

## CHEMISTRY 1101 NOTES ZUMDAHL CHAPTER 12 - CHEMICAL KINETICS

The previous chapter touched on thermodynamics which can tell us whether a reaction is inherently likely to "go". The thermodynamics of the overall reaction tell us nothing about the *rate* of a reaction. There are a number of very exothermic reactions which do not proceed at all at room temperature. Examples are the reaction of hydrogen with oxygen, hydrogen and chlorine and hydrogen and nitrogen.

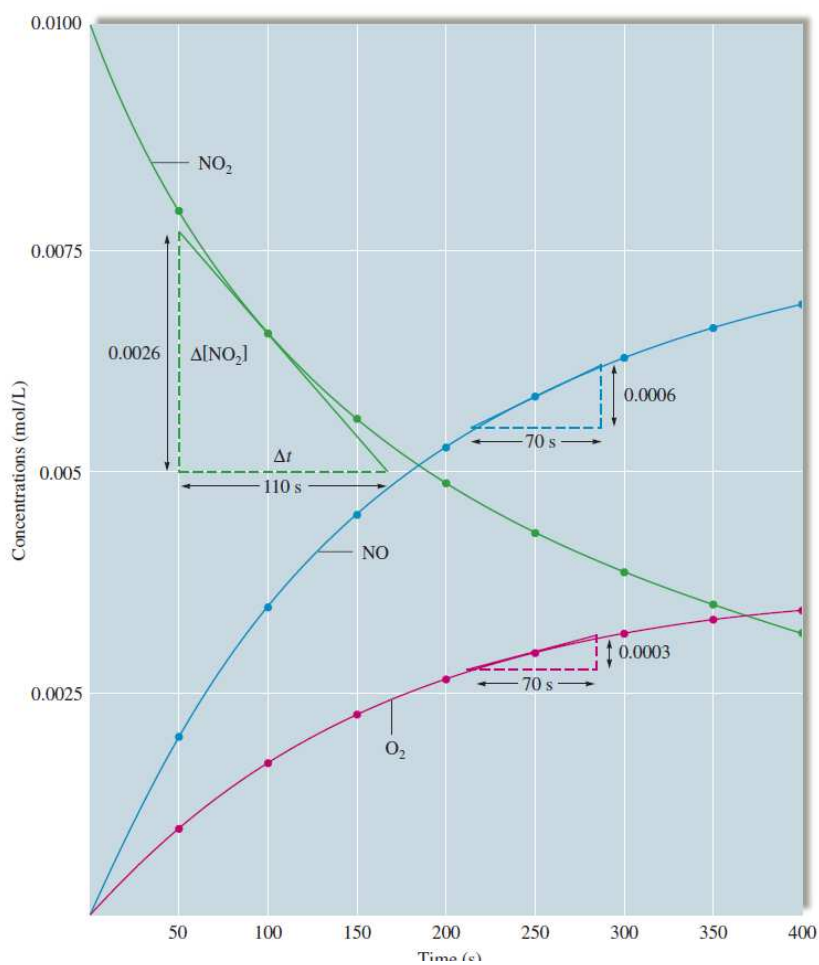
Reactions are characterized by a mechanism in which the overall reaction may actually occur in a number of steps. One or more of these steps will govern the rate at which the reaction occurs. Studying kinetics is one way to establish the mechanism, and in industrially important reactions perhaps propose other mechanisms which may be faster.

### 1. Reaction Rates

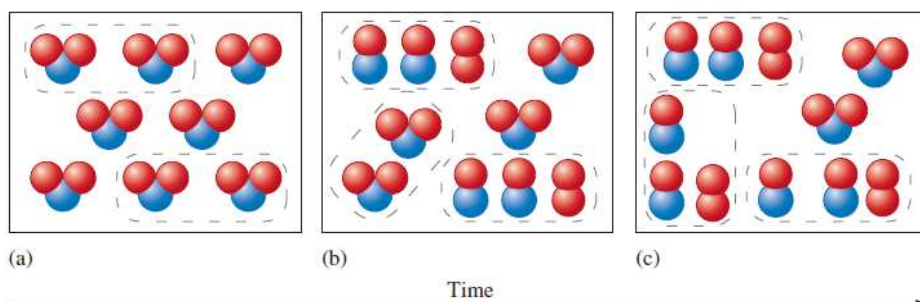
**TABLE 12.1** Concentrations of Reactant and Products as a Function of Time for the Reaction  $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$  (at  $300^\circ\text{C}$ )

Time ( $\pm 1$ s)	Concentration (mol/L)		
	$\text{NO}_2$	$\text{NO}$	$\text{O}_2$
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

See also **Figures 12.1** and **12.2**



**FIGURE 12.1**  
Starting with a flask of nitrogen dioxide at 300°C, the concentrations of nitrogen dioxide, nitric oxide, and oxygen are plotted versus time.



**FIGURE 12.2**  
Representation of the reaction  $2\text{NO}_2(g) \rightarrow 2\text{NO}(g) + \text{O}_2(g)$ . (a) The reaction at the very beginning ( $t = 0$ ). (b) and (c) As time passes,  $\text{NO}_2$  is converted to  $\text{NO}$  and  $\text{O}_2$ .

The rate can be averaged over particular periods:

$$\text{Change in } [\text{NO}_2] / \text{Time elapsed} = \Delta[\text{NO}_2] / \Delta t = [\text{NO}_2]_{50} - [\text{NO}_2]_0 / 50 = -4.2 \times 10^{-5} \text{ mol/L/s}$$

**TABLE 12.2 Average Rate (in mol/L · s) of Decomposition of Nitrogen Dioxide as a Function of Time\***

$\frac{\Delta[\text{NO}_2]}{\Delta t}$	Time Period (s)
$4.2 \times 10^{-5}$	0 → 50
$2.8 \times 10^{-5}$	50 → 100
$2.0 \times 10^{-5}$	100 → 150
$1.4 \times 10^{-5}$	150 → 200
$1.0 \times 10^{-5}$	200 → 250

\*Note that the *rate* decreases with time.

or determined as an instantaneous rate from the slope of the curves thus:

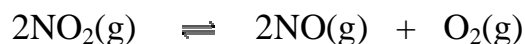
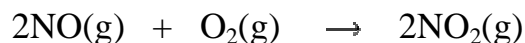
The rate of disappearance of NO<sub>2</sub> at 100 s = 0.0026/110 = -2.4x10<sup>-5</sup> mol/L/s

The rate of appearance of NO is the same at 100 s and at 250 s it is 6x10<sup>-4</sup>/70 = 8.6x10<sup>-5</sup> mol/L/s

The rate of appearance of O<sub>2</sub> would be one half of the values for NO.

