

CHEMICAL KINETICS

TOPIC 14

Chemical kinetics begins a series of topics spanning the next six chapters ending with electrochemistry, that comprises the heart and soul of what is expected for students to know for the AP examination. A thorough knowledge of these topics and their interrelationships is essential. Often students are asked to determine a rate law and its units from tabular data, use it to calculate rates and concentrations under specified conditions, and match a suitable mechanism to a rate law. Content in all sections should be mastered.

Reaction Rates

Section 14.1

Reaction rate is a measure of the speed of a chemical reaction. Rate of reaction is expressed as the change in the amount of reactants or products per unit time. Most often the unit for reaction rate is molarity per second (M/s).

Concentrations of reactants and products change with time and so does rate. Consider a simple chemical reaction where $A \rightarrow B$. Figure 14.1a illustrates how the molar concentration of A changes with time. As time increases the concentration of A decreases. The slope of the tangent line at any point $(t, [A])$ represents the instantaneous rate of the reaction. The rate is:

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

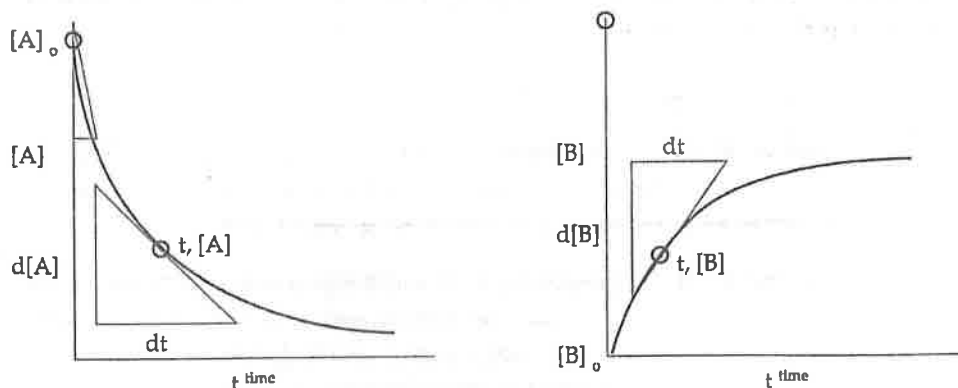


Figure 14.1. Graph of a typical reaction $A \rightarrow B$ showing how $[A]$ decreases with time and how $[B]$ increases with time.



Common Misconception: Molarity per second is often expressed as $\text{mol L}^{-1} \cdot \text{s}^{-1}$.

$$\text{M/s} = \text{Mol/L} \cdot \text{s} = \text{Mol L}^{-1} \cdot \text{s}^{-1}.$$

Reaction rate can also be expressed in pressure units per time (atm/s or torr/s) or sometimes in absorbance units per time. (For more on how absorbance can be used to monitor the changing concentration of a reactant or product, see A Closer Look: Using Spectroscopic methods to Measure Reaction Rates in Section 14.2.)

Rates are always expressed as positive quantities. Because the slope in the graph in Figure 14.1a is negative, a negative sign is used to express rate as a positive quantity. A typical reaction rate starts out fast and becomes slower as time goes on. The initial rate at time = 0, is always the largest rate.

Figure 14.1b illustrates how [B] changes with time. As time increases, the concentration of B increases. The slope of the tangent line at any point (t, [B]) represents the instantaneous rate of the reaction. The rate is:

$$\text{Rate} = +\Delta[\text{B}]/\Delta t$$

Notice that the slope of the line is positive, so a positive sign in the expression denotes a positive rate.

Section 14.2

Factors that Affect Reaction Rates

On a molecular level, reaction rates depend on the frequency of collisions between molecules and the energy with which the molecules collide. Rate of reaction increases with greater frequency of collisions, and/or greater energy with which the collisions occur.

The major factors that affect reaction rate are:

1. **Concentrations of reactants.** Higher concentrations of reactants produce a faster reaction. As concentration increases, the frequency of collisions increases, thus increasing reaction rate.
2. **Temperature.** Increasing temperature increases reaction rate. Higher temperatures provide increased kinetic energies of molecules so the molecules move more rapidly. Faster moving molecules produce more frequent and higher energy collisions. Additionally, at higher

temperatures, there is a greater fraction of collisions resulting in a reaction.

- Physical state of the reactants.** In general, homogeneous mixtures of either liquids or gases react faster than heterogeneous mixtures. A solid, for example, tends to react more slowly with either a liquid or a gas because molecular collisions are limited to the surface area of the solid. Increasing the surface area will increase the frequency of collisions, and thus increase the rate of reaction.
- The presence of a catalyst.** A catalyst increases the rate of reaction by affecting the kinds of collisions that lead to a reaction. A catalyst acts by changing the mechanism of the reaction. A reaction mechanism, to be discussed in more detail later, is a step-by-step process by which reactants become products.

Mine explosions from the ignition of powdered coal dust are relatively common, yet lumps of coal burn without exploding. Explain.

Write your answer in the space provided.

