

10

BIG IDEA 4: KINETICS

Big Idea 4

Rates of chemical reactions are determined by details of the molecular collisions.

Chemical reactions occur at different rates. A reaction may happen in the blink of an eye or it may take millennia to reach equilibrium. There are many different factors that affect the rate of reactions and the rate can provide evidence for the mechanism of a reaction. Reaction rates can be increased by suitable catalysts, as well.

You should be able to

- Identify factors which affect reaction rates.
- Calculate the rate of production of a product or consumption of a reactant using mole ratios and the given rate.
- Determine the rate law for a reaction from given data, overall order, and value of the rate constant, inclusive of units.
- Determine the instantaneous rate of a reaction.
- Use integrated rate laws to determine concentrations at a certain time, t , and create graphs to determine the order of a reaction. Also, determine the half-life of a reaction.
- Explain how collision theory supports observations of reactions and reaction rates.
- Write the rate law from a given mechanism given the speeds of each elementary step.

- Write the overall reaction for a mechanism and identify catalysts and intermediates present.
- Explain how different kinds of catalysts change reaction rates.

AP Tip

Questions on kinetics may appear in the both the multiple-choice section and free-response section. You may be asked to analyze data, plan and implement an experiment, and construct an explanation based on evidence collected in an experiment.

REACTION RATES

(Chemistry 8th ed. pages 540–545/9th ed. pages 553–557)

The reaction rate is the change in the concentration of a reactant or product per unit time.

Consider the reaction, $A \rightarrow B$.

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

The concentration of A in moles per liter is represented by [A]. The change in time is represented by Δt . The quantity, $-\Delta[A]/\Delta t$, is negative because the reactant concentrations are decreasing as products are formed.

EXAMPLE: Consider the reaction $4 \text{PH}_3(g) \rightarrow \text{P}_4(g) + 6 \text{H}_2(g)$.

If 0.0048 mol of PH_3 is consumed in a 2.0-L container during each second of the reaction, what are the rates of production for P_4 and H_2 ?

SOLUTION: The rate at which PH_3 is being consumed is $-\frac{\Delta[\text{PH}_3]}{\Delta t}$.

$$0.0048 \text{ mol PH}_3 / (2.0 \text{ L} \times \text{s}) = 0.0024 \text{ mol L}^{-1} \text{ s}^{-1} \text{ PH}_3$$

The rate at which P_4 and H_2 are being produced can be determined by using mole ratios:

$$\frac{0.0024 \text{ mol PH}_3}{\text{L} \times \text{s}} \times \frac{1 \text{ mol P}_4}{4 \text{ mol PH}_3} = 0.00060 \text{ mol L}^{-1} \text{ s}^{-1} \text{ P}_4$$

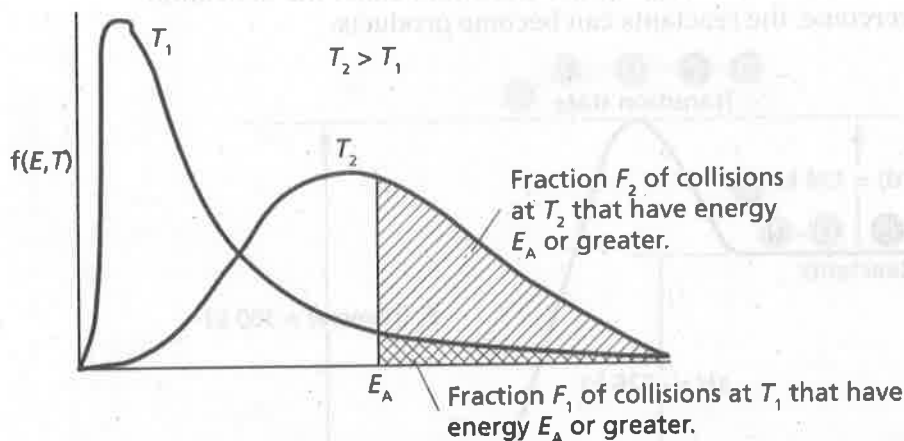
$$\frac{0.0024 \text{ mol PH}_3}{\text{L} \times \text{s}} \times \frac{6 \text{ mol H}_2}{4 \text{ mol PH}_3} = 0.0036 \text{ mol L}^{-1} \text{ s}^{-1} \text{ H}_2$$

COLLISION THEORY

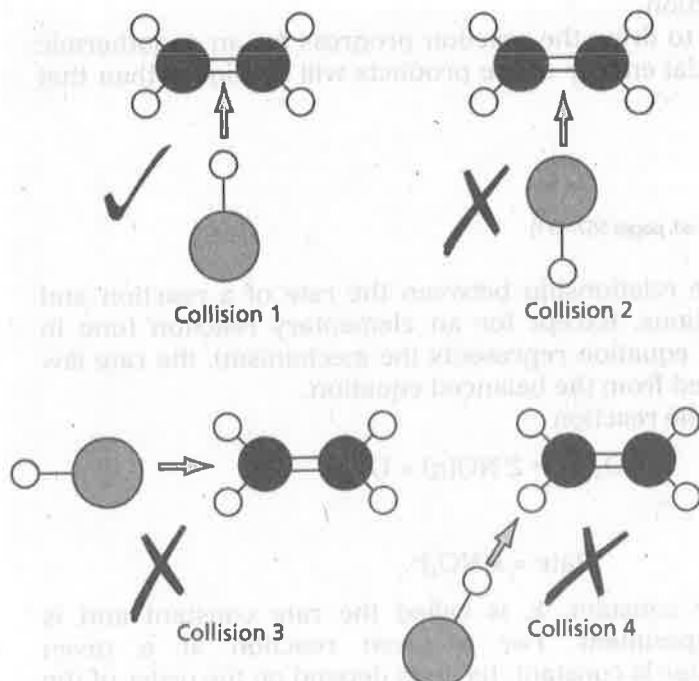
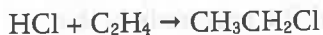
(Chemistry 8th ed. pages 565–566/9th ed. pages 577–578)

The collision theory model accounts for the observed characteristics of reaction rates. Molecules must collide in the correct orientation with sufficient energy, called the *activation energy*, for a reaction to occur. In most reactions only a small fraction of collisions meet these criteria.

The theory assumes that most reactions occur in a series of steps where one or more reactant particles collide. This sequence of collisions is called the reaction mechanism. In a unimolecular reaction, the reactant molecule may collide with a solvent particle or with other nonreactive particles that may be present. In a bimolecular reaction, two reactant particles collide. A termolecular reaction, where three particles collide simultaneously, is rare.



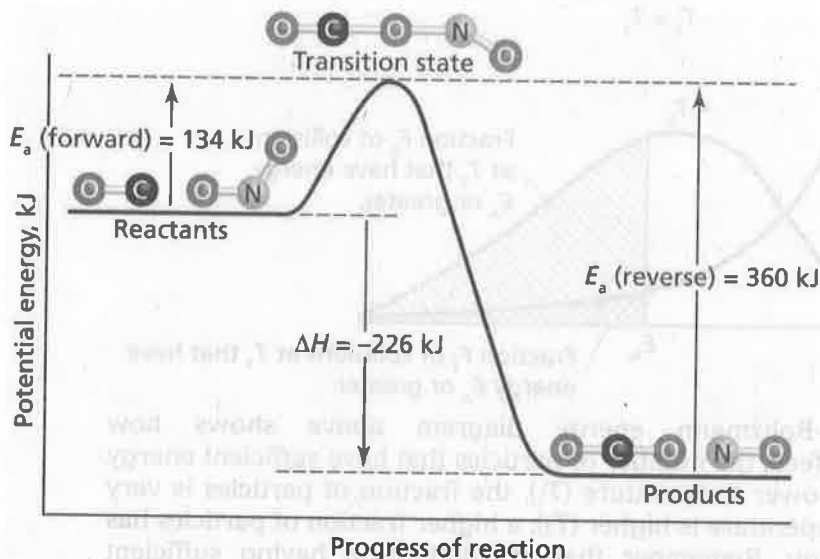
The Maxwell-Boltzmann energy diagram above shows how temperature affects the number of particles that have sufficient energy to react. At a lower temperature (T_1), the fraction of particles is very low. When temperature is higher (T_2), a higher fraction of particles has sufficient energy. Remember that in addition to having sufficient energy, the particles must collide with correct orientation. The diagram below illustrates how correct orientation is necessary for a reaction to occur.