### Rate Laws: An Introduction

All reactions are reversible. Except right at the beginning, when there are no products, the changes in concentration that we observe are dependent on the rates of the forward and reverse reaction rates.



The individual rates are dependent on a *rate law*. The rate of disappearance of NO<sub>2</sub> is governed by the equation:

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

The constants k (the *rate constant*) and n (the *order*) must be experimentally determined. The

order can be an integer, a fraction or zero. In simple cases it is usually a small integer. Important points are:

The rate law will contain the concentrations of the reactants in the process to which it applies only.

The value of the exponent must be experimentally determined.

Also we have to define exactly what rate we are writing the law for:

$$\text{Rate} = \Delta[\text{NO}_2]/\Delta t = k[\text{NO}_2]^n \quad \text{Disappearance of NO}_2$$

$$\text{Rate}' = \Delta[\text{O}_2]/\Delta t = k'[\text{NO}_2]^n \quad \text{Appearance of O}_2$$

$$\text{Rate}'' = \Delta[\text{NO}]/\Delta t = k''[\text{NO}_2]^n \quad \text{Appearance of NO}$$

$$k = k'' = 2k'$$

### **Types of Rate Laws**

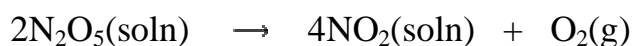
The above rate laws are called *differential rate laws* and they give rate as a function of concentration - t does not appear on the right-hand side. The other form, the *integrated rate law* gives concentrations as a function of time - t will appear on the right-hand side.

The two kinds of law can be mathematically obtained from each other so we need determine only one experimentally: whichever is more convenient.

The reason for being interested in the rate laws for a particular overall reaction is in order to obtain clues as to the individual steps in the reaction. There are very few reactions known where any one step involves more than two molecules.

### **Determining the Form of a Rate Law**

Consider the decomposition of  $\text{N}_2\text{O}_5$  in carbon tetrachloride solution at  $45^\circ\text{C}$ :



The oxygen escapes from the solution so the reverse reaction is not possible which simplifies the situation.

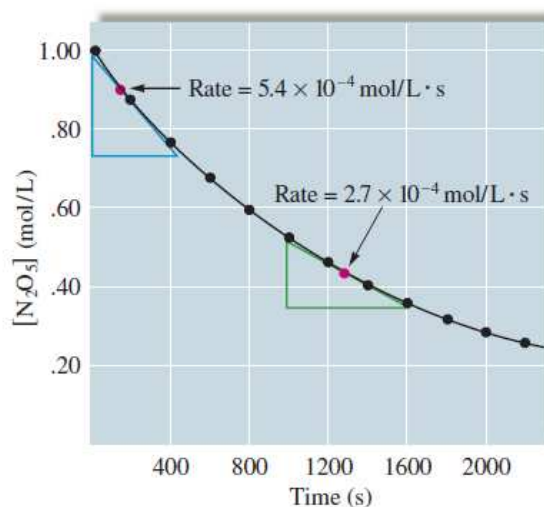
**TABLE 12.3 Concentration/Time Data for the Reaction**  
 $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$  (at 45°C)

$[\text{N}_2\text{O}_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

If we check the rates at a couple of points we can deduce a value for  $n$ . See **Figure 12.3**. When the concentration is 0.90 M the instantaneous rate (slope) is  $5.4 \times 10^{-4}$  mol/L/s, and when the concentration has halved to 0.45 M the rate becomes  $2.7 \times 10^{-4}$  mol/L/s, that is half the first. This means the rate of the reaction depends on  $[\text{N}_2\text{O}_5]$  to the first power:

$$\text{Rate} = -\Delta[\text{N}_2\text{O}_5]/\Delta t = k[\text{N}_2\text{O}_5]^1 = k[\text{N}_2\text{O}_5]$$

We could also work out  $k$  from one of these data points, but it would be better to use both and even better to use the whole plot somehow...



**FIGURE 12.3**

A plot of the concentration of  $\text{N}_2\text{O}_5$  as a function of time for the reaction  $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$  (at 45°C). Note that the reaction rate at  $[\text{N}_2\text{O}_5] = 0.90 \text{ M}$  is twice that at  $[\text{N}_2\text{O}_5] = 0.45 \text{ M}$ .

## Method of Initial Rates

The decomposition of  $\text{N}_2\text{O}_5$  had the advantage that the reverse reaction is not possible, but in most cases this is not the situation. Instead, we examine initial reaction rates at various concentrations to deduce the order:

Consider:



**TABLE 12.4 Initial Rates from Three Experiments for the Reaction  $\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$**

Experiment	Initial Concentration of $\text{NH}_4^+$	Initial Concentration of $\text{NO}_2^-$	Initial Rate (mol/L · s)
1	0.100 M	0.0050 M	$1.35 \times 10^{-7}$
2	0.100 M	0.010 M	$2.70 \times 10^{-7}$
3	0.200 M	0.010 M	$5.40 \times 10^{-7}$

The general form of the rate law is:

$$\text{Rate} = -\Delta[\text{NH}_4^+]/\Delta t = k[\text{NH}_4^+]^n[\text{NO}_2^-]^m$$

Try to find data for which only one concentration changes to deduce the exponents. This is the case with runs 1 and 2 where *only* the  $\text{NO}_2^-$  concentration doubles:

$$\text{Run 1: Rate} = 1.35 \times 10^{-7} \text{ mol/L/s} = k(0.100 \text{ mol/L})^n(0.0050 \text{ mol/L})^m$$

$$\text{Run 2: Rate} = 2.70 \times 10^{-7} \text{ mol/L/s} = k(0.100 \text{ mol/L})^n(0.0100 \text{ mol/L})^m$$

Then take the ratio:

$$\text{Run 2/Run 1: Rate}_2/\text{Rate}_1 = 2.00 = (2.0)^m$$

Obviously  $m = 1$ .