Your Turn 14.1

Concentration and Rate

Section 14.3

A rate law is a mathematical relationship that shows how rate of reaction depends on the concentrations of reactants. For any general reaction where:



the rate law takes the form:

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

k is the rate constant, $[A]$ is the molar concentration of reactant A, $[B]$ is the molar concentration of reactant B, and the exponents m and n are usually small, whole numbers that relate to the number of molecules of A and B that collide in the step-by-step mechanism.



Common misconception: The coefficients that balance the equation, a and b, are not the same as the exponents, m and n, in the rate law.

Reaction order is the sum of the exponents m and n in a rate law. For example, consider the rate law:

$$\text{Rate} = k[\text{A}]^1[\text{B}]^2$$

The reaction is said to be "first order in A" and "second order in B." The sum of $m + n$ is the overall order of the reaction. In this example, $1 + 2 = 3$, so the reaction is "third order" overall.

The rate law for any chemical reaction must be determined experimentally, often by observing the effect of changing the initial concentrations of the reactants on the initial rate of the reaction.

Consider the reaction



The rate law always takes the form:

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

A series of experiments measuring initial rate at various concentrations of reactants might give the data in Table 14.1.

Experiments 1 and 2 show that the rate is doubled when [B] is doubled. This means that the exponent of [B] is 1. ($2^1 = 2$ so $n = 1$.)

Experiments 2 and 3 show that the rate is quadrupled when [A] is doubled. This means that the exponent of [A] is 2. ($2^2 = 4$ so $m = 2$.) The data in Table 14.1 show that the rate law is:

$$\text{Rate} = k[\text{A}]^2[\text{B}]^1$$

Table 14.1. The effect of changing concentrations on the initial rate of a reaction

Experiment	[A] (M)	[B] (M)	Rate = $-\text{d}[\text{A}]/\text{d}t$ (M/s)
1	0.10	0.10	0.04
2	0.10	0.20	0.08
3	0.20	0.20	0.32

The reaction is second order in A, first order in B, and third order overall.

The data in Table 14.1 can be used to calculate the value of the rate constant.

Example:

What is the numerical value of the rate constant for the reaction described in Table 14.1? Specify its units.

Solution:

$$\text{Rate} = k[A]^2[B]^1$$

$$0.04 \text{ M/s} = k[0.1 \text{ M}]^2[0.1 \text{ M}]^1$$

$$k = (0.04 \text{ M/s}) / (0.01 \text{ M}^2 \times 0.1 \text{ M})$$

$$= 40 \text{ 1/M}^2\text{s}$$

What are the units for each rate constant for the following rate laws? Assume each rate is expressed in M/s. a. rate = $k[A]$; b. rate = $k[A]^2$; c. rate = $k[A]^3$.

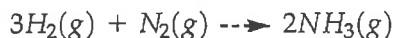
Your Turn 14.2

Write your answers in the space provided.

The coefficients that balance a chemical equation are proportional to the rates of appearance or disappearance of reactants and products. Reaction rate relates directly to stoichiometry.

Example:

Consider the reaction between gaseous hydrogen and gaseous nitrogen to produce ammonia gas.



At a particular time during the reaction $\text{H}_2(\text{g})$ disappears at the rate of 3.0 M/s.

- What is the rate of disappearance of $\text{N}_2(\text{g})$?
- What is the rate of appearance of $\text{NH}_3(\text{g})$?

Solution:

a. In the balanced equation, $N_2(g)$ has a coefficient of 1 whereas $H_2(g)$ has a coefficient of 3. $N_2(g)$ disappears at one-third the rate of $H_2(g)$.

$$1/3(3.0 \text{ M/s}) = 1.0 \text{ M/s.}$$

b. $NH_3(g)$ appears at two-thirds the rate of $H_2(g)$.

$$2/3(3.0 \text{ M/s}) = 2.0 \text{ M/s.}$$

Your Turn 14.3

If ammonia appears at 2.6 M/s, how fast does hydrogen disappear? Place your answer in the space provided.

In terms of mathematics, the following equation applies to the reaction:

$$-\Delta H_2(g)/\Delta t = -3 \Delta N_2(g)/\Delta t = +3/2 \Delta NH_3(g)/\Delta t$$

Notice the use and placement of signs and the coefficients that balance the chemical equation. If they seem counter intuitive, translate the mathematical expression into words: "The disappearance of hydrogen gas is three times the rate of the disappearance of nitrogen gas and three-halves the rate of appearance of ammonia gas."

The application of stoichiometry to the data in Table 14.1 can be used to calculate various rates.

Example:

From the data for Experiment 1 in Table 14.1, calculate the rate of appearance of C.

Solution:

The initial rate of disappearance of A in Experiment 1 is 0.04 M/s. The balanced equation shows that C has a coefficient twice that of A so the rate of appearance of C is twice that of A.

$$+\Delta C/\Delta t = -2\Delta A/\Delta t = 2(0.04 \text{ M/s}) = 0.08 \text{ M/s.}$$

The Change of Concentration with Time

Section 14.4

A first-order reaction is a reaction whose rate depends on the concentration of a single reactant raised to the first power. The rate is expressed in terms of the rate law and the slope of the tangent line at any point $t, [A]$ on the graph in Figure 14.1a.

$$\text{Rate} = k[A] = -\Delta[A]/\Delta t \quad \text{differential rate law}$$

Using calculus, this equation is transformed into the equation of the curved line in Figure 14.2a. The equation of the line is

$$\ln[A]_t = -kt + \ln[A]_0 \quad \text{integrated rate law}$$

Notice that the equation is in the form of the simple linear equation, $y = mx + b$ where $y = \ln[A]_t$, $b = \ln[A]_0$, and the slope of the line $= -k$, the rate constant.

