & > 1.6 \\ & > 1.6 \\ & > 1.4 \\ & > 1.22 \\ & > 1.01 \\ & > 1.01 \\ & > 1.01 \\ & > 1.01 \\ & > 0.560 \\ & > 101^4 \end{array} $

# Concentration of butyl chloride (C<sub>4</sub>H<sub>9</sub>Cl) as a function of time.

The dots represent the experimental data from the first two columns of Table 14.1, and the red curve is drawn to connect the data points smoothly. Lines are drawn that are tangent to the curve at t = 0 and t = 600 s. The slope of each tangent is defined as the vertical change divided by the horizontal change:  $\Delta [C_4H_9Cl]/\Delta t$ . The reaction rate at any time is related to the slope of the tangent to the curve at that time. Because C<sub>4</sub>H<sub>9</sub>Cl is disappearing, the rate is equal to the negative of the slope.

## Sample Exercise 14.2 (p. 580)

Using the reaction graphed above, calculate the instantaneous rate of disappearance of  $C_4H_9Cl$  at t = 0 (the initial rate).

(2.0 x 10<sup>-4</sup> M/s)

## Practice Exercise 1 (14.2)

Which of the following would be the instantaneous rate of the reaction in the previous figure at t = 1000 s?

- a) 1.2 x 10<sup>-4</sup> M/s
- b) 8.8 x 10<sup>-5</sup> M/s
- c)  $6.3 \times 10^{-5} \text{ M/s}$
- d) 2.7 x 10<sup>-5</sup> M/s
- e) More than one of these.

### Practice Exercise 2 (14.2)

For the reaction graphed above, calculate the instantaneous rate of disappearance of  $C_4H_9Cl$  at t = 300 s.

(1.1 x 10<sup>-4</sup> M/s)

# **Reaction Rates and Stoichiometry**

• For the reaction:

$$C_4H_9Cl_{(aq)} + H_2O_{(l)} \rightarrow C_4H_9OH_{(aq)} + HCl_{(aq)}$$

• The rate of appearance of  $C_4H_9OH$  must equal the rate of disappearance of  $C_4H_9Cl$ .

Rate = 
$$-\frac{\Delta [C_4 H_9 Cl]}{\Delta t} = \frac{\Delta [C_4 H_9 OH]}{\Delta t}$$

- What if the stoichiometric relationships are not one-to-one?
  - For the reaction:

$$2\mathrm{HI}_{(g)} \rightarrow \mathrm{H}_{2(g)} + \mathrm{I}_{2(g)}$$

• The rate may be expressed as:

Rate = 
$$-\frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H2}]}{\Delta t} = \frac{\Delta[\text{I2}]}{\Delta t}$$

- We can generalize this equation a bit.
  - For the reaction:

$$aA + bB \rightarrow cC + dD$$

• The rate may be expressed as:

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

## Sample Exercise 14.3 (p. 581)

a) How is the rate at which ozone disappears related to the rate at which oxygen appears in in the following equation?  $2 O_{3(g)} \rightarrow 3 O_{2(g)}$ 

$$\begin{pmatrix} -\underline{1} \Delta [O_3] \\ 2 \Delta t \end{bmatrix} = \underline{1} \Delta [O_2] \\ 3 \Delta t \end{pmatrix}$$

b) If the rate at which  $O_2$  appears,  $\Delta[O_2]/\Delta t$ , is 6.0 x 10<sup>-5</sup> M/s at a particular instant, at what rate is  $O_3$  disappearing at this same time,  $-\Delta[O_3]/\Delta t$ ?

(4.0 x 10<sup>-5</sup> M/s)

# Practice Exercise 1 (14.3)

At a certain time in a reaction, substance A is disappearing at a rate of  $4.0 \times 10^{-2}$  M/s, substance B is appearing at a rate of  $2.0 \times 10^{-2}$  M/s, and substance C is appearing at a rate of  $6.0 \times 10^{-2}$  M/s. Which of the following could be the stoichiometry for the reaction being studied?

- a)  $2A + B \rightarrow 3C$
- b)  $A \rightarrow 2B + 3C$
- c)  $2A \rightarrow B + 3C$
- d)  $4A \rightarrow 2B + 3C$
- e)  $A + 2B \rightarrow 3C$

# Practice Exercise 2 (14.3)

The decomposition of  $N_2O_5$  proceeds according to the following equation:

 $2 N_2 O_{5(g)} \rightarrow 4 NO_{2(g)} + O_{2(g)}$ 

If the rate of decomposition of  $N_2O_5$  at a particular instant in a reaction vessel is 4.2 x  $10^{-7}$  M/s, what is the rate of appearance of

a)  $NO_2(8.4 \times 10^{-7} \text{ M/s})$ 

b)  $O_2$  (2.1 x 10<sup>-7</sup> M/s)

# 14.3 Concentration and Rate

- In general, rates:
  - Increase when reactant concentration is increased.
  - Decrease as the concentration of reactants is reduced.
- We often examine the effect of concentration on reaction rate by measuring the way in which reaction rate at the beginning of a reaction depends on starting conditions.

TABLE 14.2 Rate Data for the Reaction of Ammonium and Nitrite Ions in Water at 25 °C			
Experiment Number	Initial NH4 <sup>+</sup> Concentration ( <i>M</i> )	Initial $NO_2^-$ Concentration ( <i>M</i> )	Observed Initial Rate (M/s)
1	0.0100	0.200	$5.4  imes 10^{-7}$
2	0.0200	0.200	$10.8 \times 10^{-7}$
3	0.0400	0.200	$21.5 \times 10^{-7}$
4	0.200	0.0202	$10.8 \times 10^{-7}$
5	0.200	0.0404	$21.6 \times 10^{-7}$
6	0.200	0.0808	$43.3 \times 10^{-7}$

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• Consider the reaction:

 $\mathrm{NH}_4^+(aq) + \mathrm{NO}_2^-(aq) \rightarrow \mathrm{N}_2(g) + 2\mathrm{H}_2\mathrm{O}(l)$ 

- We measure initial reaction rates.
- The initial rate is the instantaneous rate at time t = 0.
- We find this at various initial concentrations of each reactant.
- As  $[NH_4^+]$  doubles with  $[NO_2^-]$  constant the rate doubles.
- We conclude the rate is proportional to  $[NH_4^+]$ .
- As  $[NO_2^-]$  doubles with  $[NH_4^+]$  constant the rate doubles.
  - We conclude that the rate is proportional to  $[NO_2^-]$ .
- The overall concentration dependence of reaction rate is given in a rate law or rate expression.
  - For our example, the rate law is:

Rate = 
$$k[NH_4^+][NO_2^-]$$

- The proportionality constant k is called the **rate constant**.
- Once we have determined the rate law and the rate constant, we can use them to calculate initial reaction rates under any set of initial concentrations.