Now do the same with runs 2 and 3 where *only* the concentration of  $\text{NH}_4^+$  doubles:

$$\text{Rate}_3/\text{Rate}_2 = 2.00 = (2.0)^n$$

Thus  $n = 1$  also.

Therefore the rate law is:

$$\text{Rate} = -\Delta[\text{NH}_4^+]/\Delta t = k[\text{NH}_4^+][\text{NO}_2^-]$$

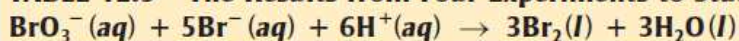
Finally we can establish a value of  $k$  from any one of the runs (or all of them graphically):

$$\text{From run 1: } 1.35 \times 10^{-7} \text{ mol/L/s} = k(0.100 \text{ mol/L})(0.0050 \text{ mol/L})$$

$$k = 2.70 \times 10^{-7} \text{ L mol}^{-1} \text{ s}^{-1}$$

### Exercise 12.1

**TABLE 12.5 The Results from Four Experiments to Study the Reaction**



Experiment	Initial Concentration of $\text{BrO}_3^-$ (mol/L)	Initial Concentration of $\text{Br}^-$ (mol/L)	Initial Concentration of $\text{H}^+$ (mol/L)	Measured Initial Rate (mol/L · s)
1	0.10	0.10	0.10	$8.0 \times 10^{-4}$
2	0.20	0.10	0.10	$1.6 \times 10^{-3}$
3	0.20	0.20	0.10	$3.2 \times 10^{-3}$
4	0.10	0.10	0.20	$3.2 \times 10^{-3}$

$$\text{Rate} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$

Consider ratios: 2/1 which gives  $n=1$ , 3/2 which gives  $m = 1$ , and 4/1 which gives  $p=2$

$$\text{ie. Rate} = k[\text{BrO}_3^-]^1[\text{Br}^-]^1[\text{H}^+]^2$$

Run 1 gives  $k$ :

$$8.0 \times 10^{-4} \text{ mol/L/s} = k(0.10 \text{ mol/L})(0.10 \text{ mol/L})(0.10 \text{ mol/L})^2$$

$$\text{Therefore: } k = (8.0 \times 10^{-4} \text{ mol/L/s}) / (1.0 \times 10^{-4} \text{ mol}^4/\text{L}^4) = 8.0 \text{ L}^3/\text{mol}^3/\text{s}$$

### The Integrated Rate Law

It is often convenient to have the variation of concentrations of reagents and products as a function of time. We need to know how to convert the differential rate law to the integrated rate law. This is simplest for reactions with but a single reactant, (and easiest to understand with a bit of calculus!)

The differential law is:  $\text{Rate} = -\Delta[A]/\Delta t = k[A]^n$

In the sections that follow, the integrated rate laws are shown for first order ( $n = 1$ ), second order ( $n = 2$ ) and zero order ( $n = 0$ ) cases. (It should be mentioned again that three-body collisions are very rare.)

### First-Order Rate Laws

For the reaction:



The rate law was:

$$\text{Rate} = -\Delta\{\text{N}_2\text{O}_5\}/\Delta t = k[\text{N}_2\text{O}_5]$$

Integration (using calculus) of this equation yields:

$$\ln([\text{N}_2\text{O}_5]_t) = -kt + \ln([\text{N}_2\text{O}_5]_o)$$

The general form of the integrated rate law for reaction which is first order in one reagent is:

$$\ln([A]_t) = -kt + \ln([A]_o)$$

- . The equation shows the variation of concentration with time if the initial concentration and the rate constant are known.
- . The equation is a straight line, ie it has the form  $y = mx + c$  where  $y = \ln[A]$ ,  $m = -k$  and  $c = \ln[A]_o$ . A plot of the natural log of concentration against time is straight if the reaction is first order (within experimental error) and taking the slope is the usual way of extracting the value of  $k$  from the complete data set rather than each point separately.
- . The equation can be rearranged:

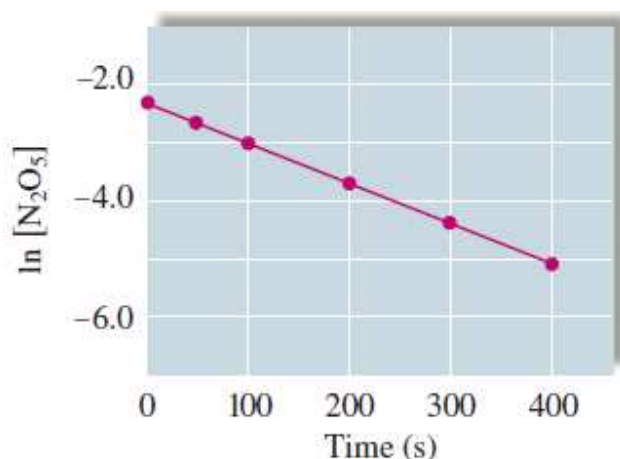
$$\ln([A]_o/[A]) = kt$$

#### Exercise 12.2

<u>[N<sub>2</sub>O<sub>5</sub>] (mol/L)</u>	<u>Time (s)</u>	<u>ln[N<sub>2</sub>O<sub>5</sub>]</u>	<u>Time (s)</u>
0.1000	0	-2.303	0
0.0707	50	-2.649	50
0.0500	100	-2.996	100
0.0250	200	-3.689	200
0.0125	300	-4.382	300
0.00625	400	-5.075	400



The data are plotted in Fig 12.4: a suspiciously perfect straight line!



**FIGURE 12.4**  
A plot of  $\ln[\text{N}_2\text{O}_5]$  versus time.

We can get the value of  $k$  from the slope using the first and last points:

$$\text{Slope} = \frac{\text{change in "y"}}{\text{change in "x"}} = \frac{\Delta \ln[\text{N}_2\text{O}_5]}{\Delta t}$$

$$\text{Slope} = \frac{-5.075 - (-2.303) \text{ (dimensionless)}}{400 - 0 \text{ (s)}} = -6.93 \times 10^{-3} \text{ s}^{-1}$$

$$k = +6.93 \times 10^{-3} \text{ s}^{-1}$$

The integrated rate law can be used to calculate the concentration at any time after the start of the reaction, for example at 150 s:

$$\ln([\text{N}_2\text{O}_5]_t) = -6.93 \times 10^{-3} \text{ (s}^{-1}) \times t \text{ (s)} + \ln([\text{N}_2\text{O}_5]_0)$$

$$\ln([\text{N}_2\text{O}_5]_{150}) = -6.93 \times 10^{-3} \text{ (s}^{-1}) \times 150 \text{ (s)} + \ln(0.100)$$

$$\ln([\text{N}_2\text{O}_5]_{150}) = -6.93 \times 10^{-3} \text{ (s}^{-1}) \times 150 \text{ (s)} + -2.303$$

$$\ln([\text{N}_2\text{O}_5]_{150}) = -3.343$$

$$\text{Therefore: } [\text{N}_2\text{O}_5]_{150} = e^{-3.343} = 0.0353 \text{ mol/L}$$

N.B. This is not halfway between 0.0500 (at  $t = 100$ ) and 0.0250 (at  $t = 200$ ) because of the logarithmic relationship.