For a **first-order reaction** a plot of $\ln[A]$ vs. time will yield a straight line with a slope of $-k$ as shown in Figure 14.2b. This is a useful graphical method for determining rate constants for first-order reactions.

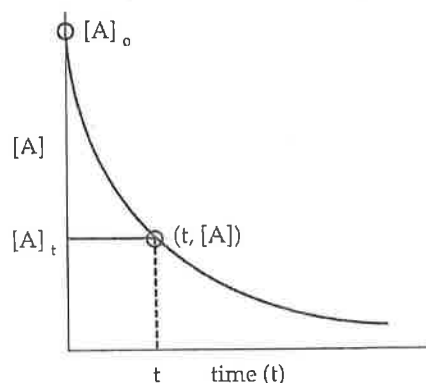


Figure 14.2a. Plot of $[A]$ vs. time for a first-order reaction.

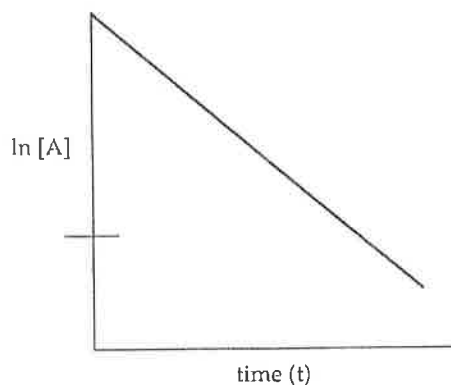


Figure 14.2b. Plot of $\ln[A]$ vs. time for a first-order reaction. The negative slope of the line equals the rate constant.

Often the equation of the line for a first-order reaction is written in the more familiar expression:

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

A simple **second-order reaction** is one whose rate depends on the concentration of the reactant raised to the second power.

The characteristic equations are:

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

and

$$1/[A]_t = kt + 1/[A]_0 \quad \text{integrated rate law}$$

Note that the integrated rate law is a linear equation of the form

$$y = mx + b$$

A plot of $1/[A]$ vs. time will yield a straight line whose slope is the rate constant k as shown in Figure 14.3b.

The **half-life** of a reaction, $t_{1/2}$, is the time required for the initial concentration of a reactant to fall to half its value.

For a first-order reaction: $t_{1/2} = 0.693/k$

For a second-order reaction: $t_{1/2} = 1/k[A]_0$

Table 14.2 summarizes the mathematical relationships of first and second-order reactions.

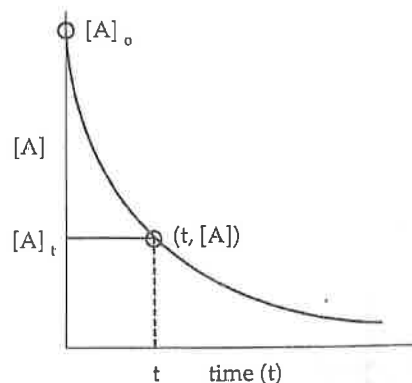


Figure 14.3a. Plot of $[A]$ vs. time for a second-order reaction.

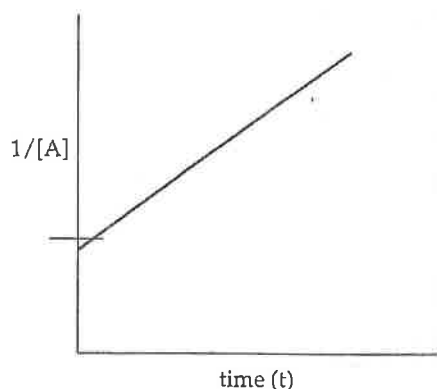


Figure 14.3b. Plot of $1/[A]$ vs. time for a second-order reaction. The slope of the line = the rate constant.

Table 14.2. Mathematical relationships of simple first- and second-order kinetics

Order or Reaction	First	Second
Differential rate law	Rate = $k[A] = -\Delta[A]/\Delta t$	Rate = $k[A]^2 = -\Delta[A]/\Delta t$
Integrated rate law	$\ln[A]_t = -kt + \ln[A]_0$ or $\ln([A]_0/[A]_t) = +kt$	$1/[A]_t = kt + 1/[A]_0$
Half-life	$t_{1/2} = 0.693/k$	$t_{1/2} = 1/k[A]_0$
Straight line plot	$\ln[A]$ vs. time	$1/[A]$ vs. time
Slope =	$-k$	k

Temperature and Rate

Section 14.5

Generally, increasing temperature increases reaction rate. The collision model, based on kinetic molecular theory, says that molecules must collide in order to react. Temperature increases the speed of molecules, and as molecules move faster they collide more frequently and with more energy, increasing reaction rates.

Figure 14.4 shows how the rate constant for a chemical reaction varies with temperature. Generally the rate constant increases with increasing temperature.