# **Reaction Orders: Exponents in the Rate Law**

- For a general reaction with rate law:
  - Rate = k[reactant 1]<sup>m</sup>[reactant 2]<sup>n</sup>
- The exponents *m* and *n* are called **reaction orders**.
  - The overall reaction order is the sum of the reaction orders.
  - The overall order of reaction is  $m + n + \dots$
  - For the reaction:

 $\mathrm{NH}_4^+(aq) + \mathrm{NO}_2^-(aq) \rightarrow \mathrm{N}_2(g) + 2\mathrm{H}_2\mathrm{O}(l)$ 

- The reaction is said to be first order in  $[NH_4^+]$ , first order in  $[NO_2^-]$ , and second order overall.
- Note that reaction orders must be determined experimentally.
  - They do not necessarily correspond to the stoichiometric coefficients in the balanced chemical equation!
  - We commonly encounter reaction orders of 0, 1 or 2.
  - Even fractional or negative values are possible.

# Units of Rate Constants

• Units of the rate constant depend on the overall reaction order.

# Using Initial Rates to Determine Rate Laws

- To determine the rate law, we observe the effect of changing initial concentrations.
  - If a reaction is zero order in a reactant, changing the initial concentration of that reactant will have no effect on rate (as long as *some* reactant is present).
  - If a reaction is first order, doubling the concentration will cause the rate to double.
  - If a reaction is second order, doubling the concentration will result in a 2<sup>2</sup> increase in rate.
    Similarly, tripling the concentration results in a 3<sup>2</sup> increase in rate.
    - A reaction is *n*th order if doubling the concentration causes a  $2^n$  increase in rate.
- Note that the rate, not the rate constant, depends on concentration.
- The rate constant IS affected by temperature and by the presence of a catalyst.

Sample Exercise 14.4 (p. 584) Consider a reaction  $A + B \rightarrow C$  for which rate =  $k[A][B]^2$ . Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as blue ones. Rank these mixtures in order of increasing rate of reaction.  $\underbrace{(1) \quad (2) \quad (2) \quad (3) \quad (3)}_{(2) \quad (2) \quad (3) \quad (3)}$ (2 < 1 < 3)  $\underbrace{Practice Exercise 1 (14.4)}_{(2) \quad (2) \quad (2) \quad (3) \quad (3)}$ 

a) 1 < 2 < 3</li>
b) 1 < 3 < 2</li>
c) 3 < 2 < 1</li>
d) 2 < 1 < 3</li>
e) 3 < 1 < 2</li>

# Practice Exercise 2 (14.4)

Assuming that the rate = k[A][B], rank the mixtures represented above in order of increasing rate.

(2 = 3 < 1)

Sample Exercise 14.5 (p. 585) a) What are the overall reaction orders for the reactions described in the following equations:  $2 \text{ N}_2\text{O}_{5(g)} \rightarrow 4 \text{ NO}_{2(g)} + \text{O}_{2(g)}$ i) Rate =  $k[N_2O_5]$  $CHCl_{3(g)} + Cl_{2(g)} \rightarrow CCl_{4(g)} + HCl_{(g)} \qquad Rate = k[CHCl_3][Cl_2]^{1/2}$ ii) b) What are the units of the rate constant for the rate law for Equation (i)? Practice Exercise 1 (14.5) Which of the following are the units of the rate constant for (ii)? a)  $M^{-1/2}s^{-1}$ b)  $M^{-1/2}s^{-1/2}$ c)  $M^{1/2}s^{-1}$ d)  $M^{-1/2}s^{-1}$ e)  $M^{-1/2}s^{-1/2}$ Practice Exercise 2 (14.5) a) What is the reaction order of the reactant H<sub>2</sub> in Equation (iii)?  $H_{2(g)} + I_{2(g)} \rightarrow 2 HI$ Rate =  $k[H_2][I_2]$ iii) (1)b) What are the units of the rate constant for Equation (iii)?  $(M^{-1}s^{-1})$ 

# Sample Exercise 14.6 (p. 586)

The initial rate of a reaction  $A + B \rightarrow C$  was measured for several different starting concentrations of A and B, and the results are as follows:

Experiment Number	[A] (M)	[B] (M)	Initial Rate (M/s)
1	0.100	0.100	$4.0  imes 10^{-5}$
2	0.100	0.200	$4.0 imes10^{-5}$
3	0.200	0.100	$16.0 \times 10^{-5}$

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Using these data, determine

- a) the rate law for the reaction  $(k[A]^2)$
- b) the magnitude of the rate constant

$$(4.0 \text{ x } 10^{-3} \text{ M}^{-1} \text{s}^{-1})$$

c) the rate of the reaction when [A] = 0.050 M and [B] = 0.100 M.  $(1.0 \times 10^{-5} \text{ M/s})$ 

# Practice Exercise 1 (14.6)

A certain reaction  $X + Y \rightarrow Z$  is described as being first order in [X] and third order overall. Which of the following statements is or are true?

- (i) The rate law for the reaction is:  $Rate = [X][Y]^2$ .
- (ii) If the concentration of X is increased by a factor of 1.5, the rate will increase by a factor of 2.25.
- (iii) If the concentration of Y is increased by a factor of 1.5, the rate will increase by a factor of 2.25.
- a) Only one statement is true.
- b) Statements (i) and (ii) are true.
- c) Statements (i) and (iii) are true.
- d) Statements (ii) and (iii) are true.
- e) All three statements are true.