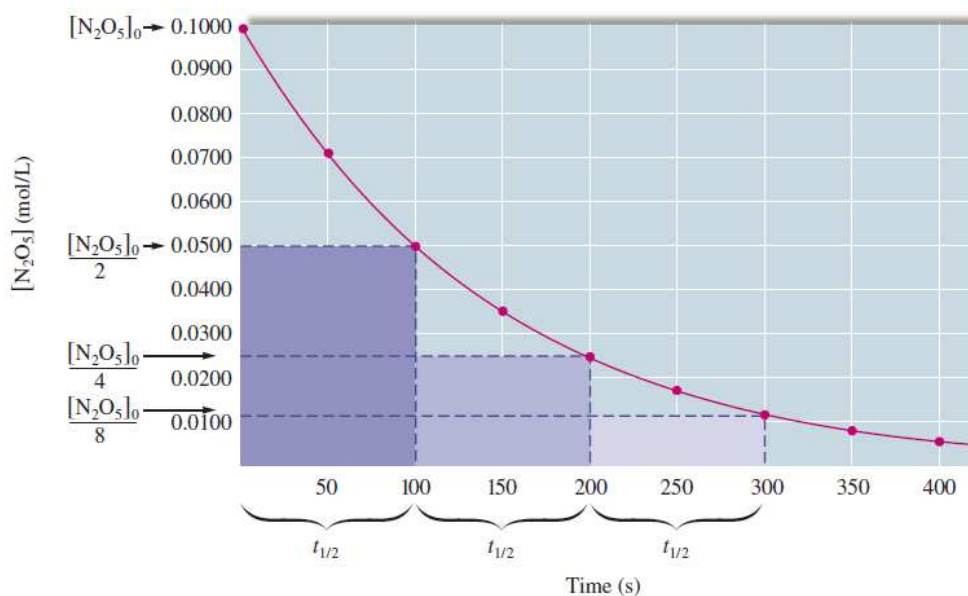
### **The Half-Life of a First-Order Reaction**

This is the time taken for a reactant to reach half its original concentration. For first order reactions this is always the same regardless of where one starts. See [Figure 12.5](#).

$[\text{N}_2\text{O}_5]$ (mol/L)	$t$ (s)
0.100	0
0.0500	100
0.0250	200
0.0125	300

$\Delta t = 100 \text{ s};$	$\frac{[\text{N}_2\text{O}_5]_{t=100}}{[\text{N}_2\text{O}_5]_{t=0}} = \frac{0.050}{0.100} = \frac{1}{2}$
$\Delta t = 100 \text{ s};$	$\frac{[\text{N}_2\text{O}_5]_{t=200}}{[\text{N}_2\text{O}_5]_{t=100}} = \frac{0.025}{0.050} = \frac{1}{2}$
$\Delta t = 100 \text{ s};$	$\frac{[\text{N}_2\text{O}_5]_{t=300}}{[\text{N}_2\text{O}_5]_{t=200}} = \frac{0.0125}{0.0250} = \frac{1}{2}$



**FIGURE 12.5**

A plot of  $[\text{N}_2\text{O}_5]$  versus time for the decomposition reaction of  $\text{N}_2\text{O}_5$ .

The data conveniently illustrate that it always takes 100 seconds to halve the concentration of  $\text{N}_2\text{O}_5$  but it is better to derive a general formula:

$$\ln\left(\frac{[A]_0}{[A]}\right) = kt$$

but by definition:

$$[A] = [A_0]/2$$

so:

$$\ln\left(\frac{[A]_0}{([A]_0/2)}\right) = kt_{1/2}$$

$$\ln(2) = kt_{1/2}$$

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

N.B. For first-order reactions the half-life is independent of the concentration.

### Exercise 12.4

A reaction has a half-life of 20.0 minutes. (a) Calculate the rate constant. (b) How much time is needed for the reaction to be 75% complete?

$$k = 0.693/20.0 = 3.47 \times 10^{-2} \text{ min}^{-1} = 5.78 \times 10^{-4} \text{ s}^{-1}$$

The quick and dirty method. Because 75% is a convenient number. Spot that that after one half-life, 50% of the reagents are left and after another half-life 50% of 50% ie 25% will be left ie 75% has been consumed. This takes 40 mins.

In general though, use the integrated rate law:

$$\ln([A]_0/[A]) = kt$$

If the reaction is 75% complete then:

$$[A]/[A]_0 = 0.25 \quad \text{or} \quad [A]_0/[A] = 4.0$$

$$\ln(4.0) = kt = 3.47 \times 10^{-2} \quad \text{or} \quad t = \ln(4.0)/3.47 \times 10^{-2} = 40 \text{ min}$$

### Second-Order Rate Laws

For a single reactant:

$$\text{Rate} = -\Delta[A]/\Delta t = k[A]^2$$

The integrated form is:

$$1/[A]_t = kt + 1/[A]_0$$

- A plot of  $1/[A]$  vs  $t$  will produce a straight line of slope  $k$ .
- Provided  $[A]_0$  and  $k$  are known, the concentration can be calculated after any time  $t$ .