The potential energy diagram, also known as the reaction progress diagram, for the reaction



is shown in the graph below. Energy must be added to break bonds of reactants in order to create a transition state at the top of the “hill,” or barrier. The transition state is the highest energy state of the reactants in the reaction. Once the energy in the transition state, the activation energy, is overcome, the reactants can become products.



Because the products have a lower potential energy than the reactants, the reaction represented in the above diagram is exothermic. Recall that $\Delta H_{\text{rxn}} = \Delta H_{\text{products}} - \Delta H_{\text{reactants}}$. The difference between the potential energies of the products and the reactants is the enthalpy of the reaction.

If you are asked to draw the reaction progress for an endothermic reaction, the potential energy of the products will be higher than that of the reactants.

RATE LAWS

(Chemistry 8th ed. pages 545–559/9th ed. pages 557–571)

Rate laws show the relationship between the rate of a reaction and reactant concentrations. Except for an elementary reaction (one in which the balanced equation represents the mechanism), the rate law cannot be determined from the balanced equation.

The rate law for the reaction



can be written as

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

The proportionality constant, k , is called the rate constant and is determined by experiment. For a given reaction at a given temperature, this value is constant. Its units depend on the order of the

reactants. The rate constant is a calculated quantity that characterizes a chemical reaction. Rate constants vary over many orders of magnitude because reaction rates vary widely.

The order, n , of the reactant must also be determined by experiment. It is the power to which the reactant concentration must be raised in the rate law. For example, if the reaction $A \rightarrow B$ is first order, then the rate law is $\text{Rate} = k[A]$; doubling the concentration of the reactant doubles the rate of the reaction. The units of a first-order reaction are s^{-1} . If the reaction is second order, then $\text{Rate} = k[A]^2$; doubling the concentration of the reactant will result in the rate quadrupling. The units for a second-order reaction are $L \text{ mol}^{-1} s^{-1}$. If the reactant concentration is changed and the rate is not affected, the order of the reactant is zero. The rate law would be $\text{Rate} = k[A]^0$ and the units are $\text{mol L}^{-1} s^{-1}$. Note that it is possible to have fractional or negative reactant orders.

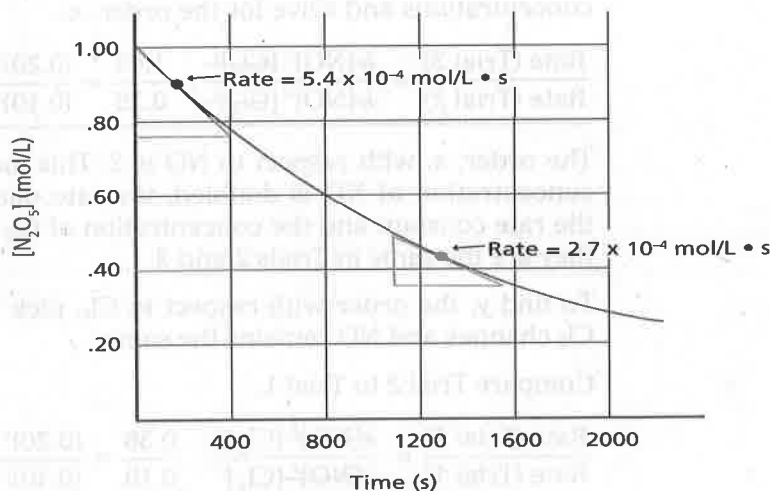
INSTANTANEOUS RATES

(Chemistry 8th ed. pages 542–543/9th ed. pages 555–556)

One way to determine the rate of a reaction at a particular time, the *instantaneous rate*, is to plot the reactant concentration versus time and take the slope of the tangent to the curve at time t .

If the slopes of tangents to the curve at two different concentrations are calculated, the rate law of a reaction can be determined by comparing the changes in rate to the changes in concentration.

In the graph to the right, when the concentration of the reactant, N_2O_5 , is halved, the rate is also halved. The reaction is first order. The rate law for the reaction is $\text{Rate} = k[N_2O_5]$.



METHOD OF INITIAL RATES

(Chemistry 8th ed. pages 548–551/9th ed. pages 560–563)

The initial rate of a reaction is the instantaneous rate just after the reaction begins (just after $t = 0$ and before the initial concentrations of the reactants have changed.)

The rate law of a reaction can be determined by performing a few trials with different reaction concentrations and measuring the initial rate for each trial. To find the order of one reactant, change its concentration while holding the concentration of the other reactants constant.

EXAMPLE: Determine the rate law and the value of the rate constant for the reaction at -10°C :



Trial	$[\text{NO}]_0$ (mol/L)	$[\text{Cl}_2]_0$ (mol/L)	Initial rate (mol L $^{-1}$ s $^{-1}$)
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.45

SOLUTION: Write the general form of the rate law:

$$\text{Rate} = k[\text{NO}]^x[\text{Cl}_2]^y$$

Your goal is to determine x and y .

To find x , the order with respect to NO, pick two trials in which NO changes and Cl_2 remains the same.

Compare Trial 3 to Trial 2.

Write a ratio of the rate law of Trial 3 to the rate of the rate law for Trial 2. Substitute the values for the rates and known concentrations and solve for the order, x .

$$\frac{\text{Rate (Trial 3)}}{\text{Rate (Trial 2)}} = \frac{k[\text{NO}]^x[\text{Cl}_2]^y}{k[\text{NO}]^x[\text{Cl}_2]^y}; \quad \frac{1.45}{0.36} = \frac{(0.20)^x}{(0.10)^x}; \quad 4.0 = 2^x; \quad x = 2.0$$

The order, x , with respect to NO is 2. This means that when the concentration of NO is doubled, the rate quadruples. Note that the rate constant and the concentration of Cl_2 cancel out because they are the same in Trials 2 and 3.

To find y , the order with respect to Cl_2 , pick two trials in which Cl_2 changes and NO remains the same.

Compare Trial 2 to Trial 1.

$$\frac{\text{Rate (Trial 2)}}{\text{Rate (Trial 1)}} = \frac{k[\text{NO}]^x[\text{Cl}_2]^y}{k[\text{NO}]^x[\text{Cl}_2]^y}; \quad \frac{0.36}{0.18} = \frac{(0.20)^y}{(0.10)^y}; \quad 2.0 = 2^y; \quad y = 1$$

The order, y , with respect to Cl_2 , is 1. This means that when the concentration of Cl_2 is doubled, the rate also doubles. Note that the rate constant and the concentration of NO cancel out because they are the same in Trials 1 and 2.

The rate law for the reaction is $\text{Rate} = k[\text{NO}]^2[\text{Cl}_2]$.

The overall order of a reaction is the sum of the reaction orders. For this example, the overall order is $2 + 1 = 3$.

Note: The order with respect to each reactant will not always be the same as the coefficients in the balanced equation and the order may be a fraction such as $1/2$. Fractional rate constants are rare but have appeared on recent exams.

To determine the value of the rate constant, including its units, use the rate law and experimental data from any given trial.

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

Using values from Trial 1:

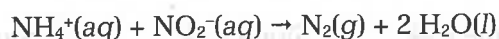
$$= (0.18 \text{ M s}^{-1})/(0.10 \text{ M})^2(0.10 \text{ M}) = 180 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

It helps to work out the units separately.

$$\left(\frac{\text{mol}}{\text{L} \cdot \text{s}}\right) \left(\frac{\text{L}^2}{\text{mol}^2}\right) \left(\frac{\text{L}}{\text{mol}}\right) = \frac{\text{L}^2}{\text{mol}^2 \cdot \text{s}}$$

If the rate constant is known and the order with respect to one of the reactants has been determined, the order with respect to the other can be calculated even if its concentration is not held constant between any of two trials.

EXAMPLE: Determine the rate law for the reaction of ammonium and nitrite ions in aqueous solution at 25°C:



Trial	$[\text{NH}_4^+]_0$ (mol/L)	$[\text{NO}_2^-]_0$ (mol/L)	Initial rate (mol L ⁻¹ s ⁻¹)
1	0.0100	0.200	5.37×10^{-7}
2	0.0400	0.200	2.15×10^{-6}

SOLUTION: Write the general form of the rate equation.

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

Using Trials 1 and 2, determine the order, m , of NH_4^+ using the technique described above. You should find that $m = 1$. Since only 2 trials were run, you must use your newly found order with respect to NH_4^+ and the concentrations given to solve for n .

$$\text{Rate (Trial 2)} = k[\text{NH}_4^+][\text{NO}_2^-]^n$$

$$\text{Rate (Trial 1)} = k[\text{NH}_4^+][\text{NO}_2^-]^n$$

$$2.15 \times 10^{-6} = k(0.200)(0.0400)^n$$

$$5.37 \times 10^{-7} = k(0.0100)(0.200)^n$$

$$4.00 = 20(0.200)^n$$

$$0.200 = (0.200)^n$$

$$n = 1$$

The reaction is first order in each reactant and the rate law is

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

INTEGRATED RATE LAWS

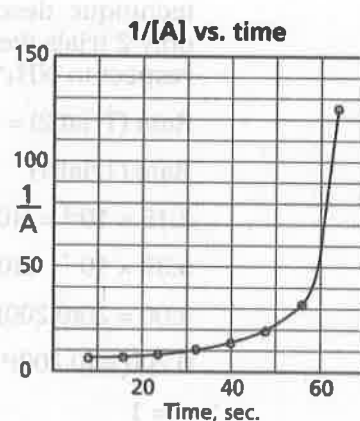
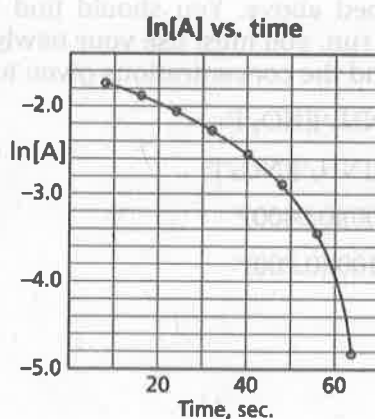
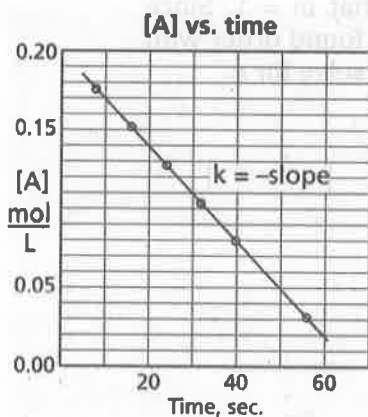
(Chemistry 8th ed. pages 551–560/9th ed. pages 563–572)

An integrated rate law, derived from the differential rate law, expresses the reactant concentration as a function of time. The table below summarizes the integrated rate laws for the reaction
 $A \rightarrow \text{Products}$.

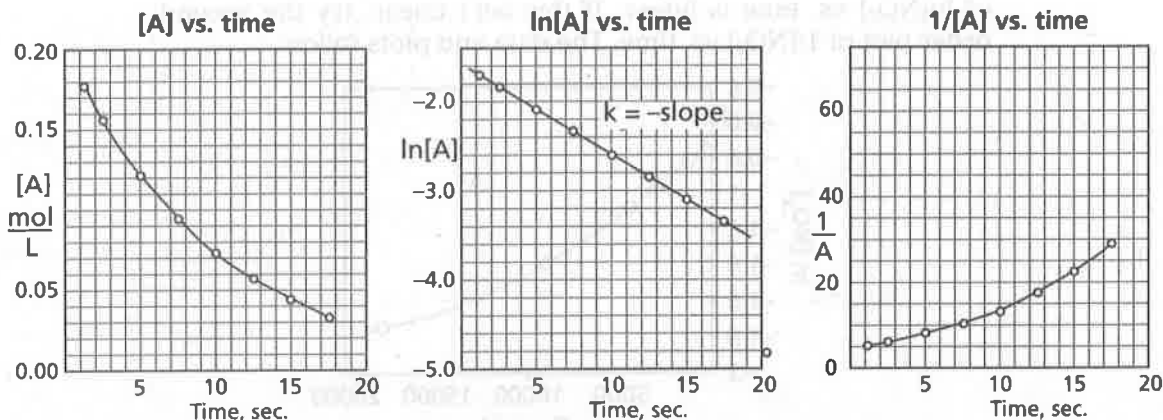
	Order		
	Zero	First	Second
Rate Law:	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated Rate Law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot Needed to Give a Straight Line:	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-Life:		$t_{1/2} = \frac{0.693}{k}$	

You can determine the order of the reactant graphically if you know the concentration of A at various times, t , during the reaction. For example, if you plot $\ln[A]$ vs. t and obtain a straight line, the reaction is first order in A. If the graph is not linear, then the reaction is not first order. The table above summarizes what is graphed to test for the order of the reactant.

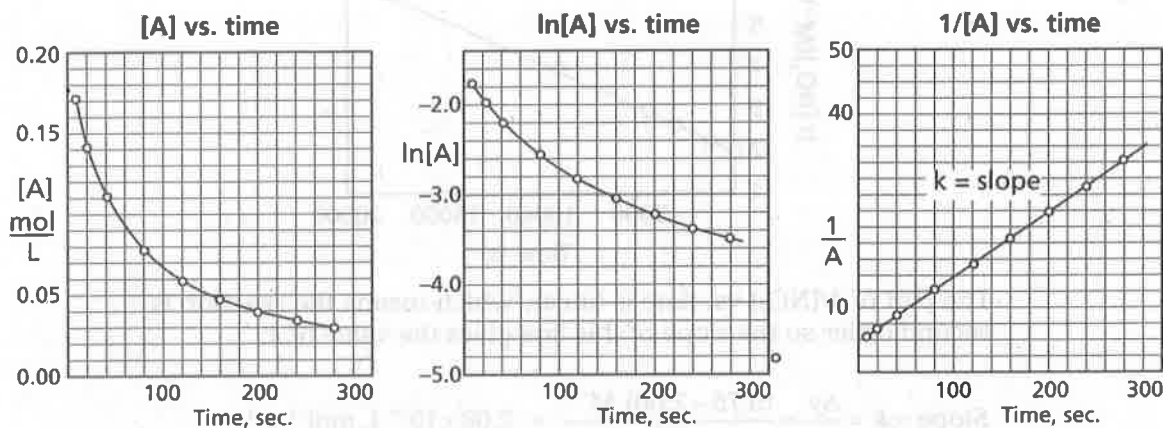
Zero Order



First Order



Second Order



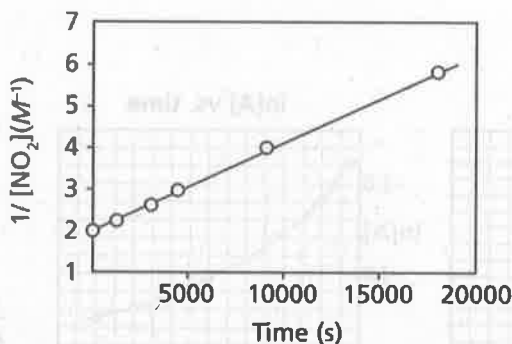
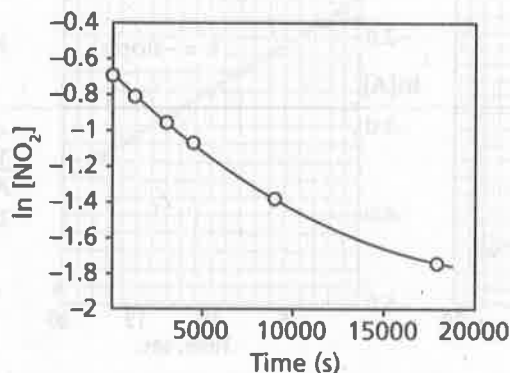
EXAMPLE: The rate of the reaction



depends only on the concentration of nitrogen dioxide below 225°C. At a temperature below 225°C, the following data were collected.

Time (s)	[NO ₂] (M)	ln[NO ₂]	1/[NO ₂] (M ⁻¹)
0	0.500	-0.693	2.00
1.20 × 10 ³	0.444	-0.812	2.25
3.00 × 10 ³	0.381	-0.965	2.62
4.50 × 10 ³	0.340	-1.079	2.94
9.00 × 10 ³	0.250	-1.386	4.00
1.80 × 10 ⁴	0.174	-1.749	5.75

SOLUTION: Assume that the data are first order and see if the plot of $\ln[\text{NO}_2]$ vs. time is linear. If this isn't linear, try the second-order plot of $1/[\text{NO}_2]$ vs. time. The data and plots follow.



The plot of $1/[\text{NO}_2]$ vs. time is linear, which means the reaction is second order so the slope of this line gives the value of k .

$$\text{Slope} = k = \frac{\Delta y}{\Delta x} = \frac{(5.75 - 2.00) \text{ M}^{-1}}{(1.8 \times 10^4 - 0) \text{ s}} = 2.08 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}$$

To determine $[\text{NO}_2]$ at $2.70 \times 10^4 \text{ s}$, use the integrated rate law where $1/[\text{NO}_2]_0 = 1/0.500 \text{ M} = 2.00 \text{ M}^{-1}$.

$$1/[\text{NO}_2] = kt + 1/[\text{NO}_2]_0$$

$$\frac{1}{[\text{NO}_2]} = \frac{2.08 \times 10^{-4} \text{ L}}{\text{mol s}} \times 2.70 \times 10^4 \text{ s} + 2.00 \text{ L mol}^{-1}$$

$$\frac{1}{[\text{NO}_2]} = 7.62 \text{ L mol}^{-1}$$

$$[\text{NO}_2] = 0.131 \text{ M}$$

The half-life of a reactant, $t_{1/2}$, is the time required for a reactant to reach half of its original concentration. The general equation for the half-life for the first order appears in the table on page 218.

THE KINETICS OF RADIOACTIVE DECAY

(Chemistry 8th ed. pages 878–888/9th ed. pages 896–907)

Radioactive decay is a common example of first-order kinetics in a real-life context. The decay of nuclides is represented by $\ln\left(\frac{N}{N_0}\right) = -kt$

where N_0 = the original mass of nuclides
 N = the mass remaining at time t
 k = the first-order rate constant
 t = time.

HALF-LIFE

(Chemistry 8th ed. page 879/9th ed. page 897)

The half-life, $t_{1/2}$, is the time required for the number of nuclides to reach half of their original value. It can be determined by the equation:

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

EXAMPLE: Iodine-131, used in the diagnosis and treatment of thyroid disease, has a half-life of 8.1 days. If a patient with thyroid disease consumes a sample containing 10 μg of iodine-131, how long will it take for the amount of iodine-131 to decrease to 1/100 of the original amount?

SOLUTION: Use the equation: $\ln(N/N_0) = -kt$

Since $N = 0.010 N_0$, substitute $0.010 N_0$ for N .

Since $t_{1/2} = 0.693/k$, substitute $0.693/8.1$ days for k .

Solving for t , you get

$$\ln(0.010) = -0.693t/8.1 \text{ days}$$

$$t = 54 \text{ days.}$$

FACTORS AFFECTING REACTION RATES

Increasing the reactant concentrations increases the chances for more molecular collisions which make products. Except for zero-order reactions, increasing reactant concentrations will usually increase the reaction rate.

Increasing the reactant's surface area increases the frequency of particle collisions. For example, granular zinc reacts more quickly with hydrochloric acid than a strip of zinc.

Increasing the reaction temperature speeds it up since the average kinetic energy of the particles is higher. More particles will have sufficient activation energy to react. Higher temperatures increase the rates of both forward and reverse reactions, increasing the number of collisions that have sufficient energy in a given period of time. The general rule-of-thumb states for each 10°C increase in temperature the reaction rate doubles and works well for reactions performed close to room temperature with activation energies of around 50 kJ mol^{-1} .

MEASURING REACTION RATES

The rate of a reaction is experimentally determined by measuring the amount of reactants converted to products in a given time. A common method of measuring the reaction rate is to use a spectrophotometer or colorimeter to monitor the absorption of light of a specific wavelength. The absorbance of the chemical is directly related to its concentration via Beer's Law.

For instance, the rate of disappearance of color from the reaction of blue food dye and bleach (NaOCl) can be analyzed. According to Beer's Law, absorbance is directly related to $[\text{dye}]$.

$$\text{Rate} = k[\text{dye}]^x[\text{OCl}]^y$$

If blue food dye is the limiting reagent and the bleach concentration is so large that it remains constant throughout the reaction, then the rate expression simplifies to

$$\text{Rate} = k_{\text{pseudo}} [\text{dye}]^x$$

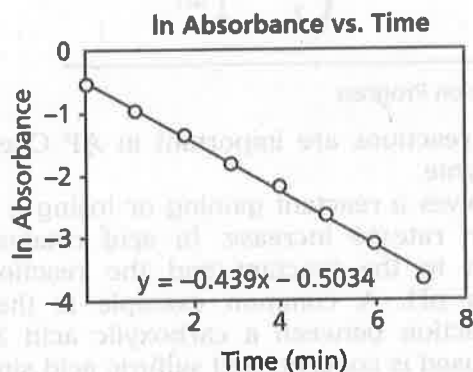
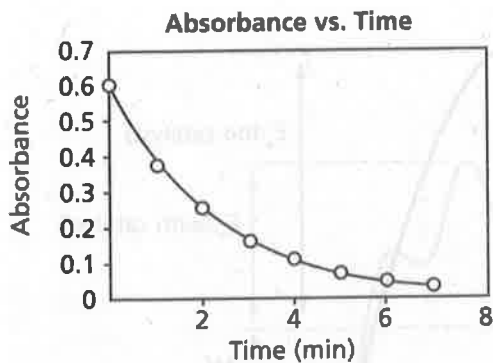
where k_{pseudo} is the pseudo rate constant for the reaction. The actual rate constant, k , can be determined by

$$k = k_{\text{pseudo}} / [\text{OCl}]^y$$

1.00 mL 0.0264 M sodium hypochlorite added to 25.00 mL of blue food dye.

Absorbance of blue food dye at 630 nm

time (min)	Abs	ln Abs
0	0.591	-0.526
1	0.369	-0.997
2	0.262	-1.339
3	0.157	-1.852
4	0.113	-2.180
5	0.071	-2.645
6	0.045	-3.101
7	0.025	-3.689



Since the graph of \ln abs vs. time is linear, the reaction is first order in dye with $k_{\text{pseudo}} = 0.439$. The experiment was carried out under the same conditions with 0.0132 M NaOCl and the slope was half meaning the reaction is also first order in OCl^- . The actual rate constant is

$$k = k_{\text{pseudo}}/[\text{OCl}^-]$$

$$k = 0.439/0.0264 = 16.6 \text{ L mol}^{-1}$$

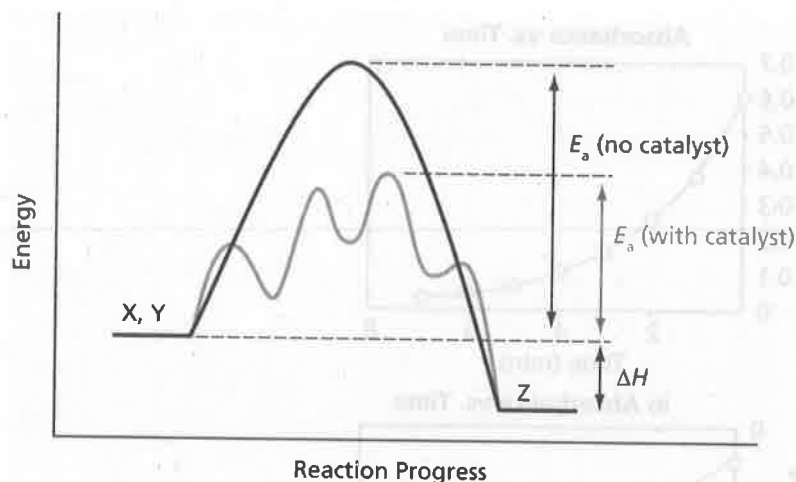
and the rate law is

$$\text{Rate} = k[\text{dye}][\text{OCl}^-]$$

CATALYSIS

(Chemistry 8th ed. pages 570–577/9th ed. pages 583–589)

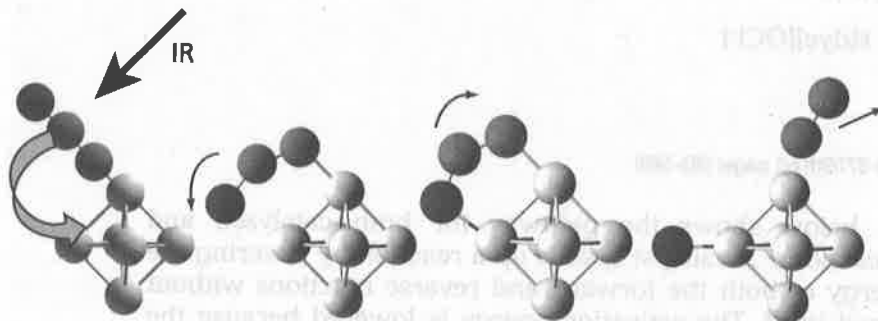
The diagram below shows the pathway for both catalyzed and uncatalyzed reactions. A catalyst speeds up a reaction by lowering the activation energy of both the forward and reverse reactions without being consumed itself. The activation energy is lowered because the mechanism of the reaction has changed and the transition state is stabilized; the pathway from reactants to products is different which is depicted by the lower squiggly line.



Three classes of catalysis reactions are important in AP Chemistry: acid-base, surface, and enzyme.

Acid-base catalysis involves a reactant gaining or losing a proton which causes the reaction rate to increase. In acid catalysis, the catalyst donates a proton to the reactant and the reaction rate increases with decreasing pH. A common example is the acid-catalyzed esterification reaction between a carboxylic acid and an alcohol. The acid typically used is concentrated sulfuric acid since this acid contains almost no water which can hydrolyse esters. In base catalysis, the reactant donates a proton to the basic catalyst causing an increase in reaction rate with increasing pH. An industrial application of base catalysis is the production of polyurethane foams.

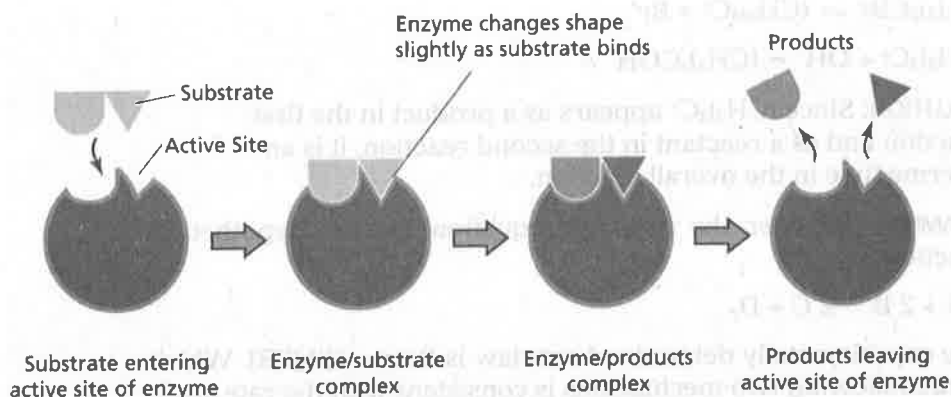
Surface catalysis involves the formation of new intermediates or an increase in the probability of successful collisions by improving the orientation of the reactants. The diagram below shows the decomposition of N_2O on rhodium clusters which mimics the chemistry in catalytic converters in automobiles.



Another example of surface catalysis includes finely divided iron in the synthesis of ammonia from nitrogen and hydrogen gas. The gases adsorb onto the surface of the iron and their bonds are weakened. Since the fragments of nitrogen and hydrogen are in close proximity, formation of new nitrogen-hydrogen bonds is favored.

Enzyme catalysis plays an important role in living organisms. Enzymes are homogenous catalysts that make products necessary for the organism. After a substrate binds to the enzyme, the shape of the enzyme changes slightly. The substrate is converted into products which then leave the enzyme to be used elsewhere in the body. The

enzyme is again available to bind with more substrate. Enzymes lower the activation energy by providing alternative pathways for biochemical reactions to occur.



MECHANISMS

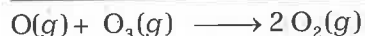
(Chemistry 8th ed. pages 562–565/9th ed. pages 574–577)

A mechanism is a series of steps by which a reaction occurs according to collision theory. The elementary steps, each step in the mechanism, must add up to give the overall balanced equation for the mechanism. The slowest step in the mechanism must agree with the experimentally determined rate law.

Once the rate law has been determined experimentally, chemists propose several mechanisms consistent with that rate law and design experiments to determine which mechanism fits the data. You will have to know how to identify catalysts and intermediates in a mechanism and write the overall equation for a mechanism. You will also need to be able to write a rate law from a given mechanism.

A catalyst is present in the reactants and also appears in the products. Recall that the catalyst is not consumed in the reaction. The catalyst does not appear in the overall reaction.

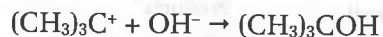
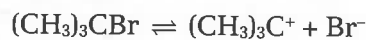
EXAMPLE: Identify the catalyst in the decomposition of ozone by atoms of chlorine.



SOLUTION: $\text{Cl}(g)$ is the catalyst because it is a reactant in the first reaction and a product in the second reaction. $\text{Cl}(g)$ does not appear in the overall reaction.

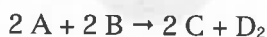
An intermediate is produced in one elementary step and then consumed in the next. It also does not appear in the overall equation for the reaction because it cancels out. The detection and identification of intermediates provides evidence that scientists use to justify one mechanism over another.

EXAMPLE: The synthesis of *t*-butyl alcohol, an octane booster in gasoline, is shown below. Identify the intermediate in the reaction.

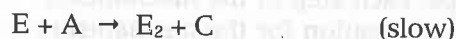


SOLUTION: Since $(\text{CH}_3)_3\text{C}^+$ appears as a product in the first reaction and as a reactant in the second reaction, it is an intermediate in the overall reaction.

EXAMPLE: Consider the balanced equation for the hypothetical reaction



The experimentally determined rate law is $\text{Rate} = k[\text{A}]^2[\text{B}]$. Which of the following two mechanisms is consistent with the rate law?

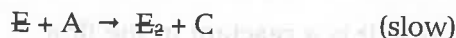


SOLUTION: For the proposed mechanism to be correct, the overall reaction and the rate law for the mechanism must agree with the given reaction and the experimentally determined rate law.

Write the overall reaction for each mechanism. Add up the elementary steps. Cancel out the catalysts and intermediates that appear. E and E_2 are intermediates because they are produced in one step and consumed in the subsequent step of the mechanism.



$2 \text{A} + 2 \text{B} \rightarrow 2 \text{C} + \text{D}_2$ is the overall reaction.



$2 \text{A} + 2 \text{B} \rightarrow 2 \text{C} + \text{D}_2$ is the overall reaction.

The overall reaction for each mechanism matches the given reaction so either mechanism could be correct.

The next step is to determine which mechanism has a rate law that matches the experimental data. Write the rate law for the slowest step in each mechanism.

Mechanism I

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

This rate law is not consistent with the rate law determined by experiment; mechanism I is not possible for this reaction.

Mechanism II

$$\text{Rate} = k[E][A]$$

[E] is an intermediate and may not be included in the rate law. Because the first step in the mechanism is reversible and fast, the rate of the forward reaction equals the rate of the reverse reaction.

$$\text{Rate (forward)} = k_f[A][B]$$

$$\text{Rate (reverse)} = k_r[E]$$

Rate (forward) = Rate (reverse), therefore $k_f[A][B] = k_r[E]$.
Rearranging the terms gives:

$$[E] = (k_f/k_r)[A][B] = k'[A][B]$$

Substitute for [E] in the rate law for the slow step in mechanism II.

$$\text{Rate} = k[E][A]$$

$$\text{Rate} = k(k'[A][B])[A]$$

Combining the rate constants gives k'' and $[A][A]$ is $[A]^2$ to get

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

Mechanism II is possible because its rate law agrees with the experimentally determined rate law and the stoichiometry also agrees with the rate determining step.

DETERMINATION OF ACTIVATION ENERGY

(Chemistry 8th ed. pages 567–570/9th ed. pages 579–583)

Activation energy can be experimentally determined using the Arrhenius equation

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

The rate constant is represented by k .

E_a is the activation energy.

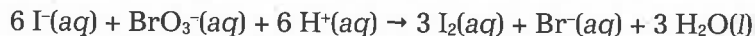
R is the gas constant, $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$.

T is the Kelvin temperature.

A is the frequency factor that is related to the collisions and is temperature dependent.

One way to determine the activation energy, E_a , is to measure the rate constant, k , at several different temperatures, and then graph $\ln(k)$ vs. $1/T$ which gives a straight line with the slope equal to $-E_a/R$.

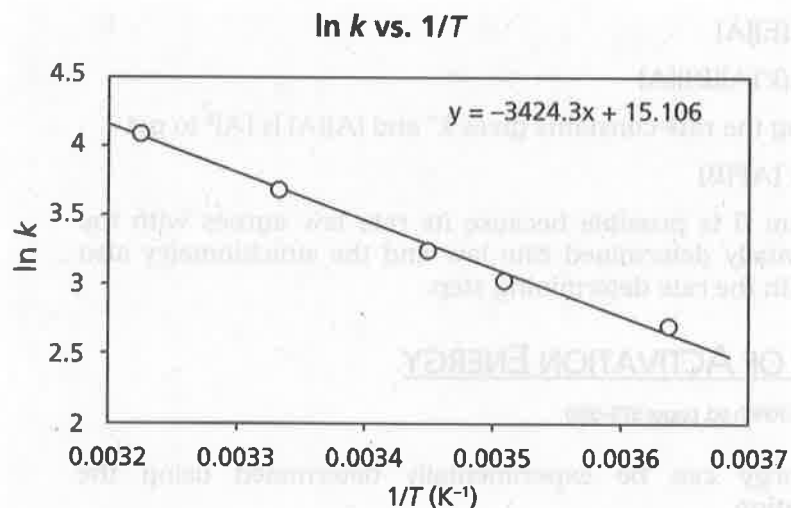
EXAMPLE: The activation energy for the following reaction was experimentally determined by varying the temperature at which the reaction was performed.



Temperature (K)	Rate constant, k ($\text{L}^3 \text{mol}^{-3} \text{s}^{-1}$)	1/Temperature (K^{-1})	$\ln k$
275	15	0.00364	2.71
285	21	0.00351	3.04
290	26	0.00345	3.26
300	40.	0.00333	3.69
310	60.	0.00323	4.09

What is the activation energy of this reaction?

SOLUTION: The data must be graphed to determine the slope of the line.



The slope of the line is equal to $-E_a/R$ and the precision is limited by 2 significant figures in the rate constant.

$$-3400 \text{ K} = -E_a/8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$E_a = 28 \text{ kJ mol}^{-1}$$

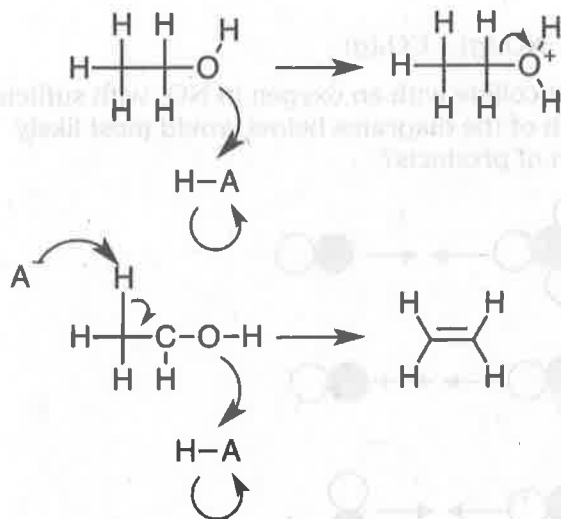
As you can see from the data, as the temperature increases, the rate constant also increases.

MULTIPLE-CHOICE QUESTIONS

No calculators are to be used in this section.

Each of the following questions or incomplete statements has four suggested responses. Select the one which best answers the question or incomplete statement.

1. The mechanism below shows how ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) is converted into ethene (CH_2CH_2).



Which explanation describes the process?

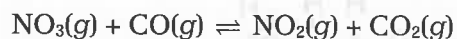
- (A) HA reacts with $\text{CH}_3\text{CH}_2\text{OH}$ to produce $\text{CH}_2\text{CH}_2 + \text{H}_2\text{O} + \text{HA}$
 (B) HA reacts with $\text{CH}_3\text{CH}_2\text{OH}$ to produce $\text{CH}_2\text{CH}_2 + \text{H}_3\text{OA}$
 (C) HA reacts with $\text{CH}_3\text{CH}_2\text{OH}$ to produce $\text{CH}_2\text{CH}_2 + \text{HA}$
 (D) HA reacts with $\text{CH}_3\text{CH}_2\text{OH}$ to produce $\text{CH}_2\text{CH}_2 + \text{H}_2\text{O}$
2. A student is trying to find the activation energy of a reaction. What technique could be used?
- (A) Vary the concentrations of all reactants in several different experiments at a constant temperature.
 (B) Choose one set of reactant concentrations and run the same reaction at different temperatures.
 (C) Use a spectrophotometer to monitor the time required for a reaction to go to completion.
 (D) Add a catalyst to the reaction to see how much quicker the reaction goes.

3. The rate law of a reaction is determined to be

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

Which statement would most likely describe this reaction?

- (A) The reaction is catalyzed by an enzyme.
 (B) The reaction involves a one-step, termolecular mechanism.
 (C) The stoichiometry of the overall reaction must be $\text{A} + 2\text{B} \rightarrow$ products.
 (D) The reaction involves the formation of intermediates.
4. In the reaction,

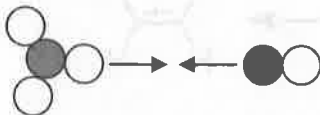


the carbon in CO must collide with an oxygen in NO_3 with sufficient energy to react. Which of the diagrams below would most likely result in the formation of products?

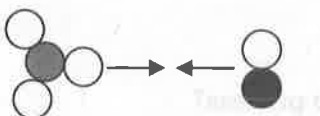
(A) -40°C



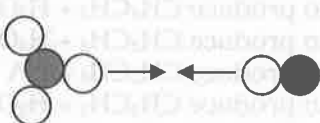
(B) 60°C



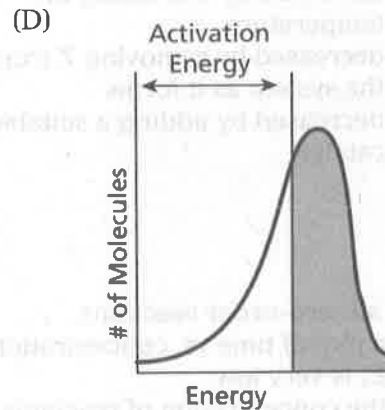
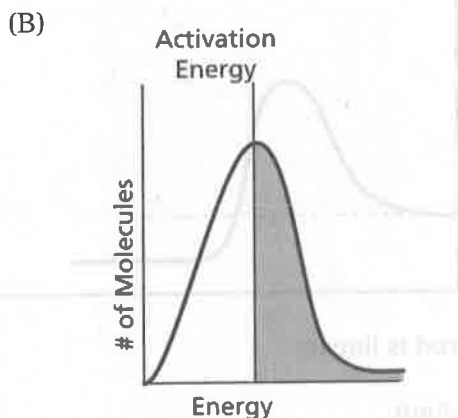
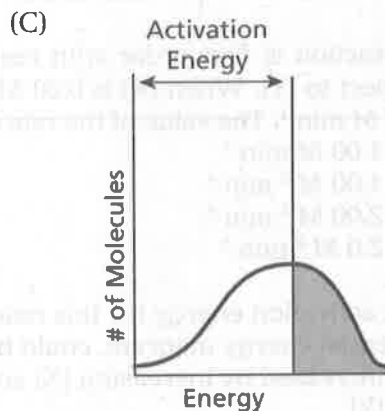
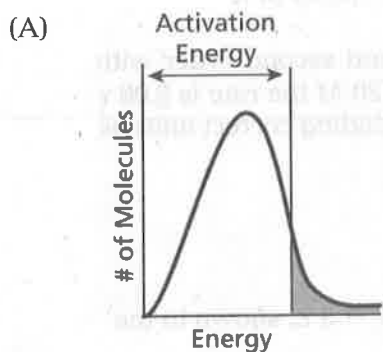
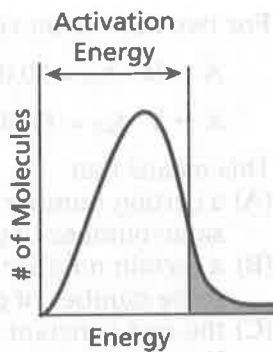
(C) 100°C



(D) 80°C

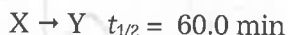
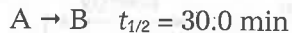


5. The graph at the right shows the number of molecules that have sufficient energy to overcome E_a for a given reaction. How would adding an enzyme change the appearance of the graph?



6. The values for the change in enthalpy, ΔH , and the activation energy, E_a , for a given reaction are known. The value of E_a for the reverse reaction equals
- E_a for the forward reaction
 - $-(E_a)$ for the forward reaction
 - the sum of $-\Delta H$ and E_a
 - the sum of ΔH and E_a

7. For two first-order reactions of different substances A and X

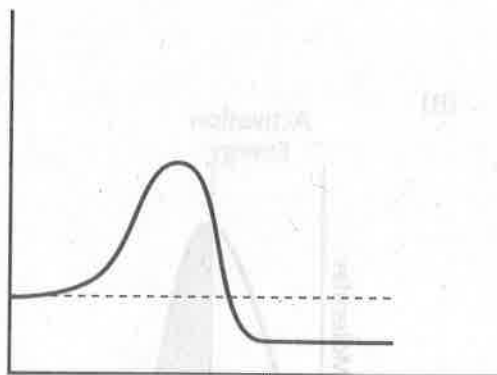


This means that

- (A) a certain number of grams of A will react twice as fast as the same number of grams of X
 (B) a certain number of grams of X will react twice as fast as the same number of grams of A
 (C) the rate constant for $A \rightarrow B$ is lower than the rate constant of $X \rightarrow Y$
 (D) 3 moles of A will react more rapidly than 3 moles of X
8. A reaction is first order with respect to [X] and second order with respect to [Y]. When [X] is 0.20 M and [Y] = 0.20 M the rate is $8.00 \times 10^{-3} \text{ M min}^{-1}$. The value of the rate constant, including correct units, is
 (A) 1.00 M min^{-1}
 (B) $1.00 \text{ M}^{-2} \text{ min}^{-1}$
 (C) $2.00 \text{ M}^{-1} \text{ min}^{-1}$
 (D) $2.0 \text{ M}^{-2} \text{ min}^{-1}$

9. The activation energy for this reaction, $X + 2 Y \rightarrow 3 Z$, shown in the potential energy diagram, could be

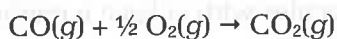
- (A) increased by increasing [X] and [Y]
 (B) increased by increasing the temperature
 (C) decreased by removing Z from the system as it forms
 (D) decreased by adding a suitable catalyst



10. For all zero-order reactions
 (A) a plot of time vs. concentration squared is linear
 (B) E_a is very low
 (C) the concentration of reactants is constant
 (D) the rate is independent of time

Use the following information to answer questions 11 through 13.

Carbon monoxide reacts with oxygen according to the equation



The rate law for the reaction is: $\text{Rate} = k[\text{CO}]^m[\text{O}_2]^n$

Experimental information for the reaction is given in the following table:

	[CO] mol L ⁻¹	[O ₂] mol L ⁻¹	Initial rate, mol L ⁻¹ min ⁻¹
Experiment 1	0.020	0.020	3.68×10^{-5}
Experiment 2	0.040	0.020	1.47×10^{-4}
Experiment 3	0.020	0.040	7.36×10^{-5}

11. Which values correspond to the reaction orders m and n for CO and O₂?

- (A) $m = 4, n = 2$
- (B) $m = 1, n = \frac{1}{2}$
- (C) $m = 1, n = 1$
- (D) $m = 2, n = 1$

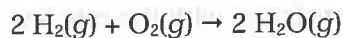
12. What is the overall reaction order?

- (A) 0
- (B) 1
- (C) 2
- (D) 3

13. What is the numerical value for the rate constant, k , for this reaction?

- (A) $3.68 \times 10^{-5} \text{ mol L}^{-1} \cdot \text{min}^{-1}$
- (B) $4.60 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$
- (C) $2.93 \times 10^{-25} \text{ mol min}^{-1}$
- (D) $1.54 \times 10^4 \text{ min}^{-1}$

14. Which of the following statements would be correct regarding the following reaction?



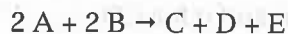
- (A) The rate of O₂ disappearance is twice the rate of H₂ disappearance.
- (B) The rate of H₂ disappearance is twice the rate of O₂ disappearance.
- (C) The rate of H₂O disappearance is twice the rate of O₂ disappearance.
- (D) The rate of H₂O appearance is equal to the rate of O₂ disappearance.

15. According to the collision theory of kinetics, which statement best describes the rate of a chemical reaction?
- All collisions result in a chemical reaction.
 - All collisions between molecules with at least a minimum kinetic energy result in reaction.
 - All collisions between molecules with at least a minimum kinetic energy and the proper orientation result in reaction.
 - The greater the difference in energy between the reactants and the products, the faster is the reaction.

FREE-RESPONSE QUESTIONS

Calculators may be used for this section.

1. The kinetics of the reaction below were studied to determine a reaction rate and to propose a mechanism.

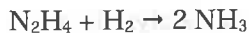
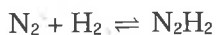


Data are presented below.

Trial	[A] ₀ (mol L ⁻¹)	[B] ₀ (mol L ⁻¹)	Initial Rate Formation (mol L ⁻¹ min ⁻¹), C
1	0.040	0.060	0.332
2	0.040	0.12	0.662
3	0.080	0.060	1.32

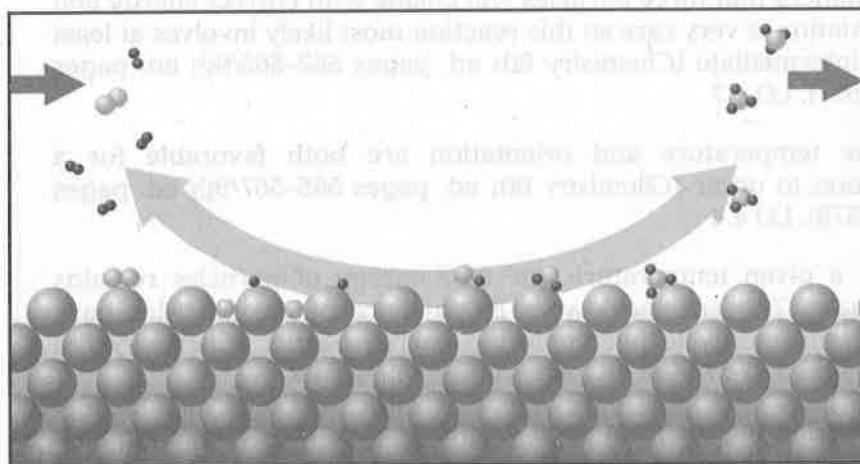
- Determine the order of reaction with respect to each reactant.
 - Write the rate law expression.
 - Calculate the value of the rate constant and include the units.
 - Calculate the initial rate of disappearance of B in experiment 3.
 - A proposed mechanism is shown below.
 - Step 1. $A + A \rightleftharpoons X$
 - Step 2. $X + B \rightarrow C + Y$
 - Step 3. $Y + B \rightarrow D + E$
 - Identify all catalysts and intermediates.
 - Determine the rate determining step.
 - Show that the mechanism is consistent with the rate law and with the overall stoichiometry of the reaction.
2. The Haber process is used to make ammonia, an important chemical feedstock for industry. Without the use of a catalyst, the reaction proceeds too slowly to be commercially viable. The basic reaction is $N_2 + 3H_2 \rightleftharpoons 2NH_3$.
- Propose a kinetic reason that the reaction does not occur in a single elementary step.

- (b) If the reaction happened in a series of bimolecular steps, this is one possibility:

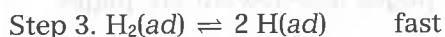
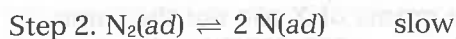


- (i) Draw the electron dot structure of N_2 and propose a reason why the reaction would be thermodynamically unfavorable.
- (ii) The decomposition of hydrazine, N_2H_4 is very exothermic. Draw the energy profile for the formation of hydrazine from N_2H_2 and H_2 . Propose a reason why this reaction would be thermodynamically unfavorable.

- (c) The actual Haber process uses an iron catalyst.

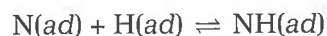


N_2 and H_2 adhere (*ad*) to the metal surface and both molecules dissociate.

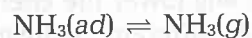


- (i) Based on the diagram, propose a reason that Step 2 is the rate determining step.

Hydrogen atoms migrate across the surface in the following series of reactions.



The final step is for the NH_3 to desorb from the catalyst.



- (ii) How does the diagram show a method to shift equilibrium to $\text{NH}_3(\text{g})$?
- (d) Describe one physical characteristic of the catalyst that would ensure its usefulness.

Answers

MULTIPLE-CHOICE QUESTIONS

- A** This is an example of an acid-catalyzed reaction. A catalyst is a reactant in the first step of the mechanism and a product in the last step of the mechanism. LO 4.9
- B** Activation energy is calculated by performing a reaction using the same concentrations of reactants at different temperatures. By graphing $\ln k$ vs $1/T$, E_a can be calculated from the slope (*Chemistry* 8th ed. pages 565–570/9th ed. pages 577–583). LO 4.6
- D** Chances that three particles will collide with correct energy and orientation is very rare so this reaction most likely involves at least one intermediate (*Chemistry* 8th ed. pages 562–565/9th ed. pages 574–577). LO 4.7
- B** The temperature and orientation are both favorable for a reaction to occur (*Chemistry* 8th ed. pages 565–567/9th ed. pages 577–579). LO 4.4
- B** At a given temperature, the free energy of particles remains constant. The enzyme lowers E_a so more of the particles have sufficient energy to overcome the energy barrier (*Chemistry* 8th ed. pages 570–576/9th ed. pages 583–588). LO 4.9
- C** Examine the diagram on p. 216. The E_a of the reverse reaction must equal the E_a of the forward reaction plus ΔH of the reaction (*Chemistry* 8th ed. pages 565–568/9th ed. pages 577–581). LO 4.6
- D** It takes half as much time for A to form B as for X to form Y, as seen by the smaller half-life. Note that option “B” would be incorrect as the grams of A and the grams of X are not the same number of moles (*Chemistry* 8th ed. pages 555–556/9th ed. pages 567–568). LO 4.3
- B** From these data, it follows that the rate law is $\text{Rate} = k[X][Y]^2$. Solving for the rate constant and substituting data for this reaction:

$$k = \text{Rate} / [X][Y]^2$$

$$= 8.00 \times 10^{-3} \text{ M/min} / (0.200 \text{ M})(0.200 \text{ M})^2$$

$$= 0.008 \text{ M/min} / 0.008 \text{ M}^3$$

$$= 1.00 \text{ M}^{-2} \text{ min}^{-1}$$
 (*Chemistry* 8th ed. pages 548–554, 562/9th ed. pages 560–566, 574)
 LO 4.2
- D** Adding a catalyst suitable for this reaction will lower the energy barrier (activation energy) by forming a different activated complex which has a lower potential energy. (*Chemistry* 8th ed. pages 565–572/9th ed. pages 577–585). LO 4.8

10. **D** For zero-order reactions, $\text{Rate} = k[X]^0$. Because anything raised to the zero power is equal to one, $\text{Rate} = k$. This is another way of saying that the rates of zero-order reactions do not change; they do not speed up and they do not slow down, they either take place or they do not (*Chemistry* 8th ed. page 559/9th ed. page 571). LO 4.2
11. **D** Compare experiments 1 and 2, doubling the concentration of CO has caused the initial rate to increase by a factor of 4 or 2^2 . Therefore $m = 2$. And comparing experiments 1 and 3, doubling the concentration of O_2 , keeping the [CO] the same, resulted in the initial rate also being doubled, or 2^1 . Therefore $n = 1$ (*Chemistry* 8th ed. pages 549–551/9th ed. pages 561–563). LO 4.2
12. **D** The overall order is simply the sum of $m + n$ or $2 + 1 = 3$ (*Chemistry* 8th ed. pages 549–551/9th ed. pages 561–563). LO 4.2
13. **B** Using experiment 1, $\text{rate} = k[\text{CO}]^2[\text{O}_2]$; $3.68 \times 10^{-5} = k(0.020)^2(0.020)$
Solving for k , $k = 4.60 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$.
(*Chemistry* 8th ed. pages 549–551/9th ed. pages 561–563) LO 4.2
14. **B** According to the balanced equation 2 moles of H_2 are used up for every mole of O_2 , so during the same time period, the rate of disappearance of the H_2 would be twice as great (*Chemistry* 8th ed. pages 540–545/9th ed. pages 553–557). LO 4.1
15. **C** Collision theory states that the molecules colliding must not only have the minimum combined activation energy required for reaction, they must also have the proper spatial orientation when they collide (*Chemistry* 8th ed. pages 565–568/9th ed. pages 577–581). LO 4.5

FREE-RESPONSE QUESTIONS

1. (a) To determine how each of the concentrations of the reactants is related to the reaction rate, only the one reactant concentration may change.
(i) Compare $[A]_0$ in Trial 1 and 3. Doubling the concentration increases the rate by a factor of about 4 which indicates the reaction is second order in A. Compare $[B]_0$ in Trials 1 and 2. Doubling the concentration doubles the rate which means that the reaction is first order in B.

$$\text{Rate} = k[A]^x[B]^y$$

$$\text{Trial 1} \quad 0.332 = k[0.040]^x[0.060]^y$$

$$\text{Trial 3} \quad 1.32 = k[0.080]^x[0.060]^y$$

$$0.252 = 0.5^x$$

$$x = 2$$

$$\text{Trial 1} \quad 0.332 = k(0.040)^x(0.060)^y$$

$$\text{Trial 2} \quad 0.662 = k(0.040)^x(0.12)^y$$

$$0.502 = 0.50^y$$

$$y = 1$$

(ii) The rate law is rate = $k[A]^2[B]$.

(b) Solving the rate law for k yields:

$$k = \text{Rate}/([A]^2[B])$$

$$= 0.332 \text{ mol L}^{-1} \text{ min}^{-1} / (0.040 \text{ mol L}^{-1})^2(0.060 \text{ mol L}^{-1})$$

$$= 3.5 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

(c) $-1/2\Delta[B]/\Delta t = \Delta[C]/\Delta t$

$$\Delta[B]/\Delta t = -2\Delta[C]/\Delta t$$

$$= (-2)(1.32 \text{ mol L}^{-1} \text{ min}^{-1})$$

$$= -2.64 \text{ mol L}^{-1} \text{ min}^{-1}$$

(d) (i) Intermediates are X and Y because they are made in one step and used in the next. There are no catalysts.

(ii) The rate law must match the rate determining step. Step 1 cannot be the RDS because that rate law would be rate = $k[A]^2$ which does not match the experimentally determined rate law.

The rate law for Step 2 would be rate = $k[X][B]$. At first glance this does not appear to agree with the experimental rate law, either. However, intermediates are not included in the rate law. Since the first reaction is an equilibrium rate forward = rate reverse.

$$\text{Rate} = k_f[A]^2 = k_r[X]$$

$$[X] = k_f[A]^2 / k_r$$

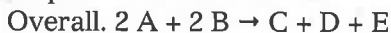
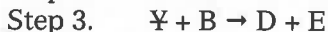
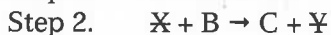
$$k_f / k_r = k'$$

$$[X] = k'[A]^2$$

Substituting into the rate law for the RDS,

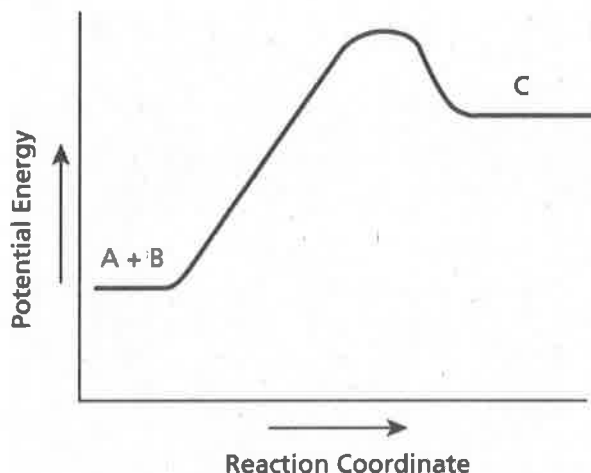
$$\text{Rate} = k_2 k'[A]^2[B] \text{ or Rate} = k[A]^2[B]$$

(iii) The experimental rate law and the rate law of the slowest step are the same. The overall stoichiometry of the mechanism is the same as reaction which indicates the mechanism is plausible,



(Chemistry 8th ed. pages 547–565/9th ed. pages 559–577)
LO 4.2, LO 4.7

2. (a) The reaction does not occur in a single elementary step because aligning 4 particles with the correct orientation and energy would not be feasible.
- (b) (i) $\text{:N}\equiv\text{N}$: The reaction is thermodynamically unfeasible because a lot of energy would need to be added to break the very stable triple bond.
- (ii) The reaction is thermodynamically unfavorable due to the high E_a .



- (c) (i) $\text{N}_2(ad) \rightleftharpoons 2 \text{N}(ad)$ may be the RDS because the nitrogen atoms fit very compactly between the iron atoms according to the diagram.
- (ii) As the $\text{NH}_3(g)$ desorbs, it is removed from the reaction vessel so it cannot dissociate back to reactants and so the equilibrium is shifted towards products.
- (d) One physical characteristic of the catalyst that will enhance its usefulness is high surface area so the reactants have lots of places to adsorb and react.

(Chemistry 8th ed. pages 361–364, 562–572, 620–624/9th ed. pages 373–376, 574–585, 633–639) LO 4.1, LO 4.4, LO 4.5, LO 4.6, LO 4.9