# Practice Exercise 2 14.6

The following data were measured for the reaction of nitric oxide with hydrogen:

 $2 \ \mathrm{NO}_{(g)} \ + \ 2 \ \mathrm{H}_{2(g)} \ \textbf{\rightarrow} \ \mathrm{N}_{2(g)} \ + \ 2 \ \mathrm{H}_{2}\mathrm{O}_{(g)}$ 

Experiment Number	[NO] (M)	[H <sub>2</sub> ] (M)	Initial Rate (M/s)
1	0.10	0.10	$1.23 \times 10^{-3}$
2	0.10	0.20	$2.46 \times 10^{-3}$
3	0.20	0.10	$4.92 \times 10^{-3}$

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a)	Determine the rate law for this reaction.	$(k[NO]^2[H_2])$
b)	Calculate the rate constant.	$(1.2 \text{ M}^{-2}\text{s}^{-1})$

c) Calculate the rate when [NO] = 0.050 M and  $[H_2] = 0.150 \text{ M}$ . (4.5 x 10<sup>-4</sup> M/s)

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# 14.4 The Change of Concentration with Time

• Goal: Convert the rate law into a convenient equation that gives concentration as a function of time.

# **First-Order Reactions**

- For a **first-order reaction**, the rate doubles as the concentration of a reactant doubles.
  - Therefore:

Integrating:

Rate = 
$$-\frac{\Delta[A]}{\Delta t} = k[A]$$
  
 $\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = -k \int_0^t dt$ 

• We get:

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

• Rearranging:

• An alternate form:

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

- A plot of  $\ln[A]_t$  versus t is a straight line with slope -k and intercept  $\ln[A]_0$ .
- Note that in this equation we use the natural logarithm, ln (log to the base *e*).



Methyl isonitrile





Acetonitrile Copyright © 2009 Preason Provider Hall Inc

# A first-order reaction.

The transformation of methyl isonitrile (CH<sub>3</sub>NC) to acetonitrile (CH<sub>3</sub>CN) is a first-order process.

Methyl isonitrile and acetonitrile are isomers, molecules that have the same atoms arranged differently.

This reaction is called an isomerization reaction.



# Kinetic data for conversion of methyl isonitrile.

- (a) Variation in the partial pressure of methyl isonitrile, CH<sub>3</sub>NC, with time during the reaction CH<sub>3</sub>NC  $\rightarrow$  CH<sub>3</sub>CN, 198.9 °C.
- (b) A plot of the natural logarithm of the  $CH_3NC$  pressure as a function of time. The fact that a straight line fits the data confirms that the rate law is first order.

### Sample Exercise 14.7 (p. 588)

The first-order rate constant for the decomposition of a certain insecticide in water at  $12^{\circ}$ C is  $1.45 \text{ yr}^{-1}$ . A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of  $5.0 \times 10^{-7} \text{ g/cm}^3$  of water. Assume that the average temperature of the lake is  $12^{\circ}$ C.

a) What is the concentration of the insecticide on June 1 of the following year?  $(1.2 \times 10^{-7} \text{ g/cm}^3)$ 

b) How long will it take for the concentration of the insecticide to drop to 3.0 x 10<sup>-7</sup> g/cm<sup>3</sup>? (0.35 yr)

# Practice Exercise 1 (14.7)

At 25°C, the decomposition of dinitrogen pentoxide,  $N_2O_{5(g)}$ , into  $NO_{2(g)}$  and  $O_{2(g)}$  follows first-order kinetics with  $k = 3.4 \times 10^{-5} \text{ s}^{-1}$ . A sample of  $N_2O_5$  with an initial pressure of 760 torr decomposes at 25°C until its partial pressure is 650 torr. How much time (in seconds) has elapsed?

- a)  $5.3 \times 10^{-6}$
- b) 2000
- c) 4600
- d) 34,000
- e) 190,000

# Practice Exercise 2 (14.7)

The decomposition of dimethyl ether, CH<sub>3</sub>OCH<sub>3</sub>, at 510<sup>o</sup>C is a first-order process with a rate constant of 6.8 x  $10^{-4} \text{ s}^{-1}$ : CH<sub>3</sub>OCH<sub>3 (g)</sub>  $\rightarrow$  CH<sub>4(g)</sub> + H<sub>2(g)</sub> + CO<sub>(g)</sub>

If the initial pressure of CH<sub>3</sub>OCH<sub>3</sub> is 135 torr, what is its partial pressure after 1420 s?

(51 torr)

# **Second-Order Reactions**

- A second-order reaction is one whose rate depends on the reactant concentration to the second power or on the concentration of two reactants, each raised to the first power.
- For a second-order reaction with just one reactant:

$$\operatorname{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

• Integrating,

$$\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = -k \int_0^t dt$$

• We get:

$$\frac{1}{\left[A\right]_t} = kt + \frac{1}{\left[A\right]_0}$$

- A plot of  $1/[A]_t$  versus t is a straight line with slope k and intercept  $1/[A]_0$ .
  - For a second order reaction, a plot of  $\ln[A]_t$  vs. *t* is not linear.

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• Note that a second-order process can have a rate constant expression of the form:

Rate = 
$$k[A][B]$$

• That is, the reaction is second order overall, but has first order dependence on A and B.

# Sample Exercise 14.8 (p. 590)

The following data were obtained for the gas phase decomposition of nitrogen dioxide at 300°C:

$$NO_{2(g)} \rightarrow NO_{(g)} + 1/2 O_{2(g)}$$

Time (s)	[NO <sub>2</sub> ] (M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Is the reaction first or second order in NO<sub>2</sub>? (Hint: use data and plots below.)



# Practice Exercise 1 (14.8)

For a certain reaction A  $\rightarrow$  products, a plot of ln[A] versus time produces a straight line with a slope of -3.0 x  $10^{-2}$  s<sup>-1</sup>. Which of the following statements is or are true?

- s . which of the following statements is of are the
- (i) The reaction follows first-order kinetics.
- (ii) The rate constant for the reaction is  $3.0 \times 10^{-2} \text{ s}^{-1}$ .
- (iii) The initial concentration of [A] was 1.0 M.
- a) Only one of the statements is true.
- b) Statements (i) and (ii) are true.
- c) Statements (i) and (iii) are true.
- d) Statements (ii) and (iii) are true.
- e) All three statements are true.