The half-life can be expressed as follows:

By definition:

$$[A] = [A]_0/2$$

$$1/([A]_0/2) = kt_{1/2} + 1/[A]_0 \quad \text{or} \quad 1/[A]_0 = kt_{1/2}$$

Therefore:

$$t_{1/2} = 1/(k[A]_0)$$

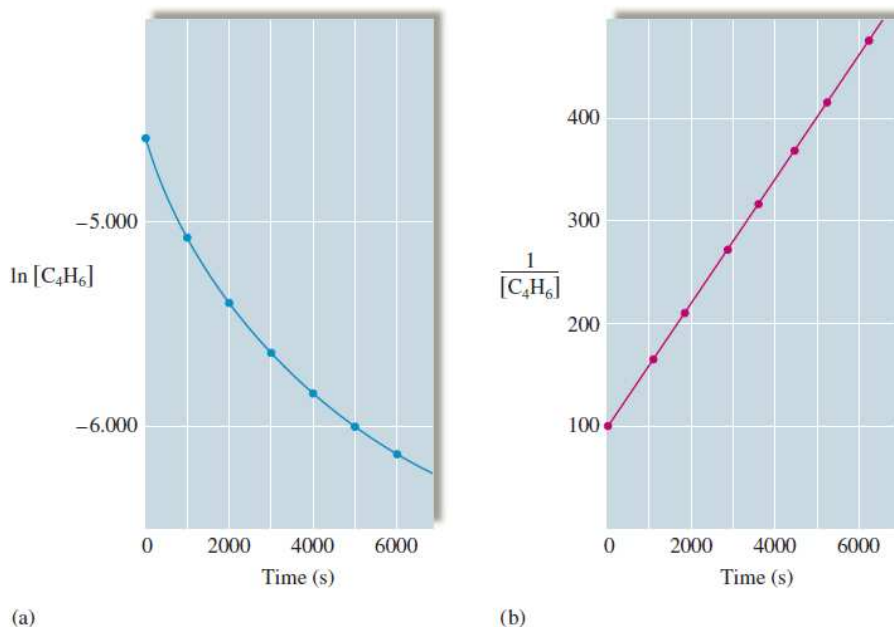
Notice the half-life is no longer constant, but is dependent on the starting concentration.

Exercise 12.5 : Data for the Dimerization of Butadiene  
 $2\text{C}_4\text{H}_6(\text{g}) \rightarrow \text{C}_8\text{H}_{12}(\text{g})$

Time ( $\pm 1$ s)	$[\text{C}_4\text{H}_6]$ (mol/L)	$\ln[\text{C}_4\text{H}_6]$	$\frac{1}{[\text{C}_4\text{H}_6]}$
0	0.01000	-4.605	100
1000	0.00625	-5.075	160
1800	0.00476	-5.348	210
2800	0.00370	-5.599	270
3600	0.00313	-5.767	320
4400	0.00270	-5.915	370
5200	0.00241	-6.028	415
6200	0.00208	-6.175	481

Find the order, the rate constant and the half life.

The data are plotted in Figures 12.6 (a) and (b). Note that the points in (a) are incorrectly marked though the curve is OK.



**FIGURE 12.6**

(a) A plot of  $\ln[\text{C}_4\text{H}_6]$  versus  $t$ . (b) A plot of  $1/[\text{C}_4\text{H}_6]$  versus  $t$ .

The log plot is not a straight line but the reciprocal one is, therefore the reaction is second order. The slope of the line is  $k$ . Using the first and last points:

$$k = (481-100 \text{ L/mol})/(6200-0 \text{ sec}) = 6.14 \times 10^{-2} \text{ L/mol/s}$$

The half life is given by:

$$t_{1/2} = 1/(k[A]_0) = 1/((6.14 \times 10^{-2})(1.000 \times 10^{-2})) = 1.63 \times 10^3 \text{ s}$$

If the initial concentration of butadiene is  $0.01000 \text{ M}$  it is halved in 1630 s. If it were half that concentration it would be halved in *double* the time!

### Zero-Order Rate Laws

$$\text{Rate} = -\Delta[A]/\Delta t = k$$

The rate is invariant with the concentration of a reagent for certain types of reactions. An example is the metal (Pt) surface catalysed decomposition of  $\text{N}_2\text{O}$  to  $\text{N}_2$  and  $\text{O}_2$ . (Figure 12.8) All the sites on the Pt surface are occupied and the rate will depend only on the number of sites (which is constant) and the rate at which the sites are liberated (which will also be constant at a particular temperature).

The integrated rate law is:

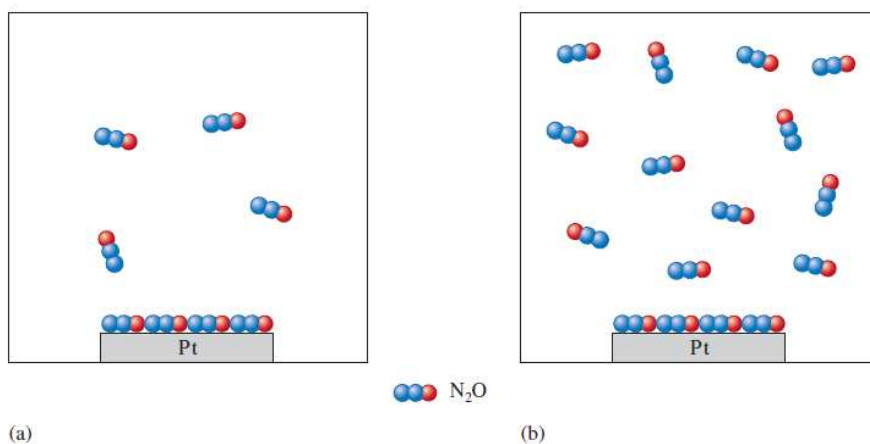
$$[A] = -kt + [A]_0$$

and the half-life is given by:

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

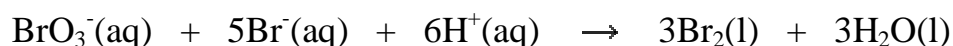
**FIGURE 12.8**

The decomposition reaction  $2\text{N}_2\text{O}(\text{g}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g})$  takes place on a platinum surface. Although  $[\text{N}_2\text{O}]$  is twice as great in (b) as in (a), the rate of decomposition of  $\text{N}_2\text{O}$  is the same in both cases because the platinum surface can accommodate only a certain number of molecules. As a result, this reaction is zero order.