The algebraic equation that describes the line in Figure 14.3 relates activation energy, E_a , to the rate constant, k , at various temperatures, T .

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

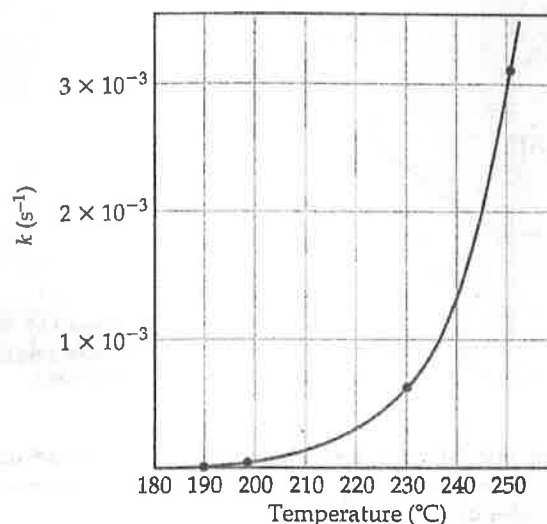


Figure 14.4. The rate constant, k , varies with temperature, T .

k_1 = the rate constant at temperature, T_1 . k_2 = the rate constant at temperature T_2 , and E_a is the activation energy. (All temperatures must be expressed in Kelvin.) $R = 8.314 \text{ J/K mol}$.

Activation energy, E_a , is the minimum amount of energy required to initiate a chemical reaction. Figure 14.5 shows the activation energy on the energy profile of a typical exothermic reaction. The activation energy can be considered to be an energy barrier that molecules must get over in order to react. On an energy profile, the activation energy is the energy difference between the reactants and the highest point of the profile.

The **activated complex** is the highest energy arrangement of molecules as they change from reactants to products. The very top of the energy profile represents the energy of the activated complex, also called the transition state.

A **catalyst** acts to lower the activation energy of a chemical reaction and thus increase the rate of reaction.

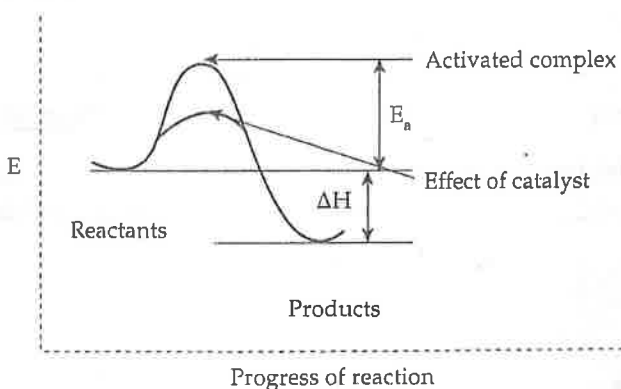


Figure 14.5. Energy profile for a typical exothermic reaction showing activation energy, E_a , change in enthalpy, ΔH , and the effect of a catalyst.

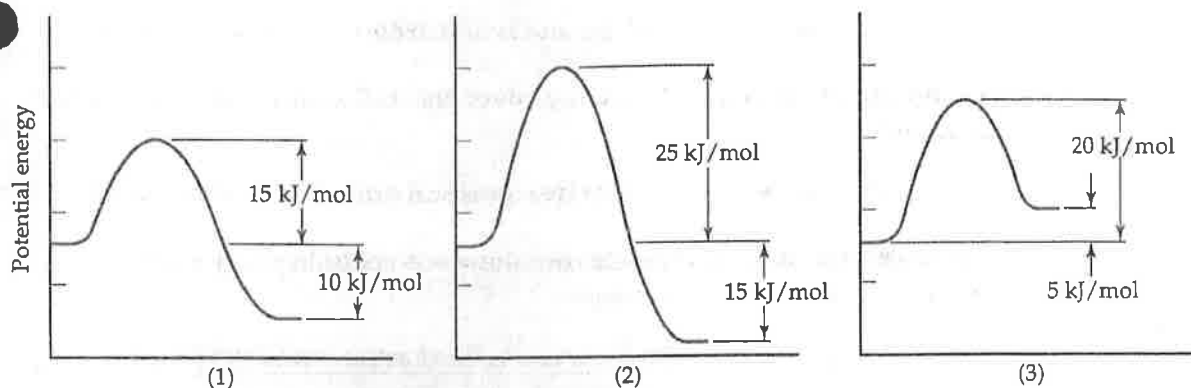


Figure 14.6. Energy profiles of two exothermic reactions and one endothermic reaction showing the activation energies. The higher the activation energy the higher the rate of reaction.

For any reaction, the higher the activation energy, the slower the rate. Very fast reactions have low activation energies and slow reactions have high activation energies. Figure 14.6 illustrates the relationship of activation energy to reaction rate. Profile 1 describes a reaction with the fastest rate, and the reaction for Profile 2 has the slowest rate.

Your Turn 14.4

Explain in terms of collision theory why temperature affects rate of reaction. Write your answer in the space provided.

Reaction Mechanisms

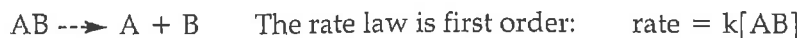
Section 14.6

A **reaction mechanism** is the step-by-step process by which a chemical reaction occurs.

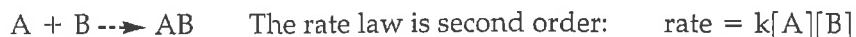
An **elementary step** is each single event or step in a mechanism.

The **molecularity** of a reaction is the number of molecules that participate as reactants in an elementary reaction.

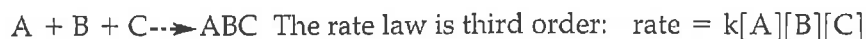
A **unimolecular** elementary reaction involves one reactant molecule.



A **bimolecular** elementary reaction involves the collision of two reactant molecules.

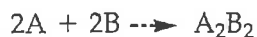


A **termolecular** reaction involves the simultaneous collision of three reactant molecules (rare but not impossible).



Commonly reactions occur in multi-step mechanisms. Each individual step is an elementary reaction and the sum of the individual steps gives the balanced chemical equation for the overall process. Usually we write each elementary step in a mechanism to be a unimolecular or bimolecular process because termolecular processes are rare.

Consider the following overall process:



A possible mechanism that can explain how reactants A and B become the product A_2B_2 is:

Elementary step	rate law for each elementary step
1. $A + A \rightarrow A_2$	$\text{rate} = k[A]^2$
2. $A_2 + B \rightarrow A_2B$	$\text{rate} = k[A_2][B]$
3. $A_2B + B \rightarrow A_2B_2$	$\text{rate} = k[A_2B][B]$
$\underline{2A + 2B \rightarrow A_2B_2}$	

Notice that the sum of the elementary steps of a mechanism gives the chemical equation for the overall process.

An **intermediate** is a chemical species that is formed in one elementary step of a multi-step mechanism and consumed in another. In the above mechanism, A_2 and A_2B are intermediates. An intermediate is never a reactant or product of the overall reaction. Intermediates never appear in the rate law for the overall reaction.

The **rate determining step** is the slowest step of a multi-step mechanism and governs the rate of the overall reaction.

The slowest step in a multi-step mechanism is reflected in the rate law. The rate law includes only those reactant molecules which react during and before the rate determining step. Therefore, the rate law must be determined experimentally and cannot be determined from the overall balanced equation.

For example, if Step 1 in the above mechanism is the slowest step, the rate law is $\text{rate} = k[\text{A}]^2$ because two molecules of A have taken part in the mechanism up to this step.

If Step 2 is slowest, the rate law will be $\text{rate} = k[\text{A}]^2[\text{B}]$ because two molecules of A and one molecule of B have taken part through Step 2 of the mechanism.

If Step 3 is slowest, the rate law will include two molecules of A and two molecules of B, because they all have taken part through Step 3 of the mechanism: $\text{rate} = k[\text{A}]^2[\text{B}]^2$.

Propose an alternate mechanism for the overall reaction: $2\text{A} + 2\text{B} \rightarrow \text{A}_2\text{B}_2$.
Write your answer in the space provided.

→ Your Turn 14.5

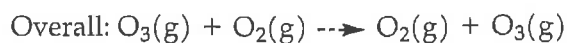
Catalysis

Section 14.7

A **catalyst** is a substance that increases the rate of a chemical reaction without undergoing a permanent change in the process. Catalysts act by changing the mechanism of a reaction so that the slowest step in the uncatalyzed reaction does not exist in the catalyzed process. The effect of a catalyst is to lower the activation energy of the overall process by replacing the slowest step with one or more faster steps having an activation energy lower than that of the uncatalyzed rate-determining step.

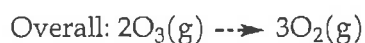
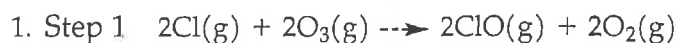
To illustrate the action of a catalyst consider the ozone cycle, the process that cycles diatomic oxygen to ozone and back to diatomic oxygen in the upper atmosphere. In its simplest form, the mechanism might look something like this:

1. Step 1 $\text{O}_2(\text{g}) + h\nu \rightarrow \text{O}(\text{g}) + \text{O}(\text{g})$
2. Step 2 $\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$
3. Step 3 $\text{O}_3(\text{g}) + h\nu \rightarrow \text{O}_2(\text{g}) + \text{O}(\text{g})$
4. Step 4 $\text{O}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{O}_2$



(Steps 1 through 4 continually repeat, producing and destroying ozone at the same rate while absorbing harmful ultraviolet radiation ($h\nu$) from the sun.)

It has been shown that chlorine atoms coming from chlorofluorocarbons released to the atmosphere catalyze the $\text{O}_3 \rightarrow \text{O}_2$ reaction. The net result is that ozone is depleted faster than it is generated by the natural cycle. Thus, chlorine atoms from chlorofluorocarbons catalytically deplete ozone in the stratosphere. In its simplest form the mechanism that catalyzes O_3 to O_2 is:



Notice that $\text{ClO}(\text{g})$ is an intermediate. $\text{ClO}(\text{g})$ is generated as a product in one elementary step and is consumed as a reactant in another later elementary step.

By contrast, Cl is a catalyst. It is consumed as a reactant in one elementary step, and is re-generated as a product in a later step. A catalyst increases the rate of a chemical reaction without undergoing a permanent change. A catalyst acts by providing a different mechanism for the reaction, one that has a lower activation energy.

(For more detailed information about the natural ozone cycle and its catalytic depletion by chlorofluorocarbons, see Section 18.3 of Chemistry the Central Science.)

Multiple Choice Questions

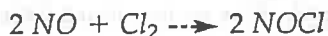
- Which of these change with time for a first-order reaction?
 - rate of reaction
 - rate constant
 - half-life
 - concentration of reactant
 - I only
 - III only
 - I and II only
 - II and III only
 - I and IV only
- Under certain conditions, the average rate of appearance of oxygen gas in the reaction:
$$2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$$
is 6.0 torr s^{-1} . What is the average rate expressed in units of torr s^{-1} for the disappearance of O_3 ?
 - 9.0
 - 6.0
 - 4.0
 - 3.0
 - 1.2
- For irreversible chemical reactions, the rate will be affected by changes in all of these factors except:
 - temperature.
 - concentration of reactants.
 - presence of a catalyst.
 - concentration of products.
 - surface area of solid reactant.
- The rate expression for a third-order reaction could be:
 - $\text{rate} = k[\text{X}]$
 - $\text{rate} = k[\text{X}]^2[\text{Y}]$
 - $\text{rate} = k[\text{X}][\text{Y}]$
 - $\text{rate} = k[\text{X}]^2[\text{Y}]^2$
 - $\text{rate} = k[\text{X}]^2$

5. The slowest step of a reaction mechanism is called the:
- A) elementary step.
 - B) inhibitor.
 - C) rate law.
 - D) rate-determining step.
 - E) catalyst.
6. The dissociation of XY molecules, as shown below, occurs at a temperature of 800 K. The rate constant, $k = 6.0 \times 10^{-3} \text{ s}^{-1}$.
- $$2\text{XY}(\text{g}) \rightleftharpoons \text{X}_2(\text{g}) + \text{Y}_2(\text{g})$$
- What is the reaction order?
- A) 0
 - B) 1
 - C) 2
 - D) 3
 - E) 4
7. The rate law of a certain reaction is $\text{rate} = k[\text{X}][\text{Y}]$. The units of k , with time measured in seconds, is:
- A) s^{-1}
 - B) $\text{M}^{-1}\text{s}^{-2}$
 - C) $\text{M}^{-2}\text{s}^{-1}$
 - D) M^{-1}
 - E) $\text{M}^{-1}\text{s}^{-1}$
8. For a first-order reaction of half-life 75 min, what is the rate constant in min^{-1} ?
- A) $(0.693)/75$
 - B) $(0.693)/1.25$
 - C) $(0.693)(75)$
 - D) $75/(0.693)$
 - E) 0.693
9. The half-life of ^{14}C is 5730 years. Approximately how many years will it take for 94% of a sample to decay?
- A) 5730
 - B) 2×5730

- C) 3×5730
 D) 4×5730
 E) 5×5730
10. A reaction between X_2 and Y was found to be described by the rate equation $\text{rate} = k[X_2][Y]^2$. What can be said about the process?
- A) The balanced chemical equation for the reaction is $X_2 + 2Y \rightarrow X_2Y_2$.
 B) The rate-determining step must be a three-atom collision.
 C) The rate-determining step must be the first step of a multi-step mechanism.
 D) The mechanism is most likely to be multi-step.
 E) The mechanism must consist of just one elementary step.

Free Response Questions

1. The overall chemical equation for the reaction of nitrogen oxide, NO , with chlorine, Cl_2 , is:



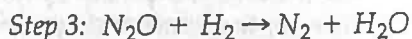
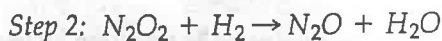
The initial rates of reaction for various concentrations of the reactants were measured and recorded at constant temperature as follows:

Experiment	$[\text{NO}](\text{M})$	$[\text{Cl}_2](\text{M})$	$-\Delta[\text{Cl}_2]/\Delta t (\text{M/hr})$
1	0.25	0.50	0.75
2	0.25	1.00	3.02
3	0.50	2.00	24.10

- a. Determine the rate law for this reaction.
 b. Calculate the numerical value for the rate constant and specify the units.
 c. What is the order of this reaction with respect to each reactant and what is the overall order of the reaction?
 d. What is the rate of disappearance of Cl_2 when the initial concentrations of the reactants are: $[\text{NO}] = 0.50 \text{ M}$ and $[\text{Cl}_2] = 0.10 \text{ M}$?
 e. When Cl_2 is disappearing at 4.5 M/hr , what is the rate of appearance of NOCl ?
 f. What is the rate of appearance of NOCl when the initial concentrations of the reactants are: $[\text{NO}] = 0.20 \text{ M}$ and $[\text{Cl}_2] = 0.30 \text{ M}$?

No calculators are permitted for Question 2.

2. Consider the proposed mechanism for the reaction between nitrogen monoxide and hydrogen gas. Assume the mechanism is correct.



- Use the steps in the mechanism to determine the overall balanced equation for the reaction. Clearly show your method.
- If Step 2 is the rate-determining step, write the rate law for the reaction. Explain your answer.
- If the observed rate law is $\text{rate} = k[\text{NO}]^2[\text{H}_2]^2$, which step is rate determining? Explain your reasoning.
- Identify all the intermediates in the mechanism.
- If the first step is the rate-determining step, what is the order of the reaction with respect to each reactant?

Additional Practice in Chemistry: The Central Science

For more practice working kinetics problems in preparation for the Advanced Placement examination, try these problems in Chapter 14 of Chemistry: The Central Science:

Additional Exercises: 14.84, 14.85, 14.86, 14.91, 14.93, 14.95, 14.97, 14.99.

Integrated Exercises: 14.104, 14.106, 14.108, 14.110, 14.111.

Multiple Choice Answers and Explanations

- E. Rate decreases with time because the concentrations of reactants decrease. The half-life of a first-order reaction remains constant as does the rate constant at constant temperature.
- C. Relative rates of disappearance of reactants and appearance of products are proportional to the stoichiometry of the reactants. Using the coefficients of the balanced equation, O_2 appears $3/2$ as fast as O_3 disappears. Thus, the rate at which O_3 disappears $= 2/3 \times 6.0 \text{ torr s}^{-1} = 4.0 \text{ torr s}^{-1}$.
- D. The frequency of collisions of reactant molecules largely determines reaction rate. Any factor that changes the frequency of collisions will affect the rate. Concentrations of products of an irreversible reaction do not affect the rate of a reaction because collisions of product molecules

- do not aid the forward reaction. Changing temperature, reactant concentrations, and the surface area of a solid reactant all change the frequency of collisions. A catalyst increases the rate of reaction by changing the reaction mechanism, eliminating the slowest step, and lowering the activation energy of the overall process.
- B. The overall order of a reaction is the sum of the exponents of the rate law.
 - D. An elementary step is each individual step in a mechanism. The rate law is a mathematical equation that relates rate to concentrations of reactants. A catalyst is a substance that increases the speed of a chemical reaction by changing the mechanism. An inhibitor is a substance that decreases the rate of a chemical reaction.
 - B. The units of the rate constant conveniently reveal the order of the reaction. The rate constant for a first-order reaction contains one unit, reciprocal time, s^{-1} . Second-order rate constants contain two units: $M^{-1}s^{-1}$. Third order contain three: $M^{-2}s^{-1}$ and so fourth. Notice that if units of a third-order reaction are given as $L^2 \text{ mol}^{-2} s^{-1}$ this relationship is often obscured. Be sure to change $L^2 \cdot \text{mol}^{-2} \cdot s^{-1}$ to the more familiar $M^{-2}s^{-1}$.
 - E. The sum of the exponents of the rate law is 2, so this is a second-order reaction. Second-order reactions are typified by one concentration unit and one time unit for a total of two units. (See the explanation to Question 6.)
 - A. The equation for the half-life of a first-order reaction is $t_{1/2} = 0.693/k$. Substituting, $75 \text{ min} = 0.693/k$ or $k = (0.693)/(75) \text{ min}^{-1}$.
 - D. Half-life is the time it takes for the amount of a reactant to lose half its value. One half-life would leave 50% of the original amount, two half-lives, 25%, 3 would leave 12.5%, and 4 would leave 6.25%. 6.25% left means that about 94% has been consumed in four half-lives. The total time elapsed is approximately 4×5730 years.
 - D. The rate equation does not necessarily relate to the balanced chemical equation in a multi-step mechanism, nor does it suggest the nature of the products. Three-atom collisions are highly unlikely so a single elementary step is not highly probable; thus while the rate determining step can be a three-atom collision, it is not required. The best that can be said is that the mechanism takes place in two or more steps, and the first step is not the rate-determining step.

Answers to Free Response Questions

1. a. The rate law will always take the form: $\text{Rate} = k[\text{Reactant 1}]^n [\text{Reactant 2}]^m$ where, in this case, Reactant 1 is NO, and Reactant 2 is Cl_2 . The object is to use the data in the given table to determine the exponents, n and m .

Experiments 1 and 2 show that the rate quadruples (apparently within experimental error) when $[\text{Cl}_2]$ doubles while $[\text{NO}]$ remains constant. Replacing Cl_2 with 2, and the rate with 4, while ignoring the remainder of the equation because nothing else changes, we get $4 = 2^n$. So $n = 2$.

Experiments 2 and 3 show that the rate increases by a factor of eight when both $[\text{NO}]$ and $[\text{Cl}_2]$ double. Replacing Cl_2 with 2, NO with 2, and the rate with 8, while ignoring the rest because nothing else changes, we get $8 = 2^m \times 2^2$. So $m = 1$.

The answer is: $\text{Rate} = k[\text{NO}]^1 [\text{Cl}_2]^2$

- b. Substitute the data from Experiment 1 (You can use any of the three experiments!) into the rate law and solve for k .

$$\text{Rate} = k[\text{NO}]^1 [\text{Cl}_2]^2$$

$$0.75 \text{ M/hr} = k(0.25 \text{ M})(0.50 \text{ M})^2$$

$$k = 0.75 \text{ M/hr} / (0.25 \text{ M})(0.25 \text{ M}^2)$$

$$k = 12/\text{M}^2 \text{ hr} = 12 \text{ L}^2 \text{ mol}^{-2} \text{ hr}^{-1}$$

- c. The order with respect to each reactant is the exponent of that reactant, and the overall order is the sum of the exponents.

The reaction is: first order in NO, second order in Cl_2 , and third order overall. (Notice that the units for the rate constant, k , are consistent with a third-order overall reaction. That is, they contain two units of M, and one unit of time, or a total of three units for a third-order reaction.)

- d. Substitute the given values and the calculated rate constant (with all units!) into the rate law and solve for rate.

$$\text{Rate} = k[\text{NO}]^1 [\text{Cl}_2]^2$$

$$\text{Rate} = 12 \text{ L}^2/\text{M}^2 \text{ hr} (0.50 \text{ M})(0.10 \text{ M})^2$$

$$\text{Rate} = 12/\text{M}^2 \text{ hr} (0.50 \text{ M})(0.01 \text{ M}^2)$$

$$\text{Rate} = 0.060 \text{ M/hr}$$

- e. The rate of one reactant or product compared to the rate of another reactant or product is always proportional to the balanced overall equation for the reaction. The balanced equation shows that two moles of NOCl appear when one mole of Cl₂ disappears. So if the rate of disappearance of Cl₂ is 4.5 M/hr then the rate of appearance of NOCl is twice that or $2 \times 4.5 \text{ M/hr} = 9.0 \text{ M/hr}$.
- f. The table and the rate law are good only for the disappearance of Cl₂. Neither is valid for the appearance of NOCl. The best you can do is substitute the given data and the calculated rate constant into the rate law and solve for the rate of disappearance of Cl₂. Then multiply your answer by two to take into account that the rate of appearance of NOCl is twice the rate of disappearance of NOCl. (Notice how the solution to Part e gives you a clue to the solution to Part f! This is often the case in multi-step quantitative problems on the AP Chemistry examination.)

$$\text{Rate} = k[\text{NO}]^1 [\text{Cl}_2]^2$$

$$\text{Rate} = 12 \text{ l/M}^2 \text{ hr}(0.20 \text{ M})(0.30 \text{ M})^2$$

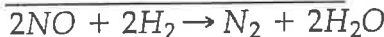
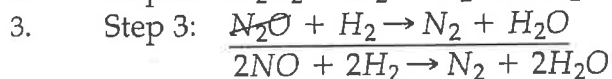
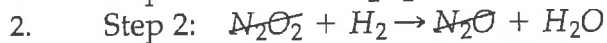
$$\text{Rate} = 12/\text{M}^2 \text{ hr}(0.20 \text{ M})(0.09 \text{ M}^2)$$

$$\text{Rate} = 0.22 \text{ M/hr}$$

This calculated rate is for the disappearance of Cl₂, because that's what the rate law calculates. To find the rate of appearance of NOCl, multiply by 2 to take into account the stoichiometry of the reaction!

$$0.22 \text{ M/hr} \times 2 = 0.44 \text{ M/hr}$$

2. a. To determine the overall reaction, add the individual steps and cancel the alike terms that appear on both sides of the equations:



- b. Through Step 2, two molecules of NO, and one molecule of H₂ have reacted, so if Step 2 is limiting, the rate law would be:

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

- c. The given rate law tells us that through the rate-determining step, two molecules of NO and two molecules of H₂ have reacted. This condition applies only if Step 3 is rate-determining.

- d. An intermediate is a substance that is produced in one elementary step and consumed in a later part. Notice that each strike-through in the solution to part a identifies an intermediate: N_2O_2 and N_2O .
- e. The order of the reaction with respect to an individual reactant is the exponent of that reactant in the rate law. If Step 1 is rate-determining, the rate law is: $\text{Rate} = k[\text{NO}]^2$. The reaction is second order in NO, and zero order in H_2 .

Your Turn Answers

14.1. The surface area of powdered coal is much greater than the surface area of lumps of coal, causing powdered coal to burn at a much more rapid rate than coal lumps. The small particle size of coal dust allows for more efficient mixing with gaseous oxygen from the air.

14.2. a. $\text{rate} = k[A]$, $k = s^{-1}$. b. $\text{rate} = k[A]^2$; $k = M^{-1}s^{-1}$. c. $\text{rate} = k[A]^3$; $k = M^{-2}s^{-1}$.

14.3. Hydrogen disappears $3/2$ as fast as ammonia appears.
 $3/2(2.6) = 3.9 \text{ M/s}$.

14.4. Increasing temperature increases the kinetic energy of atoms and molecules. The particles move faster and collide more often with greater energy resulting in more frequent collisions with sufficient energy for reaction.

14.5. 1. $B + B \rightarrow B_2$
 2. $B_2 + A \rightarrow AB_2$
 3. $AB_2 + A \rightarrow A_2B_2$

or

1. $A + B \rightarrow AB$
 2. $AB + AB \rightarrow A_2B_2$

or

1. $A + B \rightarrow AB$
 2. $AB + A \rightarrow A_2B$
 3. $A_2B + B \rightarrow A_2B_2$

Others are possible.