# Practice Exercise 2 (14.8)

Consider again the decomposition of NO<sub>2</sub> discussed above. The reaction is second order in NO<sub>2</sub> with  $k = 0.543 \text{ M}^{-1} \text{s}^{-1}$ . If the initial concentration of NO<sub>2</sub> in a closed vessel is 0.0500 M, what is the remaining concentration after 0.500 hr?

 $(1.0 \times 10^{-3} \text{ M})$ 

# Half-life

- Half-life, t<sub>1/2</sub>, is the time required for the concentration of a reactant to decrease to half its original value.
  That is, half life, t<sub>1/2</sub>, is the time taken for [A]<sub>0</sub> to reach 1/2 [A]<sub>0</sub>.
- Mathematically, the half life of a first-order reaction is:

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

So, for 
$$t = t_{1/2}$$
 and  $[A]_t = 1/2 [A]_0$   
 $\ln \frac{1/2 [A]_0}{[A]_0} = -kt_{1/2}$   
 $\ln 1/2 = -kt_{1/2}$   
 $\ln 1/2 = -kt_{1/2}$ 

• Note that the half-life of a first-order reaction is independent of the initial concentration of the reactant.

We can show that the half-life of a second order reaction is:

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

• Note that the half-life of a second-order reaction is *dependent* on the initial concentration of reactant.



# Half-life of a first-order reaction.

Pressure of methyl isonitrile as a function of time showing two successive halflives of the isomerization reaction depicted earlier in Figure 14.6.



# Practice Exercise 1 (14.9)

We noted in an earlier Practice Exercise that at 25°C the decomposition of  $N_2O_{5(g)}$  into  $NO_{2(g)}$  and  $O_{2(g)}$  follows first-order kinetics with  $k = 3.4 \times 10^{-5} \text{s}^{-1}$ . How long will it take for a sample originally containing 2.0 atm of  $N_2O_5$  to reach a partial pressure of 380 torr?

- a) 5.7 h
- b) 8.2 h
- c) 11 h
- d) 16 h
- e) 32 h

# Practice Exercise 2 (14.9)

a) Calculate  $t_{1/2}$  for the decomposition of the insecticide described in Sample Exercise 14.7. (0.478 yr = 1.51 x 10<sup>7</sup> s)

b) How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

(two half-lives = 2(0.478 yr) = 0.956 yr)

# 14.5 Temperature and Rate

- Most reactions speed up as temperature increases.
- We can illustrate this with chemiluminescent Cyalume® light sticks.
  - A chemiluminescent reaction produces light.
  - Two light sticks are placed in water, one at room temperature and one in ice.
    - The one at room temperature is brighter than the one in ice.
    - Its luminescence also fades more quickly.
  - The chemical reaction responsible for chemiluminescence is dependent on temperature, the higher the temperature, the faster the reaction and the brighter the light.



Higher temperature Lineer temperature

#### Temperature affects the rate of the chemiluminescence reaction in Cyalume® light sticks.

The light stick in hot water (left) glows more brightly than the one in cold water (right); at the higher temperature, the reaction is initially faster and produces a brighter light.

- As temperature increases, the rate increases.
- How is the relationship between temperature and rate reflected in the rate expression?
  - The rate law has no temperature term in it, so the rate constant must depend on temperature.
  - Consider the first-order reaction  $CH_3NC \rightarrow CH_3CN$ .
    - As temperature increases from 190°C to 250 °C the rate constant increases.
    - The temperature effect is quite dramatic.
    - We see an approximate doubling of the rate with each 10 °C increase in temperature.



# Dependence of rate constant on temperature.

The data show the variation in the first-order rate constant for the rearrangement of methyl isonitrile as a function of temperature. The four points indicated are used in connection with Sample Exercise 14.11.

# **The Collision Model**

- Rates of reactions are affected by **concentration** and **temperature**.
- We need to develop a model that explains this observation.
- An explanation is provided by the collision model, based on KMT.
  - In order for molecules to react they must collide.
  - The greater the number of collisions the faster the rate.
  - The more molecules present, the greater the probability of collision and the faster the rate.

#### Concentration effects:

• Thus reaction rate should  $\uparrow$  with an  $\uparrow$  in [reactant molecules].

#### Temperature effects:

- The higher the T, the more E available to the molecules and the more frequently the molecules collide.
  - Thus reaction rate should  $\uparrow$  with an  $\uparrow$  in T.

### **The Orientation Factor**

Not all collisions lead to products.

- Only a small fraction of collisions lead to products.
- In order for a reaction to occur the reactant molecules must collide in the **correct orientation** and with **enough E** to form products.
- Consider the reaction between Cl and NOCl:
  - If the Cl collides with the Cl of NOCl, the products are  $Cl_2$  and NO.
  - If the Cl collides with the O of NOCl, no products are formed.



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### Molecular collisions and chemical reactions.

Two possible ways that Cl atoms and NOCl molecules can collide are shown.

- (a) If molecules are oriented properly, a sufficiently energetic collision will lead to reaction.
- (b) If the orientation of the colliding molecules is wrong, no reaction occurs.

# **Activation Energy**

- Arrhenius: Molecules must possess a minimum amount of E to react. Why?
  - In order to form products, bonds must be broken in the reactants.
  - Bond breakage requires E.
  - Molecules moving too slowly, with too little KE, don't react when they collide.
- Activation energy,  $E_a$ , = the minimum E required to initiate a chemical reaction.
  - $E_{\rm a}$  will vary with the reaction.
- Consider the rearrangement of methyl isonitrile to form acetonitrile:
  - E is required to stretch the bond between the  $CH_3$  group and the N=C group to allow the N=C to rotate.
  - The C–C bond begins to form.
  - The E associated with the molecule drops.
  - The E barrier between the starting molecule and the highest E state found along the reaction pathway is the E<sub>a</sub>.
    - The species at the top of the barrier is called the **activated complex** or **transition state**.
  - The change in E for the reaction is the difference in E between CH<sub>3</sub>NC and CH<sub>3</sub>CN.
     ΔE<sub>rxn</sub> has no effect on reaction rate.
  - The  $E_a$  is the difference in energy between reactants, (CH<sub>3</sub>NC) and the transition state.
    - The rate depends on the magnitude of the  $E_{a}$ .
      - In general, the lower the  $E_a$ , the faster the rate.



# Energy profile for methyl isonitrile isomerization.

The methyl isonitrile molecule must surmount the activationenergy barrier before it can form the product, acetonitrile.

The horizontal axis is variously labeled "reaction pathway," as here, or "progress of reaction."

• Notice that if a forward reaction is exothermic (CH<sub>3</sub>NC  $\rightarrow$  CH<sub>3</sub>CN), then the reverse reaction is endothermic (CH<sub>3</sub>CN  $\rightarrow$  CH<sub>3</sub>NC).

# **Distribution of Kinetic Energies**



# The effect of temperature on the distribution of kinetic energies.

At the higher temperature, a larger number of molecules have higher kinetic energies. Thus, a larger fraction at any one instant will have more than the minimum energy required for reaction.

# • How does this relate to temperature?

- At any particular T, the molecules present have an average KE associated with the population.
- In the same distribution, some molecules have less E than the average while others have more than the average value.
  - The fraction of molecules with an energy equal to or greater than  $E_a$  is given by:

$$f = e^{\frac{-Ea}{RT}}$$

- Molecules that have an  $E \ge E_a$  have sufficient E to react.
  - As we  $\uparrow$  the T, the fraction of the population that has an  $E \ge E_a \uparrow$ .
  - Thus more molecules can react.

# The Arrhenius Equation (<u>calculations</u> using the Arrhenius Equation are not required on the AP Chem exam)

- Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors:
  - The number of collisions per unit time.
  - The fraction of collisions that occur with the correct orientation.
  - The fraction of the colliding molecules that have an  $E \ge E_a$ .
- From these observations Arrhenius developed the Arrhenius equation.

$$k = Ae^{\frac{-Ea}{RT}}$$

- Where k is the rate constant,  $E_a$  is the activation energy, R is the ideal-gas constant (8.314 J/K mol) and T is the temperature in K.
- *A* is called the **frequency factor**.
  - It is related to the frequency of collisions and the probability that a collision will have a favorable orientation.
- Both A and  $E_a$  are specific to a given reaction.

# **Determining the Activation Energy**

• *E*<sub>a</sub> may be determined experimentally.

$$\ln k = -\frac{E_a}{RT} + \ln A$$

- We need to take the natural log of both sides of the Arrhenius equation:
- A graph of  $\ln k$  vs 1/T will have a slope of  $-E_a/R$  and a y-intercept of  $\ln A$ .

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

• Alternatively we can use:



# Sample Exercise 14.10 (p. 597) Consider a series of reactions having the following energy profiles: $\int_{a}^{b} \int_{a}^{b} \int_{a$

Assuming that all three reactions have nearly the same frequency factors, rank the reactions from slowest to fastest.

((2) < (3) < (1))

# Practice Exercise 1 (14.10)

Which of the following statement is or are true?

- (i) The activation energies for the forward and reverse directions of a reaction can be different.
- (ii) Assuming that A is constant, ir both E<sub>a</sub> and T increase, then k will increase.
- (iii) For two different reactions, the one with the smaller value of E<sub>a</sub> will necessarily have the larger value for k.
- a) Only one of the statements is true.
- b) Statements (i) and (ii) are true.
- c) Statements (ii) and (iii) are ture.
- d) All three statements are true.

# Practice Exercise 2 (14.10)

Imagine that these reactions are reversed. Rank these reverse reactions from slowest to fastest. ( (2) < (1) < (3) )

# Sample Exercise 14.11 (p. 598)

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures:

Temperature (°C)	k (s <sup>-1</sup> )
189.7	$2.52 \times 10^{-5}$
198.9	$5.25 \times 10^{-3}$
230.3	$6.30 \times 10^{-4}$
251.2	$3.16 \times 10^{-3}$

a) From these data, calculate  $E_a$  for the reaction. (160 kJ/mol)

(Hint: make a table of T, 1/T and ln k)

b) What is the value of the rate constant at 430.0 K?  $(1.0 \times 10^{-6} \text{ s}^{-1})$ 

# Practice Exercise 1 (14.11)

Using the data in Sample Exercise 14.11, which of the following is the rate constant for the rearrangement of methyl isonitrile at 320°C?

- a) 8.1 x  $10^{-15}$  s<sup>-1</sup>
- b)  $2.2 \times 10^{-13} \text{ s}^{-1}$
- c)  $2.7 \times 10^{-9} \text{ s}^{-1}$
- d)  $2.3 \times 10^{-1} \text{ s}^{-1}$
- e)  $9.2 \times 10^3 \text{ s}^{-1}$

### Practice Exercise 2 (14.11)

Using the data in Sample Exercise 14.11, above, calculate the rate constant for the rearrangement of methyl isonitrile at 280°C.

 $(2.2 \text{ x } 10^{-2} \text{ s}^{-1})$ 

# 14.6 Reaction Mechanisms

- The balanced chemical equation provides information about substances present at the beginning and end of the reaction.
- The **reaction mechanism** is the process by which the reaction occurs.
- Mechanisms provide a picture of which bonds are broken and formed during the course of a reaction.

#### **Elementary Steps**

- Elementary steps are any processes that occur in a single step.
- The number of molecules present in an elementary step is the **molecularity** of that elementary step.
  - Unimolecular: one molecule in the elementary step
  - Bimolecular: collision of two molecules in the elementary step
  - Termolecular: simultaneous collision of three molecules in the elementary step
     very uncommon (statistically improbable)

TABLE 14.3  Elementary Reactions and Their Rate Laws			
Molecularity	Elementary Reaction	Rate Law	
<b>Unimolecular</b>	$A \longrightarrow \text{products}$	Rate = $k$ [A]	
<b>Bi</b> molecular	$A + A \longrightarrow products$	Rate = $k[A]^2$	
<b>Bimolecular</b>	$A + B \longrightarrow products$	Rate = $k[A][B]$	
Termolecular	$A + A + A \longrightarrow$ products	Rate = $k[A]^3$	
<i>Ter</i> molecular	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$	
Termolecular	$A + B + C \longrightarrow products$	Rate = $k[A][B][C]$	

# **Multistep Mechanisms**

- In a multistep process, one of the steps will be slower than all others.
- The overall reaction cannot occur faster than this slowest, rate-determining step.



# **Slow Initial Step**

 $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ 

• The rate law for this reaction is found experimentally to be

Rate =  $k[NO_2]^2$ 

• CO is necessary for this reaction to occur, but the rate of the reaction does not depend on its concentration.

This suggests the reaction occurs in two steps.

A proposed mechanism for this reaction is Step 1:  $NO_{2(g)} + NO_{2(g)} \rightarrow NO_{3(g)} + NO_{(g)}$  (slow) Step 2:  $NO_{3(g)} + CO_{(g)} \rightarrow NO_{2(g)} + CO_{2(g)}$  (fast)

The NO<sub>3</sub> intermediate is consumed in the second step.

As CO is not involved in the slow, rate-determining step, it does not appear in the rate law.

# Multistep mechanisms = sequence of elementary steps

- Elementary steps must add to give the balanced chemical equation.
- Intermediate: a species which appears in an elementary step which is not a reactant or product.
  - formed in one elementary step and consumed in another.
  - **not found** in the balanced equation for the overall reaction.

# Sample Exercise 14.12 (p. 600)

It has been proposed that the conversion of ozone into  $O_2$  proceeds via two elementary steps:

$$O_{3(g)} \rightarrow O_{2(g)} + O_{(g)}$$
$$O_{3(g)} + O_{(g)} \rightarrow 2 O_{2(g)}$$

a) Describe the molecularity of each step in this mechanism.

b) Write the equation for the overall reaction.

c) Identify the intermediate(s).

# Practice Exercise 1 (14.12)

Consider the two-step reaction mechanism:

 $\begin{array}{rrrr} A_{(g)} \ + \ B_{(g)} \ \, & \rightarrow \ \, X_{(g)} \ + \ Y_{(g)} \\ X_{(g)} \ + \ C_{(g)} \ \, & \rightarrow \ \, Y_{(g)} \ \, + \ Z_{(g)} \end{array}$ 

Which of the following statements about this mechanism is or are true?

(i) Both of the steps in this mechanism are bimolecular.

(ii) The overall reaction is A<sub>(g)</sub> + B<sub>(g)</sub> + C<sub>(g)</sub>  $\rightarrow$  Y<sub>(g)</sub> + Z<sub>(g)</sub>

(iii) The substance  $X_{(g)}$  is an intermediate in this mechanism.

a) Only one of these statements is true.

b) Statements (i) and (ii) are true.

c) Statements (i) and (iii) are true.

d) Statements (ii) and (iii) are true.

# Practice Exercise 2 (14.12)

For the reaction

 $Mo(CO)_6 + P(CH_3)_3 \rightarrow Mo(CO)_5P(CH_3)_3 + CO$ 

the proposed mechanism is

$$Mo(CO)_6 \rightarrow Mo(CO)_5 + CO$$

$$Mo(CO)_5 + P(CH_3)_3 \rightarrow Mo(CO)_5 P(CH_3)_3$$

a) Is the proposed mechanism consistent with the equation for the overall reaction?

b) Identify the intermediates.

# **Rate Laws for Elementary Steps**

- determine the overall rate law of the reaction
- The rate law of an elementary step is determined by its molecularity:
  - Unimolecular processes are first order.
  - Bimolecular processes are second order.
  - Termolecular processes are third order.

TABLE 14.3 Elementary Steps and Their Rate Laws		
Molecularity	Elementary Step	Rate Law
<b>Unimolecular</b>	$A \longrightarrow \text{products}$	Rate = $k[A]$
<b>Bimolecular</b>	$A + A \longrightarrow products$	Rate = $k[A]^2$
<b>Bimolecular</b>	$A + B \longrightarrow products$	Rate = $k[A][B]$
<i>Ter</i> molecular	A + A + A  products	Rate = $k[A]^3$
<i>Ter</i> molecular	$A + A + B \longrightarrow \text{products}$	Rate = $k[A]^2[B]$
<i>Ter</i> molecular	$A + B + C \longrightarrow products$	Rate = $k[A][B][C]$

# Sample Exercise 14.13 (p. 602)

If the following reaction occurs in a single elementary step, predict the rate law:

$$H_{2(g)} + Br_{2(g)} \rightarrow 2 HBr_{(g)}$$

# Practice Exercise 1 (14.13)

Consider the following reaction:  $2A + B \rightarrow X + 2Y$ . You are told that the first step in the mechanism of this reaction has the following rate law: Rate = k[A][B]. Which of the following could be the first step in the reaction mechanism (note that substance Z is an intermediate)?

a)  $A + A \rightarrow Y + Z$ b)  $A \rightarrow X + Z$ c)  $A + A + B \rightarrow X + Y + Y$ d)  $B \rightarrow X + Y$ e)  $A + B \rightarrow X + Z$ 

# Practice Exercise 2 (14.13)

Consider the following reaction:  $2 \text{ NO}_{(g)} + \text{Br}_{2(g)} \rightarrow 2 \text{ NOBr}_{(g)}$ .

- a) Write the rate law for the reaction, assuming it involves a single elementary step.
- b) Is a single-step mechanism likely for this reaction? Why or why not?

#### AP Chemistry

# **Rate Laws for Multistep Mechanisms**

- Most reactions occur by mechanisms with > one elementary step.
  - Rate-determining step (rate-limiting step) of the reaction = the slowest of the elementary steps.
    governs the overall rate law for the overall reaction.
- Consider the reaction:

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

- The experimentally derived rate law is: Rate =  $k[NO_2]^2$ 
  - We propose a mechanism for the reaction:
    - Step 1:  $NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)$  slow step
    - Step 2:  $NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$  fast step
    - Note that **NO**<sub>3</sub> is an **intermediate**.
  - If  $k_2 >> k_1$ , then the overall reaction rate will depend on the first step (the **rate-determining step**).
    - Rate =  $k_1[NO_2]^2$
    - This theoretical rate law is in agreement with the experimental rate law.
       → (but does not prove) our mechanism.

# Mechanisms with an Initial Fast Step

• Consider the reaction:

$$2 \operatorname{NO}(g) + \operatorname{Br}_2(g) \rightarrow 2 \operatorname{NOBr}(g)$$

• The experimentally determined rate law is:

Rate =  $k[NO]^2[Br_2]$ 

- Consider the following proposed mechanism:
  - Step 1: NO(g) + Br<sub>2</sub>(g)  $\xrightarrow{k_1}$  NOBr<sub>2</sub>(g) fast step
  - Step 2: NOBr<sub>2</sub>(g) + NO(g)  $\xrightarrow{k_2}$  2NOBr(g) slow step
  - The theoretical rate law for this mechanism is based on the rate-determining step, step 2:

Rate = 
$$k_2$$
[NOBr<sub>2</sub>][NO]

- The rate law should not depend on the [intermediate] (intermediates are usually unstable and have low/unknown concentrations.)
  - $\rightarrow$  We need to find a way to remove this term from our rate law.

#### AP Chemistry

- We can express the concentration of [NOBr<sub>2</sub>] in terms of NOBr and Br<sub>2</sub> by assuming that there is an **equilibrium** in step 1.
- In a dynamic equilibrium, the forward rate equals the reverse rate.
  - Therefore, by definition of equilibrium we get:

$$k_1[\text{NO}][\text{Br}_2] = k_{-1}[\text{NOBr}_2]$$

• Rearranging by solving for [NOBr<sub>2</sub>] we get:

$$[\text{NOBr}_2] = \frac{k_1}{k_{-1}} [\text{NO}][\text{Br}_2]$$

• Therefore, the overall rate law becomes

Rate = 
$$k_2 \frac{k_1}{k_{-1}}$$
 [NO][Br<sub>2</sub>][NO] =  $k$ [NO]<sup>2</sup>[Br<sub>2</sub>]

• Note the final rate law is consistent with the experimentally observed rate law.

# Sample Exercise 14.14 (p. 604)

The decomposition of nitrous oxide, N<sub>2</sub>O, is believed to occur by a two-step mechanism:

Step 1:  $N_2O_{(g)} \rightarrow N_{2(g)} + O_{(g)}$  (slow)

Step 2:  $N_2O_{(g)} + O_{(g)} \rightarrow N_{2(g)} + O_{2(g)}$  (fast)

- a) Write the equation for the overall reaction.
- b) Write the rate law for the overall reaction.

# Practice Exercise 1 (14.14)

Let's consider a hypothetical reaction similar to that in Practice Exercise 1 of Sample Exercise 14.13:  $2 C + D \rightarrow J + 2 K$ . You are told that the rate of this reaction is second order overall and second order in [C]. Could any of the following be a rate-determining first step in a reaction mechanism that is consistent with the observed rate law for the reaction (note that substance Z is an intermediate)?

- a)  $C + D \rightarrow K + Z$
- b)  $C \rightarrow J + Z$
- c)  $C + D \rightarrow J + Z$
- d) D  $\rightarrow$  J + K
- e) None of these are consistent with the observed rate law.

# Practice Exercise 2 (14.14)

Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:

 $O_{3(g)} + 2 NO_{2(g)} \rightarrow N_2O_{5(g)} + O_{2(g)}$ 

The reaction is believed to occur in two steps:

 $\mathrm{O}_{3(g)} \ + \ \mathrm{NO}_{2(g)} \ \textbf{\rightarrow} \ \mathrm{NO}_{3(g)} \ + \ \mathrm{O}_{2(g)}$ 

 $NO_{3(g)} + NO_{2(g)} \rightarrow N_2O_{5(g)}$ 

The experimental rate law is rate =  $k[O_3][NO_2]$ . What can you say about the relative rates of the two steps of the mechanism?

# Sample Exercise 14.15 (p. 606)

Show that the following mechanism for the equation  $2 \text{ NO}_{(g)} + \text{Br}_{2(g)} \rightarrow 2 \text{ NOBr}_{(g)}$  also produces a rate law consistent with the experimentally observed one:

Step 1: NO(g) + NO(g)  $\xrightarrow{k_1}$  N<sub>2</sub>O<sub>2(g)</sub> (fast equilibrium)  $\leftarrow k_{-1}$  Step 2: N<sub>2</sub>O<sub>2(g)</sub> + Br<sub>2(g)</sub>  $\rightarrow$  2 NOBr(g) (slow)

## Practice Exercise 1 (14.15)

Consider the following hypothetical reaction:

 $2P + Q \rightarrow 2R + S$ 

The following mechanism is proposed for this reaction:

 $P + P \leftrightarrows T \qquad (fast)$  $Q + T \rightarrow R + U \quad (slow)$  $U \rightarrow R + S \quad (fast)$ 

Substances T and U are unstable intermediates. What rate law is predicted by this mechanism?

- a) Rate =  $k[P]^2$
- b) Rate = k [P][Q]
- c) Rate =  $k[P]^2[Q]$
- d) Rate =  $k[P][Q]^2$
- e) Rate = k[U]

# Practice Exercise 2 (14.15)

The first step of a mechanism involving the reaction of bromine is

 $\begin{array}{ccc} & \stackrel{k_{1}}{\longrightarrow} \\ \text{Br}_{2(g)} & \stackrel{k_{-1}}{\longleftarrow} & 2 \text{ Br}_{(g)} & \text{(fast equilibrium)} \end{array}$ 

What is the expression relating the concentration of Br(g) to that of  $Br_2(g)$ ?

# 14.7 Catalysis

**catalyst** = a substance that changes the rate of a chemical reaction without itself undergoing a permanent chemical change in the process.

Two types of catalyst:

- Homogeneous
- Heterogeneous

Catalysts are common in the body, in the environment, and in the chemistry lab!

# **Homogeneous** Catalysis

**homogeneous catalyst** = catalyst that is present in the **same phase** as the reacting molecules.

e.g. Hydrogen peroxide decomposes very slowly in the absence of a catalyst:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

• In the **presence** of bromide ion, the decomposition occurs rapidly in acidic solution:

 $2Br^{-}(aq) + H_2O_2(aq) + 2H^{+}(aq) \rightarrow Br_2(aq) + 2H_2O(l)$ 

(Br<sub>2(aq)</sub> is brown.)

$$\operatorname{Br}_2(aq) + \operatorname{H}_2\operatorname{O}_2(aq) \rightarrow 2\operatorname{Br}^-(aq) + 2\operatorname{H}^+(aq) + \operatorname{O}_2(g)$$

- **Br** is a **catalyst** because it is regenerated at the end of the reaction.
- The net reaction is still:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$



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## How do catalysts increase reaction rates?

In general, catalysts operate by  $\downarrow$  the overall  $E_a$  for a reaction.

#### Other ways:

- by  $\uparrow$  the number of effective collisions  $\uparrow k$  by  $\uparrow A$  or  $\downarrow E_a$  (from the Arrhenius equation)
- A catalyst usually provides a completely different mechanism for the reaction, such as adding new intermediates to the reaction.
   e.g. In the absence of Br<sup>-</sup>, H<sub>2</sub>O<sub>2</sub> decomposes directly to water and oxygen.

In the presence of Br<sup>-</sup>,  $\mathbf{Br}_{2(aq)}$  is generated as an intermediate.

• When a catalyst adds an **intermediate**, the E<sub>a</sub> for **both** steps must be **lower** than the E<sub>a</sub> for the uncatalyzed reaction.



Reaction pathway

# **Heterogeneous** Catalysis

- A heterogeneous catalyst exists in a different phase than the reactants.
- e.g. gaseous reactants and products (catalytic converters in cars)
  - Many industrial catalysts are heterogeneous.
- How do they do their job?
  - The first step is **adsorption** (the binding of reactant molecules to the catalyst surface).
  - Adsorption occurs due to the high reactivity of atoms or ions on the surface of the solid.
  - Molecules are adsorbed onto active sites on the catalyst surface.
- The number of active sites on a given amount of catalyst depends on several factors such as:
  - The nature of the catalyst.
  - How the catalyst was prepared.
  - How the catalyst was treated prior to use.



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# Mechanism for reaction of ethylene with hydrogen on a catalytic surface.

(a) The hydrogen and ethylene are adsorbed at the metal surface.

(b) The H—H bond is broken to give adsorbed hydrogen atoms.

(c) These migrate to the adsorbed ethylene and bond to the carbon atoms.

(d) As C—H bonds are formed, the adsorption of the molecule to the metal surface is decreased and ethane is released.

• e.g. consider the hydrogenation of ethylene to form ethane:  $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$ 

 $\Delta H^{o} = -137 \text{ kJ/mol}$ 

- The reaction is **slow** in the absence of a catalyst.
- In the presence of a finely divided metal catalyst (Ni, Pt or Pd) the reaction occurs quickly at room temperature.
- First, the ethylene and hydrogen molecules are adsorbed onto active sites on the metal surface.
- The H–H bond breaks and the H atoms migrate about the metal surface.
- When an H atom collides with an ethylene molecule on the surface, the C–C  $\pi$  bond breaks and a C–H  $\sigma$  bond forms.
- An *ethyl group*,  $C_2H_5$ , is weakly bonded to the metal surface with a metal-carbon  $\sigma$  bond.
- When  $C_2H_6$  forms it **desorbs** from the surface.
- When ethylene and hydrogen are adsorbed onto a surface, less E is required to break the bonds.
- $E_a$  for the reaction  $\downarrow \rightarrow \uparrow$  reaction rate

#### Enzymes

- Enzymes are **biological** catalysts.
- Most enzymes are **protein molecules** with large molecular masses  $(10,000 \text{ to } 10^6 \text{ amu})$
- Enzymes have very specific shapes.
- Most enzymes catalyze very specific reactions.
- Substrates undergo reaction at the **active site** of an enzyme.
- A substrate locks into an enzyme and a fast reaction occurs.
- The products then move away from the enzyme.
- Only substrates that fit into the enzyme lock can be involved in the reaction.
- If a molecule binds tightly to an enzyme so that another substrate cannot displace it, then the active site is blocked and the catalyst is inhibited (enzyme inhibitors).
- Enzymes are extremely efficient catalysts.
  - The number of individual catalytic events occurring at an active site per unit time is called the *turnover number*.
  - Large turnover numbers correspond to very low  $E_a$  values.
  - For enzymes, turnover numbers are very large (typically  $10^3 10^7$  per second).



# The lock-and-key model for enzyme action.

The correct substrate is recognized by its ability to fit the active site of the enzyme, forming the enzyme–substrate complex. After the reaction of the substrate is complete, the products separate from the enzyme.

# Acid-Base Catalysts

- Proton transfers to or from charged intermediates or transition states that would otherwise break down to their reactants. Water is often produced or involved, acting as a Brønsted-Lowry acid or base.
- Stabilizes the intermediate long enough to go on to the next step.
- The acid or base participates in one of the early steps in a multi-step reaction before or during the slow step, then is regenerated in a later step.
- Acid-base catalysis is one of the mechanisms by which enzymes catalyze reactions, via amino acid acidic or basic side-chains in the active site. (general acid-base catalysis)
- Specific acid-base catalysis occurs when the reaction rate is dependent on pH only, i.e. the solvent acts as an acid or base.
- Examples organic chemistry, such as ester hydrolysis (enzymatic) or decomposition of hydrocarbons in the conversion of petroleum to gasoline (industrial)

# Sample Integrative Exercise 14: Putting Concepts Together (p. 613)

Formic acid (HCOOH) decomposes in the gas phase at elevated temperatures as follows:

$$\text{HCOOH}_{(g)} \rightarrow \text{CO}_{2(g)} + \text{H}_{2(g)}$$

The decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in the figure below. When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies as shown by the blue curve in the figure below.



- a) Estimate the half-life and first-order rate constant for formic acid decomposition.
- b) What can you conclude from the effect of added ZnO on the decomposition of formic acid?
- c) The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, we had plotted the concentration of formic acid in units of mol/L. What effect would this have had on the calculated value of *k*?

d) The pressure of formic acid vapor at the start of the reaction is  $3.00 \times 10^2$  torr. Assuming constant temperature and ideal-gas behavior, what is the pressure in the system at the end of the reaction? If the volume of the reaction chamber is 436 cm<sup>3</sup>, how many moles of gas occupy the reaction chamber at the end of the reaction?

e) The standard heat of formation of formic acid vapor is  $\Delta H^o_f = -378.6 \text{ kJ/mol}$ . Calculate  $\Delta H^o$  for the overall reaction. Assuming that the activation energy (E<sub>a</sub>) for the reaction is 184 kJ/mol, sketch an approximate energy profile for the reaction, and label E<sub>a</sub>,  $\Delta H^o$ , and the transition state.