### Integrated Rate Laws for Reactions with More than One Reactant

The example given is:



We already know the (differential) rate law is:

$$\text{Rate} = -\Delta[\text{BrO}_3^-]/\Delta t = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

The integrated rate law for such a reaction causes mathematical problems unless we do the reaction under conditions where two of the reagents are present in such excess that their concentration is constant within experimental error. The book suggests 1 M for  $\text{Br}^-$  and  $\text{H}^+$  and 0.001 M for  $\text{BrO}_3^-$  in order to obtain *pseudo first-order* conditions.

The new rate law is:

$$\text{Rate} = -\Delta[\text{BrO}_3^-]/\Delta t = k'[\text{BrO}_3^-]$$

As for any other first-order reaction,  $k'$  can be obtained from the -slope of the log plot, and then  $k$  obtained because the concentrations of bromide and proton are known:

$$k' = k[\text{Br}^-]_0[\text{H}^+]_0$$

### • Rate Laws: a Summary

<b>(Table 12.6) Summary of the Kinetics for Reactions of the Type aA → Products</b>			
	<b>Zero Order</b>	<b>First Order</b>	<b>Second Order</b>
Rate Law	Rate = k	Rate = k[A]	Rate = k[A] <sup>2</sup>
Integrated Rate Law	[A] = -kt + [A] <sub>0</sub>	ln[A] = -kt + ln[A] <sub>0</sub>	1/[A] = kt + 1/[A] <sub>0</sub>
Straight Line Plot	[A] vs t	ln[A] vs t	1/[A] vs t

Significance of the Slope	-k	-k	k
Half-life	$t_{1/2} = [A]_0/2k$	$t_{1/2} = 0.693/k$	$t_{1/2} = 1/k[A]_0$

- . The treatment we have seen assumes that only the forward reaction is important (and only one process determines the rate).
- . There are two forms of rate law:
  - Differential rate law*: Usually just *rate law* relates rate to concentration of reactant(s)
  - Integrated rate law*: relates concentration to time.
- . The two types of rate law are mathematically related and only one has to be established by suitable experiments.
- . The method of initial rates is the most common method for determining the differential rate law.
- . The method of measuring the concentration over an extended period leads to the integrated rate law in the sense that the shape of the plots determines the order.
- . A rate law for reactions involving several reactants can always usually reduced to pseudo nth order in one reactant by making sure there is a healthy excess of the others.

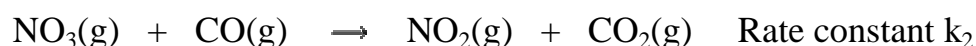
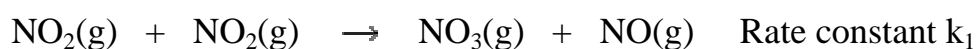
### Reaction Mechanisms

Consider the reaction:



$$\text{Rate} = k[\text{NO}_2]^2$$

The reaction is actually thought to proceed by a rather more complex mechanism than the overall equation indicates:



$\text{NO}_3$  is an *intermediate*. It does not appear in the overall reaction.

Each reaction is called an *elementary step*.

The *molecularity* of an elementary step which can be *unimolecular*, *bimolecular* or very rarely *termolecular* is associated with a specific rate law for that step.

**TABLE 12.7 Examples of Elementary Steps**

Elementary Step	Molecularity	Rate Law
$A \rightarrow \text{products}$	<i>Unimolecular</i>	Rate = $k[A]$
$A + A \rightarrow \text{products}$ ( $2A \rightarrow \text{products}$ )	<i>Bimolecular</i>	Rate = $k[A]^2$
$A + B \rightarrow \text{products}$	<i>Bimolecular</i>	Rate = $k[A][B]$
$A + A + B \rightarrow \text{products}$ ( $2A + B \rightarrow \text{products}$ )	<i>Termolecular</i>	Rate = $k[A]^2[B]$
$A + B + C \rightarrow \text{products}$	<i>Termolecular</i>	Rate = $k[A][B][C]$

Elementary steps above termolecular are virtually impossible.

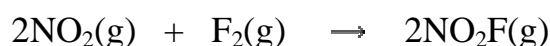
1. The sum of the elementary steps must sum to the overall balanced equation.

The mechanism must agree with the experimentally determined rate law.

The first criterion is clearly true. The second requires the introduction of the idea of a *rate determining step*. In this case the rate determining step is the first one, which gives us the experimentally observed rate law. This does not confirm that this is the actual mechanism: there may be another that is chemically reasonable but that we have not thought of.

#### Exercise 12.6

The balance equation for the reaction of nitrogen dioxide and fluorine in the gas phase is:



and the experimental rate law is:

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

A suggested mechanism is:

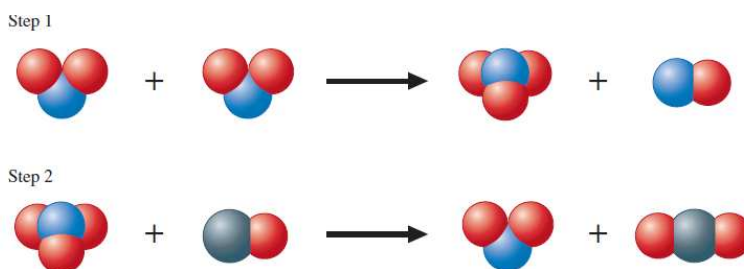
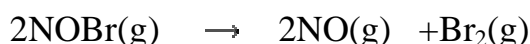


This is an acceptable mechanism on both the above criteria.

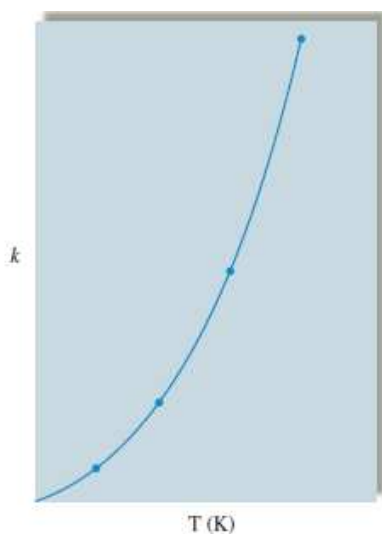


## A Model for Chemical Kinetics

The *collision model* requires that a collision has to happen for a reaction step to occur. This is enough to explain the rate laws if we choose a suitable mechanism, but there is also a temperature effect which causes reaction rates to rise dramatically (usually) as the temperature is raised: the effect is actually exponential (Figure 12.9). The effect can be explained by assuming that reactions have a threshold *activation energy* (Svante Arrhenius, 1880's) This activation energy is like a barrier that the reaction has to "go over" to get to the products. Figure 12.10 illustrates this for:



**FIGURE 12.9**  
A molecular representation of the elementary steps in the reaction of NO<sub>2</sub> and CO.



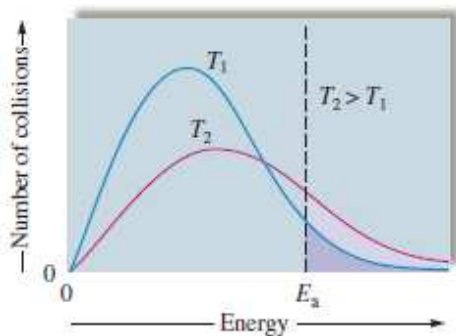
**FIGURE 12.10**  
A plot showing the exponential dependence of the rate constant on absolute temperature. The exact temperature dependence of *k* is different for each reaction. This plot represents the behavior of a rate constant that doubles for every increase in temperature of 10 K.

The reaction (step) proceeds through an *activated complex* or *transition state* which is proposed to explain the kinetics. In addition two factors allow us to understand the actual rates observed:

0. The number of collisions with energy greater than the necessary threshold:

$$\text{Number of collisions with the necessary minimum energy} = z \cdot \exp(-E_a/RT)$$

1. The fraction of the number of collisions (*p*) where the orientation of the colliding molecules is correct. This will depend on the reaction step. In some cases the stereochemistry is very demanding and in others not so demanding, but the rate will always be somewhat lower than the total number of collisions with adequate energy. See Figure 12.12 for appropriate and inappropriate orientations for reaction.



**FIGURE 12.12**  
Plot showing the number of collisions with a particular energy at  $T_1$  and  $T_2$ , where  $T_2 > T_1$ .

The rate constant is given by:

$$k = z.p.\exp(-E_a/RT) = A.\exp(-E_a/RT)$$

where  $A$  is the *frequency factor* replacing the product of the *steric factor* ( $p$ ) and the *collision frequency* ( $z$ ). This equation is called the *Arrhenius equation*. Taking logs of both sides gives:

$$\ln(k) = -(E_a/R)(1/T) + \ln(A)$$

With a couple of data points it is already possible to extract the activation energy:

$$\ln(k_2) - \ln(k_1) = [-(E_a/R)(1/T_2) + \ln(A)] - [-(E_a/R)(1/T_1) + \ln(A)]$$

$$\ln(k_2/k_1) = E_a/R(1/T_1 - 1/T_2)$$

### Exercise 12.8

Data for the reaction:



At  $550^\circ\text{C}$  ( $T_1$ )  $k_1 = 1.1 \text{ L/mol/s}$  and at  $625^\circ\text{C}$  ( $T_2$ )  $k_2 = 6.4 \text{ L/mol/s}$ . Calculate  $E_a$ .

$$\ln(6.4/1.1) = E_a/8.3145 \text{ J/K/mol} \times (1/823 \text{ K} - 1/898 \text{ K})$$

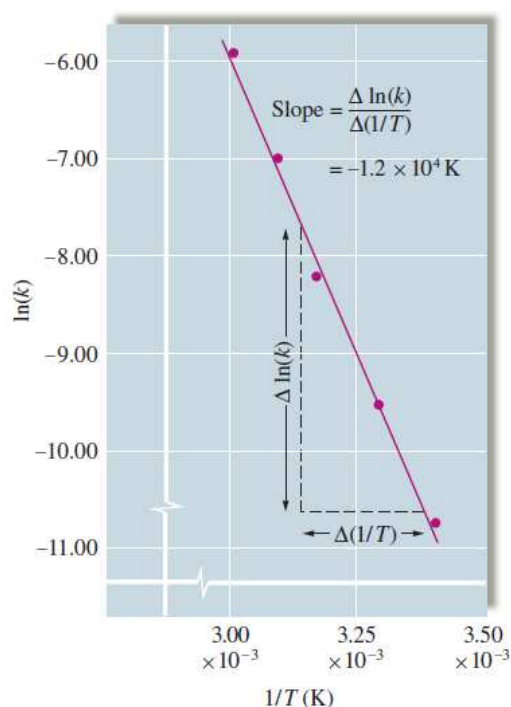
$$E_a = 1.4 \times 10^2 \text{ kJ/mol}$$

Normally a plot of  $\ln(k)$  vs  $1/T$ , called an *Arrhenius plot* with  $-(E_a/R)$  as its slope would be used for a more extended set of data.

## Exercise 12.7

$T$ (°C)	$T$ (K)	$1/T$ (K)	$k$ (s <sup>-1</sup> )	$\ln(k)$
20	293	$3.41 \times 10^{-3}$	$2.0 \times 10^{-5}$	-10.82
30	303	$3.30 \times 10^{-3}$	$7.3 \times 10^{-5}$	-9.53
40	313	$3.19 \times 10^{-3}$	$2.7 \times 10^{-4}$	-8.22
50	323	$3.10 \times 10^{-3}$	$9.1 \times 10^{-4}$	-7.00
60	333	$3.00 \times 10^{-3}$	$2.9 \times 10^{-3}$	-5.84

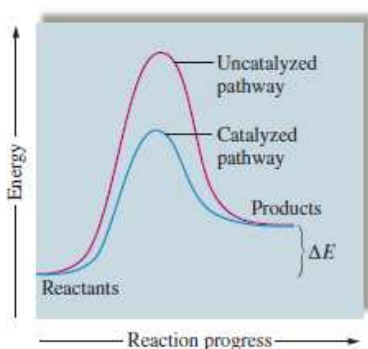
Figure 12.14 shows the plot. The slope is  $-1.2 \times 10^4$  K and the value of  $E_a$  is  $-\text{slope} \times R = 1.0 \times 10^3$  kJ/mol.



**FIGURE 12.14**

Plot of  $\ln(k)$  versus  $1/T$  for the reaction  $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ . The value of the activation energy for this reaction can be obtained from the slope of the line, which equals  $-E_a/R$ .

