SAMPLE EXERCISE 14.1 Calculating an Average Rate of Reaction

From the data given in the caption of Figure 14.3, calculate the average rate at which A disappears over the time interval from 20 s to 40 s.

Solution

Analyze: We are given the concentration of A at 20 s (0.54 *M*) and at 40 s (0.30 *M*) and asked to calculate the average rate of reaction over this time interval.

Plan: The average rate is given by the change in concentration, Δ[A], divided by the corresponding change in time, Δ*t*. Because A is a reactant, a minus sign is used in the calculation to make the rate a positive quantity.

Solve:

$$\text{Average rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{0.30\ M - 0.54\ M}{40\ s - 20\ s} = 1.2 \times 10^{-2}\ M/s$$

PRACTICE EXERCISE

For the reaction pictured in Figure 14.3, calculate the average rate of appearance of B over the time interval from 0 to 40 s. (The necessary data are given in the figure caption.)

Answer: $1.8 \times 10^{-2}\ M/s$

SAMPLE EXERCISE 14.2 Calculating an Instantaneous Rate of Reaction

Using Figure 14.4, calculate the instantaneous rate of disappearance of C_4H_9Cl at $t = 0$ (the initial rate).

Solution

Analyze: We are asked to determine an instantaneous rate from a graph of concentration versus time.

Plan: To obtain the instantaneous rate at $t = 0$ we must determine the slope of the curve at $t = 0$. The tangent is drawn on the graph. The slope of this straight line equals the change in the vertical axis divided by the corresponding change in the horizontal axis (that is, change in molarity over change in time).

Solve: The straight line falls from $[C_4H_9Cl] = 0.100\ M$ to $0.060\ M$ in the time change from 0 s to 200 s, as indicated by the tan triangle shown in Figure 14.4. Thus, the initial rate is

$$\text{Rate} = -\frac{\Delta[C_4H_9Cl]}{\Delta t} = -\frac{(0.060 - 0.100)\ M}{(200 - 0)\ s} = 2.0 \times 10^{-4}\ M/s$$

PRACTICE EXERCISE

Using Figure 14.4, determine the instantaneous rate of disappearance of C_4H_9Cl at $t = 300$ s.

Answer: $1.1 \times 10^{-4}\ M/s$

SAMPLE EXERCISE 14.3 Relating Rates at Which Products Appear and Reactants Disappear

(a) How is the rate at which ozone disappears related to the rate at which oxygen appears in the reaction $2 O_3(g) \longrightarrow 3 O_2(g)$?

(b) If the rate at which O_2 appears, $\Delta[O_2]\square\Delta t$, is 6.0×10^{-5} M/s at a particular instant, at what rate is O_3 disappearing at this same time, $-\Delta[O_3]\square\Delta t$?

Solution

Analyze: We are given a balanced chemical equation and asked to relate the rate of appearance of the product to the rate of disappearance of the reactant.

Plan: We can use the coefficients in the chemical equation as shown in Equation 14.4 to express the relative rates of reactions.

Solve: (a) Using the coefficients in the balanced equation and the relationship given by Equation 14.4, we have:

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$$

(b) Solving the equation from part (a) for the rate at which O_3 disappears, $-\Delta[O_3]\square\Delta t$ we have:

$$-\frac{\Delta[O_3]}{\Delta t} = \frac{2}{3}\frac{\Delta[O_2]}{\Delta t} = \frac{2}{3}(6.0 \times 10^{-5} \ M/s) = 4.0 \times 10^{-5} \ M/s$$
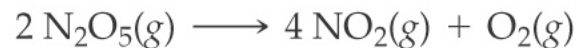
Check: We can directly apply a stoichiometric factor to convert the O_2 formation rate to the rate at which the O_3 disappears:

$$-\frac{\Delta[O_3]}{\Delta t} = \left(6.0 \times 10^{-5}\frac{\text{mol } O_2/L}{s}\right)\left(\frac{2 \text{ mol } O_3}{3 \text{ mol } O_2}\right) = 4.0 \times 10^{-5}\frac{\text{mol } O_3/L}{s}$$

$$= 4.0 \times 10^{-5} \ M/s$$

PRACTICE EXERCISE

The decomposition of N_2O_5 proceeds according to the following equation:

$$2\,N_2O_5(g) \longrightarrow 4\,NO_2(g) + O_2(g)$$

If the rate of decomposition of N_2O_5 at a particular instant in a reaction vessel is $4.2 \times 10^{-7}\,M/s$, what is the rate of appearance of (a) NO_2, (b) O_2?

Answers: **(a)** $8.4 \times 10^{-7}\,M/s$, **(b)** $2.1 \times 10^{-7}\,M/s$

SAMPLE EXERCISE 14.4 Relating a Rate Law to the Effect of Concentration on Rate

Consider a reaction $A + B \longrightarrow C$ for which rate = $k[A][B]^2$. Each of the following boxes represents a reaction mixture in which A is shown as red spheres and B as purple ones. Rank these mixtures in order of increasing rate of reaction.

(1)   (2)   (3)
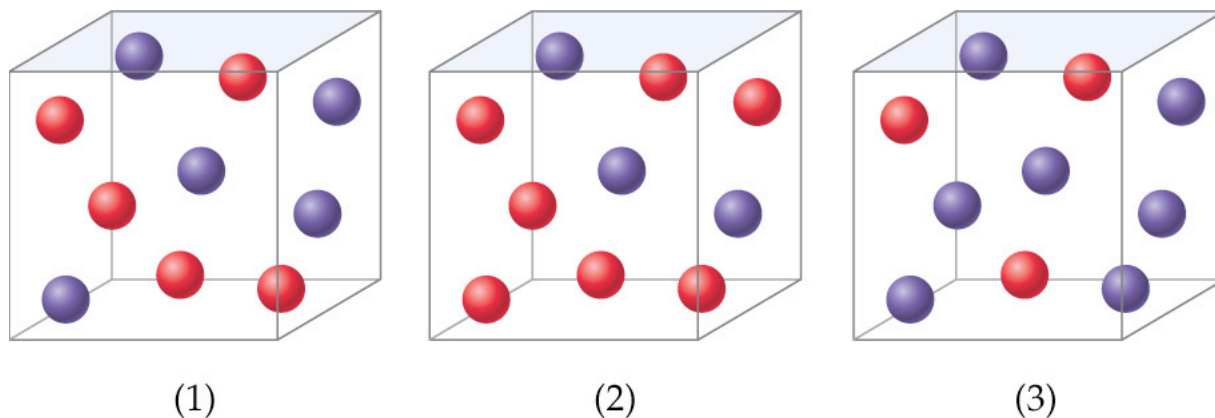
Solution

Analyze: We are given three boxes containing different numbers of spheres representing mixtures containing different reactant concentrations. We are asked to use the given rate law and the compositions of the boxes to rank the mixtures in order of increasing reaction rates.

Plan: Because all three boxes have the same volume, we can put the number of spheres of each kind into the rate law and calculate the rate for each box.

Solve: Box 1 contains 5 red spheres and 5 purple spheres, giving the following rate:

$$\text{Box 1: Rate} = k(5)(5)^2 = 125k$$

Box 2 contains 7 red spheres and 3 purple spheres:

$$\text{Box 2: Rate} = k(7)(3)^2 = 63k$$

Box 3 contains 3 red spheres and 7 purple spheres:

$$\text{Box 3: Rate} = k(3)(7)^2 = 147k$$

The slowest rate is $63k$ (box 2), and the highest is $147k$ (box 3). Thus, the rates vary in the order $2 < 1 < 3$.

Check: Each box contains 10 spheres. The rate law indicates that in this case [B] has a greater influence on rate than [A] because B has a higher reaction order. Hence, the mixture with the highest concentration of B (most purple spheres) should react fastest. This analysis confirms the order $2 < 1 < 3$.

PRACTICE EXERCISE
Assuming that rate = k[A][B], rank the mixtures represented in this Sample Exercise in order of increasing rate.

Answer: $2 = 3 < 1$

SAMPLE EXERCISE 14.5 Determining Reaction Orders and Units for Rate Constants

(a)What are the overall reaction orders for the rate laws described in Equations 14.9 and 14.10? **(b)** What are the units of the rate constant for the rate law for Equation 14.9?

Solution

Analyze: We are given two rate laws and asked to express **(a)** the overall reaction order for each and **(b)** the units for the rate constant for the first reaction.

Plan: The overall reaction order is the sum of the exponents in the rate law. The units for the rate constant, k, are found by using the normal units for rate (M/s) and concentration (M) in the rate law and applying algebra to solve for k.

Solve: (a) The rate of the reaction in Equation 14.9 is first order in N_2O_5 and first order overall. The reaction in Equation 14.10 is first order in $CHCl_3$ and one-half order in Cl_2. The overall reaction order is three halves.
  (b) For the rate law for Equation 14.9, we have

$$\text{Units of rate} = (\text{units of rate constant})(\text{units of concentration})$$

So

$$\text{Units of rate constant} = \frac{\text{units of rate}}{\text{units of concentration}} = \frac{M/s}{M} = s^{-1}$$

Notice that the units of the rate constant change as the overall order of the reaction changes.

PRACTICE EXERCISE

(a) What is the reaction order of the reactant H_2 in Equation 14.11? **(b)** What are the units of the rate constant for Equation 14.11?

Answers: **(a)** 1, **(b)** $M^{-1} s^{-1}$

SAMPLE EXERCISE 14.6 Determining a Rate Law from Initial Rate Data

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

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

Using these data, determine **(a)** the rate law for the reaction, **(b)** the magnitude of the rate constant, **(c)** the rate of the reaction when $[A] = 0.050\ M$ and $[B] = 0.100\ M$.

Solution

Analyze: We are given a table of data that relates concentrations of reactants with initial rates of reaction and asked to determine
(a) the rate law, **(b)** the rate constant, and **(c)** the rate of reaction for a set of concentrations not listed in the table.

Plan: **(a)** We assume that the rate law has the following form: Rate $= k[A]^m[B]^n$, so we must use the given data to deduce the reaction orders m and n. We do so by determining how changes in the concentration change the rate. **(b)** Once we know m and n, we can use the rate law and one of the sets of data to determine the rate constant k. **(c)** Now that we know both the rate constant and the reaction orders, we can use the rate law with the given concentrations to calculate rate.

Solve: **(a)** As we move from experiment 1 to experiment 2, [A] is held constant and [B] is doubled. Thus, this pair of experiments shows how [B] affects the rate, allowing us to deduce the order of the rate law with respect to B. Because the rate remains the same when [B] is doubled, the concentration of B has no effect on the reaction rate. The rate law is therefore zero order in B (that is, $n = 0$).

In experiments 1 and 3, [B] is held constant so these data show how [A] affects rate. Holding [B] constant while doubling [A] increases the rate fourfold. This result indicates that rate is proportional to $[A]^2$ (that is, the reaction is second order in A). Hence, the rate law is

$$\text{Rate} = k[A]^2[B]^0 = k[A]^2$$

This rate law could be reached in a more formal way by taking the ratio of the rates from two experiments:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{4.0 \times 10^{-5} \, M/s}{4.0 \times 10^{-5} \, M/s} = 1$$

Using the rate law, we have

$$1 = \frac{\text{rate 2}}{\text{rate 1}} = \frac{k[0.100 \, M]^m[0.200 \, M]^n}{k[0.100 \, M]^m[0.100 \, M]^n} = \frac{[0.200]^n}{[0.100]^n} = 2^n$$

2^n equals 1 under only one condition:

$$n = 0$$

We can deduce the value of m in a similar fashion

$$\frac{\text{Rate 3}}{\text{Rate 1}} = \frac{16.0 \times 10^{5} \, M/s}{4.0 \times 10^{-5} \, M/s} = 4$$

Using the rate law gives

$$4 = \frac{\text{rate 3}}{\text{rate 1}} = \frac{k[0.200 \, M]^m[0.100 \, M]^n}{k[0.100 \, M]^m[0.100 \, M]^n} = \frac{[0.200]^m}{[0.100]^m} = 2^m$$

Because $2^m = 4$, we conclude that

$$m = 2$$

(b) Using the rate law and the data from experiment 1, we have

$$k = \frac{\text{rate}}{[A]^2} = \frac{4.0 \times 10^{-5} \, M/s}{(0.100 \, M)^2} = 4.0 \times 10^{-3} \, M^{-1} s^{-1}$$

(c) Using the rate law from part (a) and the rate constant from part (b), we have

$$\text{Rate} = k[A]^2 = (4.0 \times 10^{-3} \, M^{-1} s^{-1})(0.050 \, M)^2 = 1.0 \times 10^{-5} \, M/s$$

Because [B] is not part of the rate law, it is irrelevant to the rate, provided that there is at least some B present to react with A.

Check: A good way to check our rate law is to use the concentrations in experiment 2 or 3 and see if we can correctly calculate the rate. Using data from experiment 3, we have

$$\text{Rate} = k[A]^2 = (4.0 \times 10^{-3} \, M^{-1} s^{-1})(0.200 \, M)^2 = 1.60 \times 10^{-4} \, M/s$$

Thus, the rate law correctly reproduces the data, giving both the correct number and the correct units for the rate.

PRACTICE EXERCISE

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

$$2\,NO(g) + 2\,H_2(g) \longrightarrow N_2(g) + 2\,H_2O(g)$$

Experiment Number	[NO] (M)	[H$_2$] (M)	Initial Rate (M/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

(a) Determine the rate law for this reaction. **(b)** Calculate the rate constant. **(c)** Calculate the rate when [NO] = 0.050 M and [H$_2$] = 0.150 M.

Answers: **(a)** rate = $k[NO]^2[H_2]$; **(b)** k =1.2 $M^{-2}s^{-1}$; **(c)** rate = 4.5×10^{-4} M/s

SAMPLE EXERCISE 14.7 Using the Integrated First-Order Rate Law

The decomposition of a certain insecticide in water follows first-order kinetics with a rate constant of 1.45 yr^{-1} at 12°C. A quantity of this insecticide is washed into a lake on June 1, leading to a concentration of 5.0×10^{-7} g/cm³. Assume that the average temperature of the lake is 12°C. **(a)** What is the concentration of the insecticide on June 1 of the following year? **(b)** How long will it take for the concentration of the insecticide to drop to 3.0×10^{-7} g/cm³?

Solution

Analyze: We are given the rate constant for a reaction that obeys first-order kinetics, as well as information about concentrations and times, and asked to calculate how much reactant (insecticide) remains after one year. We must also determine the time interval needed to reach a particular insecticide concentration. Because the exercise gives time in (a) and asks for time in (b), we know that the integrated rate law, Equation 14.13, is required.

Plan: (a) We are given $k = 1.45$ yr^{-1}, $t = 1.00$ yr, and $[\text{insecticide}]_0 = 5.0 \times 10^{-7}$ g/cm³, and so Equation 14.13 can be solved for $\ln[\text{insecticide}]_t$. **(b)** We have $k = 1.45 yr^{-1}$, $[\text{insecticide}]_0 = 5.0 \times 10^{-7}$ g/cm³, and $[\text{insecticide}]_t = 3.0 \times 10^{-7}$ g/cm³, and so we can solve Equation 14.13 for t.

Solve: (a) Substituting the known quantities into Equation 14.13, we have

$$\ln[\text{insecticide}]_{t=1\text{ yr}} = -(1.45 \text{ yr}^{-1})(1.00 \text{ yr}) + \ln(5.0 \times 10^{-7})$$

We use the ln function on a calculator to evaluate the second term on the right, giving

$$\ln[\text{insecticide}]_{t=1\text{ yr}} = -1.45 + (-14.51) = -15.96$$

To obtain $[\text{insecticide}]_{t=1\text{ yr}}$, we use the inverse natural logarithm, or e^x, function on the calculator:

$$[\text{insecticide}]_{t=1\text{ yr}} = e^{-15.96} = 1.2 \times 10^{-7} \text{ g/cm}^3$$

Note that the concentration units for $[A]_t$ and $[A]_0$ must be the same.

(b) Again substituting into Equation 14.13, with $[\text{insecticide}]_t = 3.0 \times 10^{-7}$ g/cm³, gives

$$\ln(3.0 \times 10^{-7}) = -(1.45 \text{ yr}^{-1})(t) + \ln(5.0 \times 10^{-7})$$

Solving for t gives

$$t = -[\ln(3.0 \times 10^{-7}) - \ln(5.0 \times 10^{-7})]/1.45 \text{ yr}^{-1}$$
$$= -(-15.02 + 14.51)/1.45 \text{ yr}^{-1} = 0.35 \text{ yr}$$

Check: In part (a) the concentration remaining after 1.00 yr (that is, 1.2×10^{-7} g/cm³) is less than the original concentration (5.0×10^{-7} g/cm³), as it should be. In (b) the given concentration (3.0×10^{-7} g/cm³) is greater than that remaining after 1.00 yr, indicating that the time must be less than a year. Thus, $t = 0.35$ yr is a reasonable answer.

PRACTICE EXERCISE

The decomposition of dimethyl ether, $(CH_3)_2O$, at 510°C is a first-order process with a rate constant of $6.8 \times 10^{-4} \text{s}^{-1}$:

$$(CH_3)_2O(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$
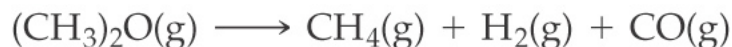
If the initial pressure of $(CH_3)_2O$ is 135 torr, what is its partial pressure after 1420 s?

Answer: 51 torr

SAMPLE EXERCISE 14.8 Determining Reaction Order from the Integrated Rate Law

The following data were obtained for the gas-phase decomposition of nitrogen dioxide at 300°C,
$NO_2(g) \longrightarrow NO(g) + \frac{1}{2} O_2(g)$:

Time (s)	$[NO_2]$ (M)
0.0	0.01000
50.0	0.00787
100.0	0.00649
200.0	0.00481
300.0	0.00380

Is the reaction first or second order in NO_2?

Solution

Analyze: We are given the concentrations of a reactant at various times during a reaction and asked to determine whether the reaction is first or second order.

Plan: We can plot $\ln[NO_2]$ and $1/[NO_2]$ against time. One or the other will be linear, indicating whether the reaction is first or second order.

Solve: In order to graph $\ln[NO_2]$ and $1/[NO_2]$ against time, we will first prepare the following table from the data given:

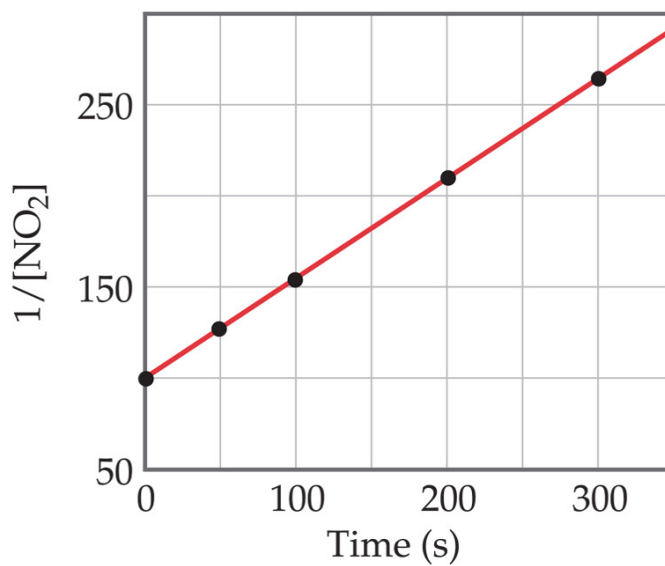| Time (s)	$[NO_2]$ (M)	$\ln[NO_2]$	$1/[NO_2]$
0.0	0.01000	−4.610	100
50.0	0.00787	−4.845	127
100.0	0.00649	−5.038	154
200.0	0.00481	−5.337	208
300.0	0.00380	−5.573	263

As Figure 14.8 shows, only the plot of $1/[NO_2]$ versus time is linear. Thus, the reaction obeys a second-order rate law: Rate $= k[NO_2]^2$. From the slope of this straight-line graph, we determine that $k = 0.543$ M^{-1} s^{-1} for the disappearance of NO_2.
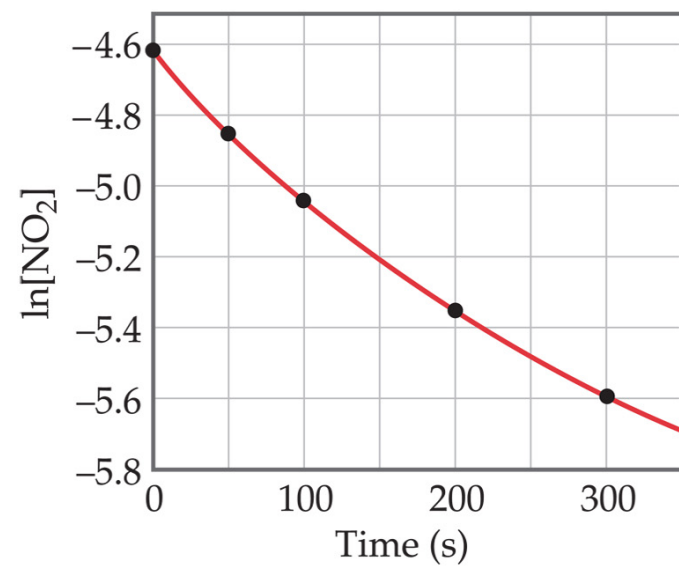
Figure 14.8 **Kinetic data for decomposition of NO₂.** The reaction is $NO_2(g) \longrightarrow NO(g) + \frac{1}{2}O_2(g)$, and the data were collected at 300°C. (a) A plot of $[NO_2]$ versus time is not linear, indicating that the reaction is not first order in NO_2. (b) A plot of $1/[NO_2]$ versus time is linear, indicating that the reaction is second order in NO_2.

PRACTICE EXERCISE

Consider again the decomposition of NO_2 discussed in the Sample Exercise. The reaction is second order in NO_2 with $k = 0.543$ $M^{-1}s^{-1}$. If the initial concentration of NO_2 in a closed vessel is 0.0500 M, what is the remaining concentration after 0.500 h?

Answer: Using Equation 14.14, we find $[NO2] = 1.00 \times 10^{-3}$ M

SAMPLE EXERCISE 14.9 Determining the Half-life of a First-Order Reaction

The reaction of C_4H_9Cl with water is a first-order reaction. Figure 14.4 shows how the concentration of C_4H_9Cl changes with time at a particular temperature. **(a)** From that graph, estimate the half-life for this reaction. **(b)** Use the half-life from (a) to calculate the rate constant.

Solution

Analyze: We are asked to estimate the half-life of a reaction from a graph of concentration versus time and then to use the half-life to calculate the rate constant for the reaction.

Plan: (a) To estimate a half-life, we can select a concentration and then determine the time required for the concentration to decrease to half of that value. **(b)** Equation 14.15 is used to calculate the rate constant from the half-life.

Solve: (a) From the graph, we see that the initial value of $[C_4H_9Cl]$ is 0.100 M. The half-life for this first-order reaction is the time required for $[C_4H_9Cl]$ to decrease to 0.050 M, which we can read off the graph. This point occurs at approximately 340 s.

    (b) Solving Equation 14.15 for k, we have

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{340\ \text{s}} = 2.0 \times 10^{-3}\ \text{s}^{-1}$$

Check: At the end of the second half-life, which should occur at 680 s, the concentration should have decreased by yet another factor of 2, to 0.025 M. Inspection of the graph shows that this is indeed the case.

PRACTICE EXERCISE

(a) Using Equation 14.15, calculate $t_{1/2}$ for the decomposition of the insecticide described in Sample Exercise 14.7. **(b)** How long does it take for the concentration of the insecticide to reach one-quarter of the initial value?

Answers: **(a)** 0.478 yr $= 1.51 \times 10^{-7}$ s; **(b)** it takes two half-lives, $2(0.478\ \text{yr}) = 0.956$ yr

Consider a series of reactions having the following energy profiles:
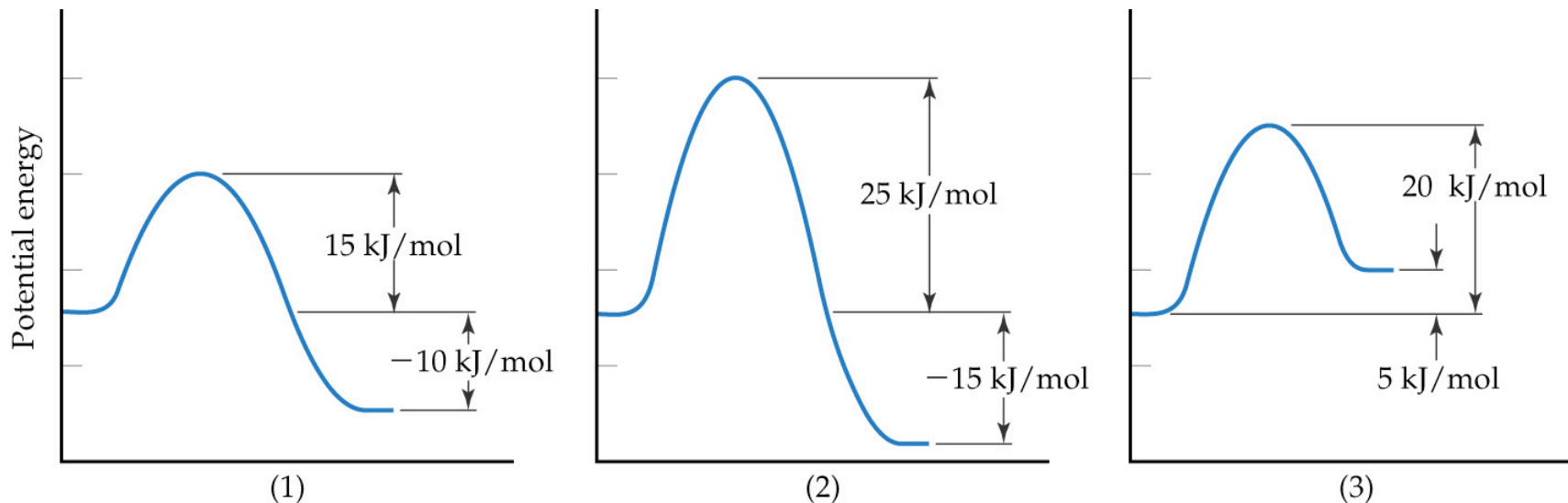
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Assuming that all three reactions have nearly the same frequency factors, rank the reactions from slowest to fastest.

Solution The lower the activation energy, the faster the reaction. The value of ΔE does not affect the rate. Hence the order is $(2) < (3) < (1)$.

PRACTICE EXERCISE
Imagine that these reactions are reversed. Rank these reverse reactions from slowest to fastest.

Answer: $(2) < (1) < (3)$ because E_a values are 40, 25, and 15 kJ/mol, respectively

The following table shows the rate constants for the rearrangement of methyl isonitrile at various temperatures (these are the data in Figure 14.12):

Temperature (°C)	$k(s^{-1})$
189.7	2.52×10^{-5}
198.9	5.25×10^{-5}
230.3	6.30×10^{-4}
251.2	3.16×10^{-3}

(a) From these data, calculate the activation energy for the reaction. **(b)** What is the value of the rate constant at 430.0 K?

Solution

Analyze: We are given rate constants, k, measured at several temperatures and asked to determine the activation energy, E_a, and the rate constant, k, at a particular temperature.

Plan: We can obtain E_a from the slope of a graph of $\ln k$ versus $1/T$. Once we know E_a, we can use Equation 4.21 together with the given rate data to calculate the rate constant at 430.0 K.
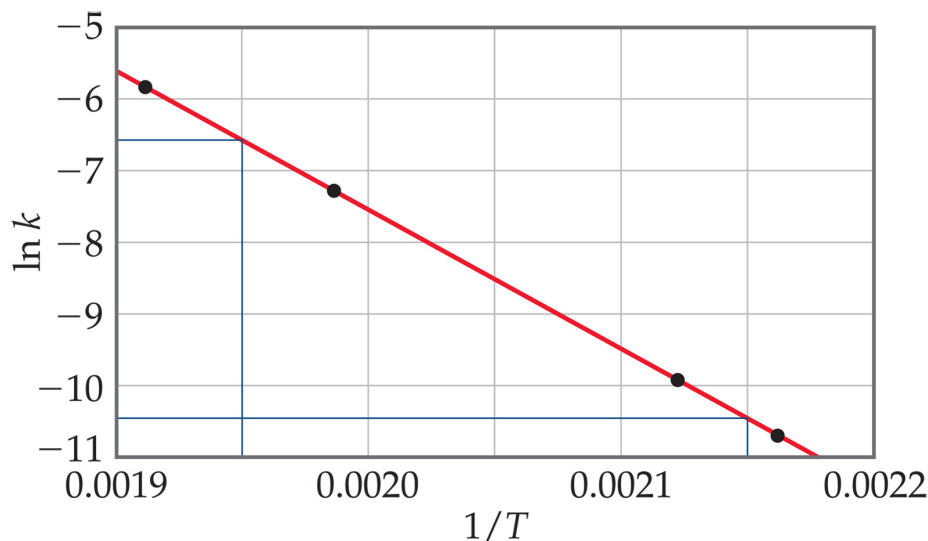
Solve: **(a)** We must first convert the temperatures from degrees Celsius to kelvins. We then take the inverse of each temperature, $1/T$, and the natural log of each rate constant, $\ln k$. This gives us the table shown at the right:

T(K)	$1/T$ (K^{-1})	$\ln k$
462.9	2.160×10^{-3}	-10.589
472.1	2.118×10^{-3}	-9.855
503.5	1.986×10^{-3}	-7.370
524.4	1.907×10^{-3}	-5.757

A graph of $\ln k$ versus $1/T$ results in a straight line, as shown in Figure 14.17.

Figure 14.17 Graphical determination of activation energy. The natural logarithm of the rate constant for the rearrangement of methyl isonitrile is plotted as a function of $1/T$. The linear relationship is predicted by the Arrhenius equation giving a slope equal to $-E_a/R$.

The slope of the line is obtained by choosing two well-separated points, as shown, and using the coordinates of each:

$$\text{Slope} = \frac{\Delta y}{\Delta x} = \frac{-6.6 - (-10.4)}{0.00195 - 0.00215} = -1.9 \times 10^4$$

Because logarithms have no units, the numerator in this equation is dimensionless. The denominator has the units of $1/T$, namely, K^{-1}. Thus, the overall units for the slope are K. The slope equals $-E_a/R$. We use the value for the molar gas constant R in units of J/mol-K (Table 10.2). We thus obtain

$$\text{Slope} = -\frac{E_a}{R}$$

$$E_a = -(\text{slope})(R) = -(-1.9 \times 10^4 \, K)\left(8.314\frac{J}{\text{mol-K}}\right)\left(\frac{1 \, kJ}{1000 \, J}\right)$$

$$= 1.6 \times 10^2 \, kJ/mol = 160 \, kJ/mol$$

We report the activation energy to only two significant figures because we are limited by the precision with which we can read the graph in Figure 14.17.

(b) To determine the rate constant, k_1, at $T = 430.0$ K, we can use Equation 14.21 with $E_a = 160$ kJ/ mol, and one of the rate constants and temperatures from the given data, such as $k_2 = 2.52 \times 10^{-5}s^{-1}$ and $T_2 = 462.9$ K:

$$\ln\left(\frac{k_1}{2.52 \times 10^{-5} \, s^{-1}}\right) = \left(\frac{160 \, kJ/mol}{8.314 \, J/mol\text{-}K}\right)\left(\frac{1}{462.9 \, K} - \frac{1}{430.0 \, K}\right)\left(\frac{1000 \, J}{1 \, kJ}\right) = -3.18$$

Thus,

$$\frac{k_1}{2.52 \times 10^{-5}\,\text{s}^{-1}} = e^{-3.18} = 4.15 \times 10^{-2}$$

$$k_1 = (4.15 \times 10^{-2})(2.52 \times 10^{-5}\,\text{s}^{-1}) = 1.0 \times 10^{-6}\,\text{s}^{-1}$$

Note that the units of k_1 are the same as those of k_2.

PRACTICE EXERCISE

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

Answer: $2.2 \times 10^{-2}\,\text{s}^{-1}$

SAMPLE EXERCISE 14.12 Determining Molecularity and Identifying Intermediates

It has been proposed that the conversion of ozone into O_2 proceeds by a two-step mechanism:

$$O_3(g) \longrightarrow O_2(g) + O(g)$$
$$O_3(g) + O(g) \longrightarrow 2\,O_2(g)$$
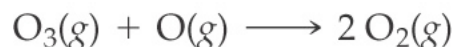
(a) Describe the molecularity of each elementary reaction in this mechanism. **(b)** Write the equation for the overall reaction. **(c)** Identify the intermediate(s).

Solution

Analyze: We are given a two-step mechanism and asked for **(a)** the molecularities of each of the two elementary reactions, **(b)** the equation for the overall process, and **(c)** the intermediate.

Plan: The molecularity of each elementary reaction depends on the number of reactant molecules in the equation for that reaction. The overall equation is the sum of the equations for the elementary reactions. The intermediate is a substance formed in one step of the mechanism and used in another and therefore not part of the equation for the overall reaction.

Solve: **(a)** The first elementary reaction involves a single reactant and is consequently unimolecular. The second reaction, which involves two reactant molecules, is bimolecular.

(b) Adding the two elementary reactions gives

$$2\,O_3(g) + O(g) \longrightarrow 3\,O_2(g) + O(g)$$

Because $O(g)$ appears in equal amounts on both sides of the equation, it can be eliminated to give the net equation for the chemical process:

$$2\,O_3(g) \longrightarrow 3\,O_2(g)$$

(c) The intermediate is $O(g)$. It is neither an original reactant nor a final product, but is formed in the first step of the mechanism and consumed in the second.
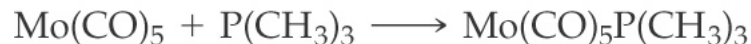
PRACTICE EXERCISE

For the reaction

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

the proposed mechanism is

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

$$Mo(CO)_5 + P(CH_3)_3 \longrightarrow Mo(CO)_5P(CH_3)_3$$

(a) Is the proposed mechanism consistent with the equation for the overall reaction? (b) What is the molecularity of each step of the mechanism? (c) Identify the intermediate(s).

Answers: (a) Yes, the two equations add to yield the equation for the reaction. (b) The first elementary reaction is unimolecular, and the second one is bimolecular. (c) $Mo(CO)_5$

SAMPLE EXERCISE 14.13 Predicting the Rate Law for an Elementary Reaction

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

$$H_2(g) + Br_2(g) \longrightarrow 2\,HBr(g)$$
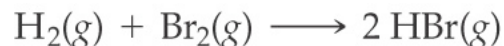
Solution

Analyze: We are given the equation and asked for its rate law, assuming that it is an elementary process.

Plan: Because we are assuming that the reaction occurs as a single elementary reaction, we are able to write the rate law using the coefficients for the reactants in the equation as the reaction orders.

Solve: The reaction is bimolecular, involving one molecule of H_2 with one molecule of Br_2. Thus, the rate law is first order in each reactant and second order overall:

$$Rate = k[H_2][Br_2]$$

Comment: Experimental studies of this reaction show that the reaction actually has a very different rate law:

$$Rate = k[H_2][Br_2]^{1/2}$$

Because the experimental rate law differs from the one obtained by assuming a single elementary reaction, we can conclude that the mechanism must involve two or more elementary steps.

PRACTICE EXERCISE

Consider the following reaction: $2\,NO(g) + Br_2(g) \longrightarrow 2\,NOBr(g)$. **(a)** Write the rate law for the reaction, assuming it involves a single elementary reaction. **(b)** Is a single-step mechanism likely for this reaction?

Answers: **(a)** Rate = $k[NO]^2[Br_2]$ **(b)** No, because termolecular reactions are very rare

SAMPLE EXERCISE 14.14 Determining the Rate Law for a Multistep Mechanism

The decomposition of nitrous oxide, N_2O, is believed to occur by a two-step mechanism:

$$N_2O(g) \longrightarrow N_2(g) + O(g) \quad \text{(slow)}$$
$$N_2O(g) + O(g) \longrightarrow N_2(g) + O_2(g) \quad \text{(fast)}$$
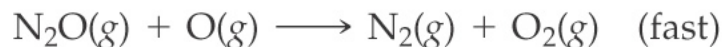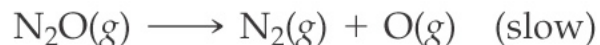
(a) Write the equation for the overall reaction. **(b)** Write the rate law for the overall reaction.

Solution

Analyze: Given a multistep mechanism with the relative speeds of the steps, we are asked to write the overall reaction and the rate law for that overall reaction.

Plan: **(a)** The overall reaction is found by adding the elementary steps and eliminating the intermediates.
(b) The rate law for the overall reaction will be that of the slow, rate-determining step.

Solve: **(a)** Adding the two elementary reactions gives

$$2\,N_2O(g) + O(g) \longrightarrow 2\,N_2(g) + O_2(g) + O(g)$$
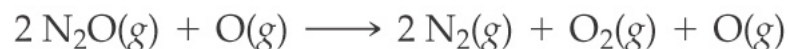
Omitting the intermediate, $O(g)$, which occurs on both sides of the equation, gives the overall reaction:

$$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$$
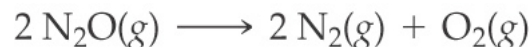
(b) The rate law for the overall reaction is just the rate law for the slow, rate-determining elementary reaction. Because that slow step is a unimolecular elementary reaction, the rate law is first order:

$$\text{Rate} = k[N_2O]$$

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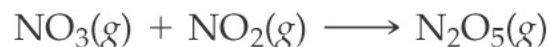
Ozone reacts with nitrogen dioxide to produce dinitrogen pentoxide and oxygen:

$$O_3(g) + 2 NO_2(g) \longrightarrow N_2O_5(g) + O_2(g)$$

The reaction is believed to occur in two steps

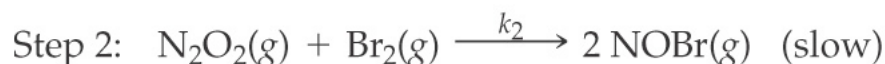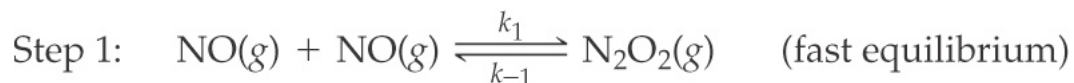$$O_3(g) + NO_2(g) \longrightarrow NO_3(g) + O_2(g)$$

$$NO_3(g) + NO_2(g) \longrightarrow N_2O_5(g)$$

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

Answer: Because the rate law conforms to the molecularity of the first step, that must be the rate-determining step. The second step must be much faster than the first one.

Show that the following mechanism for Equation 14.24 also produces a rate law consistent with the experimentally observed one:

Step 1: $NO(g) + NO(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2(g)$ (fast equilibrium)

Step 2: $N_2O_2(g) + Br_2(g) \overset{k_2}{\longrightarrow} 2\,NOBr(g)$ (slow)

Solution

Analyze: We are given a mechanism with a fast initial step and asked to write the rate law for the overall reaction.

Plan: The rate law of the slow elementary step in a mechanism determines the rate law for the overall reaction. Thus, we first write the rate law based on the molecularity of the slow step. In this case the slow step involves the intermediate N_2O_2 as a reactant. Experimental rate laws, however, do not contain the concentrations of intermediates, but are expressed in terms of the concentrations of starting substances. Thus, we must relate the concentration of N_2O_2 to the concentration of NO by assuming that an equilibrium is established in the first step.

Solve: The second step is rate determining, so the overall rate is

$$Rate = k2[N_2O_2][Br_2]$$

We solve for the concentration of the intermediate N_2O_2 by assuming that an equilibrium is established in step 1; thus, the rates of the forward and reverse reactions in step 1 are equal:

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$[N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$
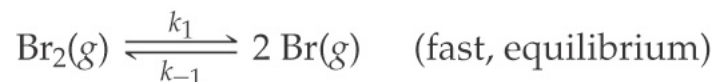
Substituting this expression into the rate expression gives

$$\text{Rate} = k_2 \frac{k_1}{k_{-1}}[\text{NO}]^2[\text{Br}_2] = k[\text{NO}]^2[\text{Br}_2]$$

Thus, this mechanism also yields a rate law consistent with the experimental one.

PRACTICE EXERCISE

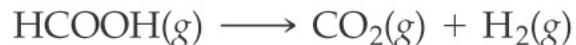The first step of a mechanism involving the reaction of bromine is

$$\text{Br}_2(g) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,\text{Br}(g) \quad \text{(fast, equilibrium)}$$

What is the expression relating the concentration of $\text{Br}(g)$ to that of $\text{Br}_2(g)$?

Answer: $[\text{Br}] = \left(\dfrac{k_1}{k_{-1}}[\text{Br}_2] \right)^{1/2}$

SAMPLE INTEGRATIVE EXERCISE Putting Concepts Together

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

$$HCOOH(g) \longrightarrow CO_2(g) + H_2(g)$$

The decomposition reaction is determined to be first order. A graph of the partial pressure of HCOOH versus time for decomposition at 838 K is shown as the red curve in Figure 14.28. When a small amount of solid ZnO is added to the reaction chamber, the partial pressure of acid versus time varies as shown by the blue curve in Figure 14.28.
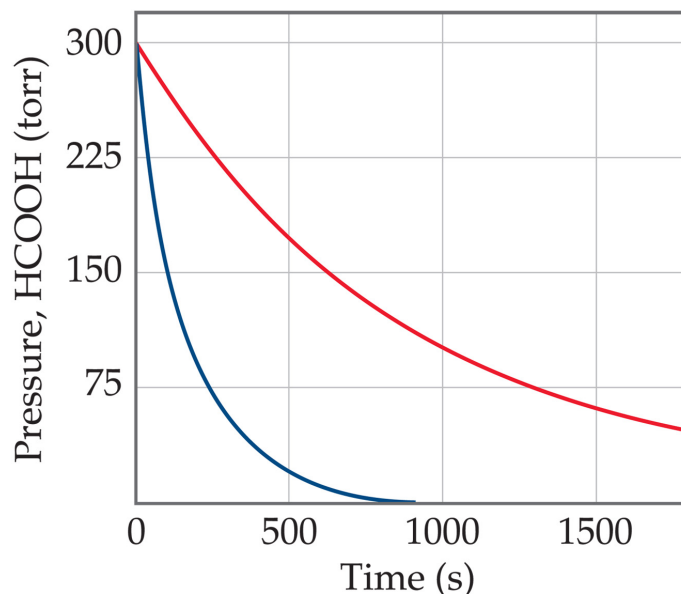

Figure 14.28 Variation in pressure of HCOOH(g) as a function of time at 838 K. The red line corresponds to decomposition when only gaseous HCOOH is present. The blue line corresponds to decomposition in the presence of added ZnO(s).

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(a) Estimate the half-life and first-order rate constant for formic acid decomposition.
(b) What can you conclude from the effect of added ZnO on the decomposition of formic acid?

(c) The progress of the reaction was followed by measuring the partial pressure of formic acid vapor at selected times. Suppose that, instead, we had plotted the concentration of formic acid in units of mol/L. What effect would this have had on the calculated value of k?

(d) The pressure of formic acid vapor at the start of the reaction is 3.00×10^2 torr. Assuming constant temperature and ideal-gas behavior, what is the pressure in the system at the end of the reaction? If the volume of the reaction chamber is 436 cm³, how many moles of gas occupy the reaction chamber at the end of the reaction?

(e) The standard heat of formation of formic acid vapor is $\Delta H_f^\circ = -378.6 \text{ kJ/mol}$. Calculate ΔH° for the overall reaction. Assuming that the activation energy (E_a) for the reaction is 184 kJ/mol, sketch an approximate energy profile for the reaction, and label E_a, ΔH°, and the transition state.

Solution (a) The initial pressure of HCOOH is 3.00×10^2 torr. On the graph we move to the level at which the partial pressure of HCOOH is 150 torr, half the initial value. This corresponds to a time of about 6.60×10^2s, which is therefore the half-life. The first-order rate constant is given by Equation 14.15: $k = 0.693/t_{1/2} = 0.693/660 \text{ s} = 1.05 \times 10^{-3} \text{ s}^{-1}$.

(b) The reaction proceeds much more rapidly in the presence of solid ZnO, so the surface of the oxide must be acting as a catalyst for the decomposition of the acid. This is an example of heterogeneous catalysis.

(c) If we had graphed the concentration of formic acid in units of moles per liter, we would still have determined that the half-life for decomposition is 660 seconds, and we would have computed the same value for k. Because the units for k are s⁻¹, the value for k is independent of the units used for concentration.

(d) According to the stoichiometry of the reaction, two moles of product are formed for each mole of reactant. When reaction is completed, therefore, the pressure will be 600 torr, just twice the initial pressure, assuming ideal-gas behavior. (Because we are working at quite high temperature and fairly low gas pressure, assuming ideal-gas behavior is reasonable.) The number of moles of gas present can be calculated using the ideal-gas equation (Section 10.4):
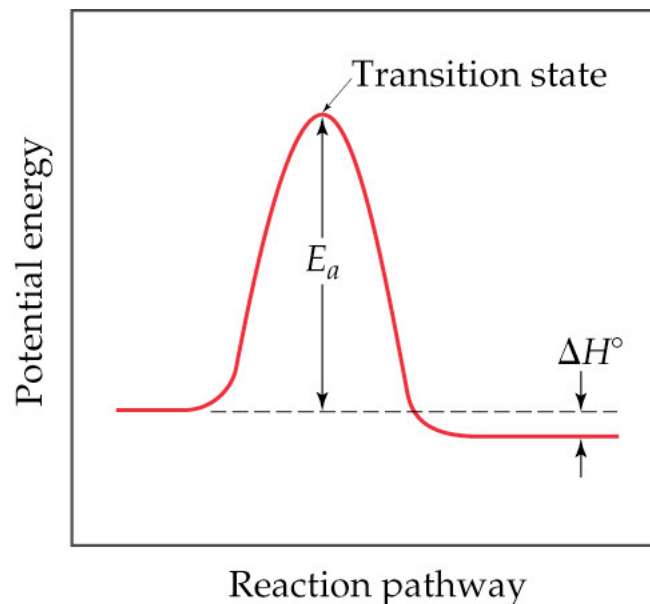
$$n = \frac{PV}{RT} = \frac{(600/760 \text{ atm}) (0.436 \text{ L})}{(0.0821 \text{ L-atm/mol-K})(838 \text{ K})} = 5.00 \times 10^{-3} \text{ moles}$$

(e) We first calculate the overall change in energy, ΔH° (Section 5.7 and Appendix C), as in

$$\Delta H^\circ = \Delta H_f^\circ(CO_2(g)) + \Delta H_f^\circ(H_2(g)) - \Delta H_f^\circ(HCOOH(g))$$
$$= -393.5 \text{ kJ/mol} + 0 - (-378.6 \text{ kJ/mol})$$
$$= -14.9 \text{ kJ/mol}$$

From this and the given value for E_a, we can draw an approximate energy profile for the reaction, in analogy to Figure 14.15.

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