## 6. Catalysis



**FIGURE 12.15**

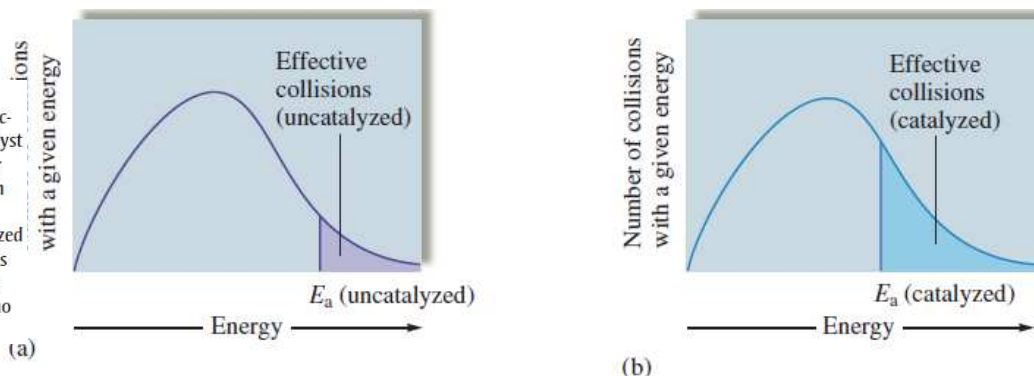
Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction.

We can make reactions go faster by working a higher temperatures, but this is very energy-expensive. Biological systems overcome this cost with catalysts called enzymes. In industry, almost all processes involve catalysts which can help reactions go at lower temperatures and even favour certain reaction over other less desirable ones.

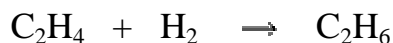
Figures 12.15 and 12.16 illustrate the the effect of catalysis in thermodynamic terms.

**FIGURE 12.16**

Effect of a catalyst on the number of reaction-producing collisions. Because a catalyst provides a reaction pathway with a lower activation energy, a much greater fraction of the collisions is effective for the catalyzed pathway (b) than for the uncatalyzed pathway (a) (at a given temperature). This allows reactants to become products at a much higher rate, even though there is no temperature increase.



◇ **Example:** Hydrogenation of ethylene on nickel, palladium or platinum:



There are three steps (Figure 12.17):

1-Adsorption and activation of the reactants.

2-Migration of the adsorbed species.

3-Reaction of the activated reactants and desorption of the product.

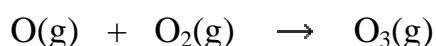
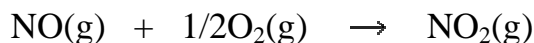
This particular reaction is not a major industrial process, but the hydrogenation of unsaturated oils to make solid fats (margarine for example is).

**Example:** Oxidation of sulphur dioxide to sulphur trioxide. This process is catalysed fortuitously and undesirably by water and dust particles in the air (smog). The reaction is performed deliberately in the contact process with vanadium pentoxide for the manufacture of sulphuric acid.

**Example:** Catalytic converters on cars convert  $\text{CO}$  to  $\text{CO}_2$ ,  $\text{NO}_x$  to  $\text{N}_2$  and hydrocarbons to  $\text{CO}_2$ . Unfortunately they also convert  $\text{SO}_2$  to  $\text{SO}_3$  so sulphur must not be present in fuel. Several catalysts are used and they are subject to gradual degradation (poisoning) notably by lead.

## Homogeneous Catalysis

**Example:** Nitric oxide catalysis of ozone production in the lower atmosphere (troposphere). The reaction of  $\text{N}_2$  with  $\text{O}_2$  at high temperature and pressure in internal combustion engines produces  $\text{NO}$ . The compound can participate in a chain reaction leading to  $\text{O}_3$  production:



At levels near the ground this is really bad because ozone is a very toxic and irritant substance, and can oxidize other things. Note that by adding the equations the net result is:

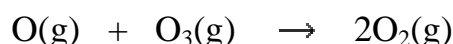


Thus  $\text{NO}$  is a true catalyst.

Conversely, in the stratosphere, where there are plenty of oxygen atoms, the  $\text{NO}$  catalyses the decomposition of  $\text{O}_3$ :



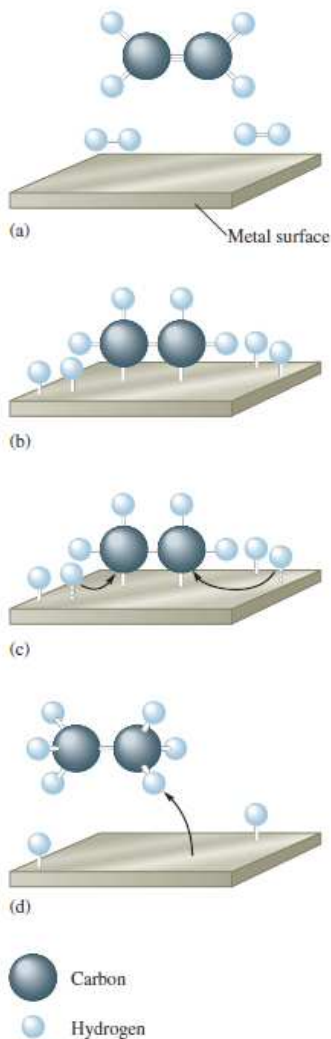
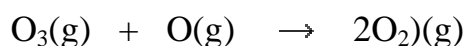
The net result is:



**Example:** The action of freons is another catalytic process:



The net reaction from the catalytic cycle (the above *two* steps) is:



**FIGURE 12.17**

Heterogeneous catalysis of the hydrogenation of ethylene. (a) The reactants above the metal surface. (b) Hydrogen is adsorbed onto the metal surface, forming metal-hydrogen bonds and breaking the  $\text{H}-\text{H}$  bonds. The  $\pi$  bond in ethylene is broken and metal-carbon bonds are formed during adsorption. (c) The adsorbed molecules and atoms migrate toward each other on the metal surface, forming new  $\text{C}-\text{H}$  bonds. (d) The  $\text{C}$  atoms in ethane ( $\text{C}_2\text{H}_6$ ) have completely saturated bonding capacities and so cannot bind strongly to the metal surfaces. The  $\text{C}_2\text{H}_6$  molecule thus escapes.

**Final Example:** The "oxo" process. The hydroformylation of  $C_2H_4$  by  $H_2$  and  $CO$  to give  $CH_3CH_2CHO$  is catalysed by  $HCo(CO)_3$  in solution:

