Chemistry 2e
12: Kinetics
12.1: Chemical Reaction Rates

1. What is the difference between average rate, initial rate, and instantaneous rate?

Solution

The instantaneous rate is the rate of a reaction at any particular point in time, a period of time that is so short that the concentrations of reactants and products change by a negligible amount. The initial rate is the instantaneous rate of reaction as it starts (as product just begins to form). Average rate is the average of the instantaneous rates over a time period.

3. In the nuclear industry, chlorine trifluoride is used to prepare uranium hexafluoride, a volatile compound of uranium used in the separation of uranium isotopes. Chlorine trifluoride is prepared by the reaction $\mathrm{Cl_2}(g) + 3\mathrm{F_2}(g) \longrightarrow 2\mathrm{ClF_3}(g)$. Write the equation that relates the rate expressions for this reaction in terms of the disappearance of Cl_2 and F_2 and the formation of ClF_3.

Solution

Write the rate of change with a negative sign for substances decreasing in concentration (reactants) and a positive sign for those substances being formed (products). Multiply each term by the reciprocal of its coefficient:

$$\text{rate} = +\frac{1}{2}\frac{\Delta[\mathrm{ClF_3}]}{\Delta t} = -\frac{\Delta[\mathrm{Cl_2}]}{\Delta t} = -\frac{1}{3}\frac{\Delta[\mathrm{F_2}]}{\Delta t}$$

5. A study of the rate of the reaction represented as $2A \longrightarrow B$ gave the following data:

Time (s)	0.0	5.0	10.0	15.0	20.0	25.0	35.0
[*A*] (*M*)	1.00	0.775	0.625	0.465	0.360	0.285	0.230

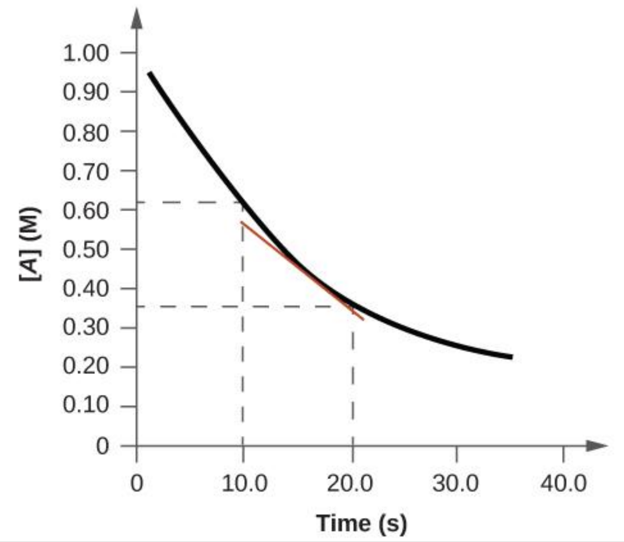
(a) Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.

(b) Estimate the instantaneous rate of disappearance of *A* at 15.0 s from a graph of time versus [*A*]. What are the units of this rate?

(c) Use the rates found in parts (a) and (b) to determine the average rate of formation of *B* between 0.00 s and 10.0 s, and the instantaneous rate of formation of *B* at 15.0 s.

Solution

Plot the concentration against time and determine the required slopes:



(a) Average rates are computed directly from the reaction's rate expression and the specified concentration/time data:

$$\text{average rate, } 0 - 10 \text{ s} = -\frac{0.625\ M - 1.00\ M}{10.0 \text{ s} - 0.00 \text{ s}} = 0.0375 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{average rate, } 10 - 20 \text{ s} = -\frac{0.360\ M - 0.625\ M}{20.0 \text{ s} - 10.0 \text{ s}} = 0.0265 \text{ mol L}^{-1} \text{ s}^{-1};$$

(b) The instantaneous rate is estimated as the slope of a line tangent to the curve at 15 s. Such a line is drawn in the plot, and two concentration/time data pairs are used to estimate the line's slope:

$$\text{instantaneous rate, } 15 \text{ s} = -\frac{0.35\ M - 0.58\ M}{20.0 \text{ s} - 10.0 \text{ s}} = 0.023 \text{ mol L}^{-1} \text{ s}^{-1};$$

(c) To derive rates for the formation of *B* from the previously calculated rates for the disappearance of *A*, we consider the stoichiometry of the reaction, namely, *B* will be produced at one-half the rate of the disappearance of *A*:

$$\text{rate} = -\frac{1}{2}\frac{\Delta[\text{A}]}{\Delta t} = \frac{\Delta[\text{B}]}{\Delta t}$$

$$\text{average rate for B formation} = \frac{0.0375 \text{ mol L}^{-1} \text{ s}^{-1}}{2} = 0.0188 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\text{instantaneous rate for B formation} = \frac{0.023 \text{ mol L}^{-1} \text{ s}^{-1}}{2} = 0.0120 \text{ mol L}^{-1} \text{ s}^{-1}$$

Chemistry 2e
12: Kinetics
12.2: Factors Affecting Reaction Rates

7. Describe the effect of each of the following on the rate of the reaction of magnesium metal with a solution of hydrochloric acid: the molarity of the hydrochloric acid, the temperature of the solution, and the size of the pieces of magnesium.

Solution

Higher molarity increases the rate of the reaction. Higher temperature increases the rate of the reaction. Smaller pieces of magnesium metal will react more rapidly than larger pieces because more reactive surface exists.

9. Go to the Reactions & Rates (https://openstaxcollege.org/l/16PHETrecation) interactive. Use the Single Collision tab to represent how the collision between monatomic oxygen (O) and carbon monoxide (CO) results in the breaking of one bond and the formation of another. Pull back on the red plunger to release the atom and observe the results. Then, click on “Reload Launcher” and change to “Angled shot” to see the difference.

(a) What happens when the angle of the collision is changed?

(b) Explain how this is relevant to rate of reaction.

Solution

(a) Depending on the angle selected, the atom may take a long time to collide with the molecule and, when a collision does occur, it may not result in the breaking of the bond and the forming of the other. (b) Particles of reactant must come into contact with each other before they can react.

11. In the PhET Reactions & Rates (https://openstaxcollege.org/l/16PHETrecation)interactive, on the Many Collisions tab, set up a simulation with 15 molecules of A and 10 molecules of BC. Select “Show Bonds” under Options.

(a) Leave the Initial Temperature at the default setting. Observe the reaction. Is the rate of reaction fast or slow?

(b) Click “Pause” and then “Reset All,” and then enter 15 molecules of A and 10 molecules of BC once again. Select “Show Bonds” under Options. This time, increase the initial temperature until, on the graph, the total average energy line is completely above the potential energy curve. Describe what happens to the reaction.

Solution

(a) At the default temperature, the rate of reaction is very slow. Even though *A* molecules collide with *BC* molecules quite frequently, very few of them have enough energy to bond. (b) As the temperature is increased, the reaction proceeds at a faster rate. The amount of reactants decreases, and the amount of products increases. After a while, there is a roughly equal amount of *BC*, *AB*, and *C* in the mixture and a slight excess of *A*.

Chemistry 2e
12: Kinetics
12.3: Rate Laws

13. Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:
(a) What is the order of the reaction with respect to that reactant?
(b) Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

Solution
(a) Since the concentration of the reactant doubled and the rate quadrupled, we can conclude that the order with respect to the reactant is 2, since $2^2 = 4$.

$$\text{rate } = k\left[\text{reactant}\right]^{m}$$

$$4\left(\text{rate}\right) = k\left[2\left(\text{reactant}\right)\right]^{2};$$

(b) Since the concentration of the reactant and the rate both tripled, we can conclude that $m=1$, and the order with respect to this reactant is 1.

$$\text{rate } = k\left[\text{reactant}\right]^{m}$$

$$3\left(\text{rate}\right) = k\left[3\left(\text{reactant}\right)\right]^{1}$$

15. How will the rate of reaction change for the process:

$\text{CO}(g) + \text{NO}_2(g) \longrightarrow \text{CO}_2(g) + \text{NO}(g)$ if the rate law for the reaction is $\text{rate } = k\left[\text{NO}_2\right]^2$?

(a) Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
(b) Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

Solution

(a) $\dfrac{\text{rate}_2}{\text{rate}_1} = \dfrac{k[0.25\ \text{NO}_2]^2}{k[0.50\ \text{NO}_2]^2} = \dfrac{0.0625}{0.25} = \dfrac{1}{4}$

Since rate_1 is four times as large as rate_2, the process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

17. Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $\text{NO} + \text{O}_3 \longrightarrow \text{NO}_2 + \text{O}_2$ is first order with respect to both NO and O_3 with a rate constant of 2.20×10^7 L/mol/s. What is the instantaneous rate of disappearance of NO when $[\text{NO}] = 3.3 \times 10^{-6}\ M$ and $[\text{O}_3] = 5.9 \times 10^{-7}\ M$?

Solution
$\text{Rate} = k[\text{NO}][\text{O}_3] = 2.20 \times 10^7\ \text{L/mol/s}[3.3 \times 10^{-6}\ M][5.9 \times 10^{-7}\ M] = 4.3 \times 10^{-5}\ \text{mol/L/s}$

19. The rate constant for the radioactive decay of ^{14}C is 1.21×10^{-4} year^{-1}. The products of the decay are nitrogen atoms and electrons (beta particles):

$${}^{14}_{6}\text{C} \longrightarrow {}^{14}_{6}\text{N} + \text{e}^-$$

$$\text{rate} = k\left[{}^{14}_{6}\text{C}\right]$$

What is the instantaneous rate of production of N atoms in a sample with a carbon–14 content of $6.5 \times 10^{-9}\ M$?

Solution

rate = 1.21×10^{-4} year^{-1} [6.5×10^{-9} *M*] = 7.9×10^{-13} mol/L/year

21. Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

[C_2H_5OH] (*M*)	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}
Rate (mol L^{-1} h^{-1})	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Determine the rate law, the rate constant, and the overall order for this reaction.

Solution

The rate is independent of the concentration. Therefore, rate = *k*; *k* = 2.0×10^{-2} mol L^{-1} h^{-1} (about 0.9 g L^{-1} h^{-1}for the average male); The reaction is zero order—that is, it does not depend on the concentration of any reagent.

23. Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2\text{NOCl}(g) \longrightarrow 2\text{NO}(g) + \text{Cl}_2(g)$$

Determine the rate law, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (*M*)	0.10	0.20	0.30
Rate (mol L^{-1} h^{-1})	8.0×10^{-10}	3.2×10^{-9}	7.2×10^{-9}

Solution

The object of this problem is to use the general rate expression: rate = *k*[NOCl]^m, first to determine the value of *m* and then, by substituting data from one experiment into the equation, to find the value of *k*. The data listed as substituted into the rate law give:

Experiment 1: 8.0×10^{-10} mol/L/h = *k*[0.10 mol/L]^m
Experiment 2: 3.20×10^{-9} mol/L/h = *k*[0.20 mol/L]^m
Experiment 3: 7.2×10^{-9} mol/L/h = *k*[0.30 mol/L]^m

The value of *m* can be found by inspection. Examining Experiments 1 and 2, it is found that the rate increases by a factor of four as the concentration increases by a factor of two; from Experiments 1 and 3, the rate increases by a factor of nine while the concentration increases by a factor of three. This can happen only if *m* is 2. The value of *k* as calculated from the first set of data is:

$$k = \frac{8.0 \times 10^{-10}\ \text{mol L}^{-1}\ \text{h}^{-1}}{[0.10\ \text{mol L}^{-1}]^2} = 8.0 \times 10^{-8}\ \text{L mol}^{-1}\ \text{h}^{-1}$$

rate = *k*[NOCl]^2; *k* = 8.0×10^{-8} L/mol/h; second order

25. Nitrogen monoxide reacts with chlorine according to the equation:

$$2\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g)$$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L)	[Cl_2] (mol/L)	Rate (mol L^{-1} h^{-1})
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate law that describes the rate’s dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

Solution

The rate law has the general form:

$$\text{rate} = k\left[\text{NO}\right]^m\left[\text{Cl}_2\right]^n$$

Comparing the data in rows 1 and 2, [Cl_2] remains constant, [NO] doubles, and the rate becomes four times as large, so $m = 2$. Comparing data in rows 2 and 3, [NP] remains constant, [Cl_2] doubles, and the rate doubles, so $n = 1$. The rate law is:

$$\text{rate} = k\left[\text{NO}\right]^2\left[\text{Cl}_2\right]$$

Data from row 1 are used to determine *k*.

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{Cl}_2]} = \frac{1.14\text{ mol L}^{-1}\text{ h}^{-1}}{(0.50\text{ mol L}^{-1})^2(0.50\text{ mol L}^{-1})} = 9.1\text{ L}^2\text{ mol}^{-2}\text{ h}^{-1}$$

$\text{rate} = k\left[\text{NO}\right]^2\left[\text{Cl}_2\right]$; second order in NO; first order in Cl_2]

27. For the reaction $A \longrightarrow B + C$, the following data were obtained at 30 °C:

[*A*] (*M*)	0.230	0.356	0.557
Rate (mol L^{-1} s^{-1})	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

(a) What is the order of the reaction with respect to [*A*], and what is the rate law?
(b) What is the rate constant?

Solution

(a) The rate law will be of the form rate = $k[\text{A}]^m$ and *m* will be the same for all three sets of experimental data. Therefore, we can write:

Experiment 1: 4.17×10^{-4} mol/L/s = $k[0.230\ M]^m$
Experiment 2: 9.99×10^{-4} mol/L/s = $k[0.356\ M]^m$
Experiment 3: 2.44×10^{-3} mol/L/s = $k[0.557\ M]^m$

The first two experiments can be set up so as to cancel one of the unknowns (that is, *k*) and solve for the other unknown (that is, *m*):

$$\frac{4.17\times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}}{9.99\times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}} = \frac{(0.230\ M)^m}{(0.356\ M)^m}$$

$$0.4174 = \frac{(0.230\ M)^m}{(0.356\ M)^m}$$

Taking the natural log of each side gives:

$\ln 0.4174 = m(\ln 0.230) - m(\ln 0.356)$
$-0.8737 = -1.4697m + 1.0328m$
$-0.8737 = -0.4369m$

$$m = \frac{-0.8737}{-0.4369} = 2.00$$

Therefore, the rate law is second order in A and is written as rate = $k[A]^2$. (b) The rate constant can be calculated from any of the three sets of data by using the rate law in conjunction with data found by substituting any of the three sets of data into the rate law. Using the data from Equation 1 gives:

4.17×10^{-4} mol/L/s = $k[0.230\ M]^2$

$$k = \frac{4.17 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}}{(0.059\text{ mol}^2\text{ L}^{-2})} = 7.88 \times 10^{-3}\text{ L mol}^{-1}\text{ s}^{-1}$$

29. The rate constant for the first–order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is 6.2×10^{-4} min^{-1}.

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

What is the rate of the reaction when $[N_2O_5] = 0.40\ M$?

Solution

(a) The rate of reaction for a first-order reaction in N_2O_5 is written as rate = $k[N_2O_5]$ where k, the rate constant at 45 °C, is $6.2 \times 10^{-4}\ \text{min}^{-1}$. When $[N_2O_5] = 0.40\ M$,
rate = $6.2 \times 10^{-4}\ \text{min}^{-1}\ (0.40\ \text{mol/L}) = 2.5 \times 10^{-4}\ \text{mol/L/min}$

31. The following data have been determined for the reaction:

$I^- + OCl^- \longrightarrow IO^- + Cl^-$

	1	2	3
$[I^-]_{\text{initial}}$ (M)	0.10	0.20	0.30
$[OCl^-]_{\text{initial}}$ (M)	0.050	0.050	0.010
Rate (mol L^{-1} s^{-1})	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate law and the rate constant for this reaction.

Solution

The rate law has the form rate = $k[I^-]^m[OCl^-]^n$ and the values for m and n must be determined.
Comparing data from columns 1 and 2, $[OCl^-]$ remains constant and $[I^-]$ doubles. As $[I^-]$ doubles, the rate doubles, so $m = 1$.
Comparing data from columns 1 and 3,
$3.05 \times 10^{-4} = k[0.10]^1[0.05]^n \longrightarrow 3.05 \times 10^{-3} = k[0.05]^n$
$1.83 \times 10^{-4} = k[0.30]^1[0.01]^n \longrightarrow 6.1 \times 10^{-4} = k[0.01]^n$
The first numerical value is five times larger than the second, corresponding to a fivefold increase in concentration. Therefore, $n = 1$; rate = $k[I^-][OCl^-]$
The rate constant is determined by putting the data from column 2 into the rate law:

$$k = \frac{\text{rate}}{[I^-][OCl^-]} = \frac{6.10 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}{(0.20\ \text{mol L}^{-1})(0.050\ \text{mol L}^{-1})} = 6.1 \times 10^{-2}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

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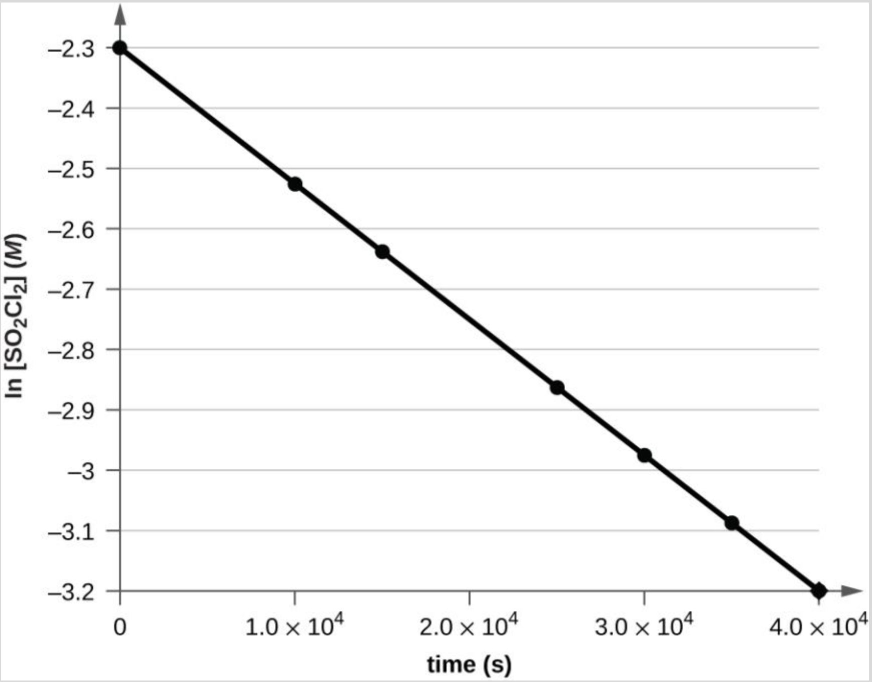
12: Kinetics
12.4: Integrated Rate Laws

33. Use the data provided to graphically determine the order and rate constant of the following reaction: $SO_2Cl_2 \longrightarrow SO_2 + Cl_2$

Time (s)	0	5.00 × 10^3	1.00 × 10^4	1.50 × 10^4	2.50 × 10^4	3.00 × 10^4	4.00 × 10^4
[SO_2Cl_2] (*M*)	0.100	0.0896	0.0802	0.0719	0.0577	0.0517	0.0415

Solution

Plotting a graph of ln[SO_2Cl_2] versus *t* reveals a linear trend; therefore, we know this is a first-order reaction:



The value of *k* is found from the slope of the line since $\ln[A] = -kt + \ln[A]_0$ is in the form of a straight line, *y* = *mx* + *b*.

$$\frac{\Delta y}{\Delta x} = \frac{\ln 0.0896 - \ln 0.100}{5.00 \times 10^3 - 0\text{ s}} = \frac{-0.1098}{5.00 \times 10^3\text{ s}} = -2.20 \times 10^{-5}\text{ s}^{-1}$$

Since the slope of this plot is equal to –*k*, $k = 2.20 \times 10^{-5}\text{ s}^{-1}$.

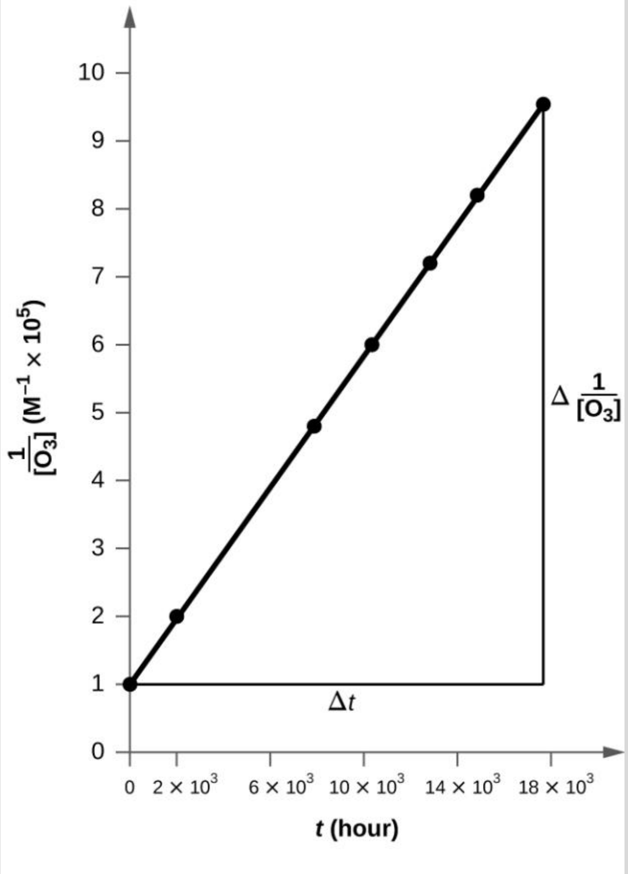
34. Pure ozone decomposes slowly to oxygen, $2O_3(g) \longrightarrow 3O_2(g)$. Use the data provided in a graphical method and determine the order and rate constant of the reaction.

Time (h)	0	2.0 × 10^3	7.6 × 10^3	1.00 × 10^4
[O_3] (*M*)	1.00 × 10^{-5}	4.98 × 10^{-6}	2.07 × 10^{-6}	1.66 × 10^{-6}
Time (h)	1.23 × 10^4	1.43 × 10^4	1.70 × 10^4	
[O_3] (*M*)	1.39 × 10^{-6}	1.22 × 10^{-6}	1.05 × 10^{-6}	

Solution

To distinguish a first-order reaction from a second-order reaction, we plot ln[P] against t and compare that plot with a plot of $\frac{1}{[P]}$ versus t. The values needed for these plots are abbreviated to include only the data needed for a second-order plot, as the data do not seem to support a first-order reaction:

$\frac{1}{[O_3]}$ (M^{-1})	1.00×10^5	2.01×10^5	4.83×10^5	6.02×10^5	7.19×10^5	8.20×10^5	9.52×10^5



The plot is nicely linear, so the reaction is second order.

$$\text{slope} = k = \frac{9.52 \times 10^5 - 1.00 \times 10^5}{17 \times 10^3 - 0} = 50.1 \text{ L mol}^{-1} \text{ h}^{-1}$$

36. What is the half-life for the first-order decay of phosphorus–32? ($^{32}_{15}\text{P} \longrightarrow {}^{32}_{16}\text{S} + \text{e}^-$) The rate constant for the decay is 4.85×10^{-2} day^{-1}.

Solution

The half-life is $t_{1/2} = \frac{0.693}{k}$, where k is the rate constant:

$$k = \frac{0.693}{t_{1/2}} = 4.85 \times 10^{-2} \text{ d}^{-1}$$

$$t_{1/2} = \frac{0.693}{4.85 \times 10^{-2} \text{ d}^{-1}} = 14.3 \text{ d}$$

38. What is the half-life for the decomposition of NOCl when the concentration of NOCl is 0.15 M? The rate constant for this second-order reaction is 8.0×10^{-8} L mol^{-1} s^{-1}.

Solution

In a second-order reaction, the rate is concentration-dependent, $t_{1/2} = \dfrac{1}{k[A]_0}$.

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{8.0 \times 10^{-8}\ \text{L mol}^{-1}\ \text{s}^{-1}\ [0.15\ M]} = 8.3 \times 10^{7}\ \text{s}$$

40. The reaction of compound A to give compounds C and D was found to be second-order in A. The rate constant for the reaction was determined to be 2.42 L mol^{-1} s^{-1}. If the initial concentration is 0.500 mol/L, what is the value of $t_{1/2}$?

Solution

For a second-order reaction, the half-life is concentration-dependent:

$$t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{2.42\ \text{L mol}^{-1}\ \text{s}^{-1} \times 0.500\ \text{mol L}^{-1}} = 0.826\ \text{s}$$

42. Some bacteria are resistant to the antibiotic penicillin because they produce penicillinase, an enzyme with a molecular weight of 3×10^4 g/mol that converts penicillin into inactive molecules. Although the kinetics of enzyme-catalyzed reactions can be complex, at low concentrations this reaction can be described by a rate law that is first order in the catalyst (penicillinase) and that also involves the concentration of penicillin. From the following data: 1.0 L of a solution containing 0.15 µg (0.15×10^{-6} g) of penicillinase, determine the order of the reaction with respect to penicillin and the value of the rate constant.

[Penicillin] (M)	Rate (mol L^{-1} min^{-1})
2.0×10^{-6}	1.0×10^{-10}
3.0×10^{-6}	1.5×10^{-10}
4.0×10^{-6}	2.0×10^{-10}

Solution

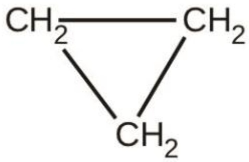
The reaction is first order with respect to penicillinase, and the rate doubles as [penicillin] doubles. Thus the rate equation is:

rate = k[penicillinase][penicillin]

Using the data in the first row,

$$k = \frac{1.0 \times 10^{-10}\ \text{mol L}^{-1}\ \text{min}^{-1}}{\left(\dfrac{0.15 \times 10^{-6}\ \text{g L}^{-1}}{3.0 \times 10^{4}\ \text{g mol}^{-1}}\right)(2.0 \times 10^{-6}\ \text{mol L}^{-1})} = 1.0 \times 10^{7}\ \text{L mol}^{-1}\ \text{min}^{-1}$$

44. There are two molecules with the formula C_3H_6. Propene, $CH_3CH=CH_2$, is the monomer of the polymer polypropylene, which is used for indoor-outdoor carpets. Cyclopropane is used as an anesthetic:



When heated to 499 °C, cyclopropane rearranges (isomerizes) and forms propene with a rate constant of 5.95×10^{-4} s^{-1}. What is the half-life of this reaction? What fraction of the cyclopropane remains after 0.75 h at 499 °C?

Solution

The provided rate constant’s unit is s^{-1}, indicating the reaction is first-order, and so

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.95\times10^{-4}\ \text{s}^{-1}} = 1.16\times10^{3}\ \text{s}$$

The fraction remaining after 0.75 h may be determined from the integrated rate law:

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

Rearranging this equation to isolate the fraction remaining yields

$$\ln\frac{[A]_t}{[A]_0} = e^{-kt}$$

Converting the time to seconds and substituting values for k and t gives

$$\ln\frac{[A]_t}{[A]_0} = e^{-kt} = e^{-\left(5.95\times10^{-4}\ \text{s}^{-1}\right)(0.75\ \text{h})\left(\frac{60\ \text{m}}{1\ \text{hr}}\right)\left(\frac{60\ \text{s}}{1\ \text{min}}\right)} = 0.20$$

And so, 20% of the reactant remains.

46. Suppose that the half-life of steroids taken by an athlete is 42 days. Assuming that the steroids biodegrade by a first-order process, how long would it take for $\frac{1}{64}$ of the initial dose to remain in the athlete’s body?

Solution

$\frac{1}{64} = \frac{1}{2^x}$ where x represents the number of half-life periods $x = 6$, so (6)(42) = 252 days.

48. Nitroglycerine is an extremely sensitive explosive. In a series of carefully controlled experiments, samples of the explosive were heated to 160 °C and their first-order decomposition studied. Determine the average rate constants for each experiment using the following data:

Initial $[C_3H_5N_3O_9]$ (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

Solution

From the first-order rate law, calculate the value of $[A]$, $\ln\left(\frac{[A]_0}{[A]}\right)$, and k. The values are tabulated:

$[A]_0$ (M)	$[A]$ (M)	$\ln\left(\frac{[A]_0}{[A]}\right)$	t (s)	$k \times 10^3$ (s^{-1})
4.88	2.34	0.734	300	2.45
3.52	1.66	0.752	300	2.51
2.29	1.07	0.761	300	2.53
1.81	0.834	0.775	300	2.58
5.33	3.49	0.423	180	2.36

4.05	2.61	0.439	180	2.47
2.95	1.89	0.445	180	2.48
1.72	1.11	0.438	180	2.43

Chemistry 2e
12: Kinetics
12.5: Collision Theory

50. Chemical reactions occur when reactants collide. What are two factors that may prevent a collision from producing a chemical reaction?

Solution

The reactants either may be moving too slowly to have enough kinetic energy to exceed the activation energy for the reaction, or the orientation of the molecules when they collide may prevent the reaction from occurring.

52. What is the activation energy of a reaction, and how is this energy related to the activated complex of the reaction?

Solution

The activation energy is the minimum amount of energy necessary to form the activated complex in a reaction. It is usually expressed as the energy necessary to form one mole of activated complex.

54. Describe how graphical methods can be used to determine the activation energy of a reaction from a series of data that includes the rate of reaction at varying temperatures.

Solution

After finding *k* at several different temperatures, a plot of ln *k* versus $\frac{1}{T}$ gives a straight line with the slope $\frac{-E_a}{R}$, from which E_a may be determined.

56. The rate of a certain reaction doubles for every 10 °C rise in temperature.

(a) How much faster does the reaction proceed at 45 °C than at 25 °C?

(b) How much faster does the reaction proceed at 95 °C than at 25 °C?

Solution

(a) The rate doubles for each 10 °C rise in temperature; 45 °C is a 20 °C increases over 25 °C. Thus, the rate doubles two times, or 2^2 (rate at 25 °C) = 4-times faster. (b) 95 °C is a 70 °C increases over 25 °C. Thus the rate doubles seven times, or 2^7 (rate at 25 °C) = 128-times faster.

58. The rate constant at 325 °C for the decomposition reaction $C_4H_8 \longrightarrow 2C_2H_4$ is 6.1×10^{-8} s^{-1}, and the activation energy is 261 kJ per mole of C_4H_8. Determine the frequency factor for the reaction.

Solution

The rate constant *k* is related to the activation energy E_a by a relationship known as the Arrhenius equation. Its form is:

$$k = A \times 10^{-(E_a/2.303RT)} = A \times e^{-(E_a/RT)}$$

where *A* is the frequency factor. Using the data provided, and converting kilojoules to joules:

$$\begin{aligned} 6.1 \times 10^{-8}\ \text{s}^{-1} &= A \times 10^{-\left[+261.000\ \text{J}/2.303(8.314\ \text{J K}^{-1})(325+273)\text{K}\right]} \\ &= A \times 10^{-22.8} \end{aligned}$$

$$A = \frac{6.1 \times 10^{-8}\ \text{s}^{-1}}{1.58 \times 10^{-23}} = 3.9 \times 10^{15}\ \text{s}^{-1}$$

60. An elevated level of the enzyme alkaline phosphatase (ALP) in human serum is an indication of possible liver or bone disorder. The level of serum ALP is so low that it is very difficult to measure directly. However, ALP catalyzes a number of reactions, and its relative concentration

can be determined by measuring the rate of one of these reactions under controlled conditions. One such reaction is the conversion of p-nitrophenyl phosphate (PNPP) to p-nitrophenoxide ion (PNP) and phosphate ion. Control of temperature during the test is very important; the rate of the reaction increases 1.47 times if the temperature changes from 30 °C to 37 °C. What is the activation energy for the ALP–catalyzed conversion of PNPP to PNP and phosphate?

Solution

Note that $e^{-x} = 10^{-x/2.303}$. Changes in rate brought about by temperature changes are governed by the Arrhenius equation: $k = A \times 10^{-E_a/2.303RT}$. In this particular reaction, k increases by 1.47 as T changes from 30 °C (303 K). The Arrhenius equation may be solved for A under both sets of conditions and then A can be eliminated between the two equations. Eliminating k from both sides, taking logs, and rearranging gives:

$$\frac{-E_a}{2.303 \times 8.314 \text{ J mol}^{-1}\text{ K}^{-1}(310\text{ K})} = \log 1.47 - \frac{E_a}{2.303 \times 8.314 \text{ J mol}^{-1}\text{ K}^{-1}(303\text{ K})}$$

$$\frac{-E_a}{5935.6 \text{ J mol}^{-1}} = 0.1673 - \frac{E_a}{5801.6 \text{ J mol}^{-1}}$$

$$\frac{E_a}{5801.6} - \frac{E_a}{5935.6} = 0.1673 \text{ J mol}^{-1}$$

$E_a(1.72366 \times 10^{-4} - 1.68474 \times 10^{-4}) = 0.1673$ J/mol

$3.892 \times 10^{-6} E_a = 0.1673$ J/mol

$E_a = 42986$ J/mol = 43.0 kJ/mol

62. Hydrogen iodide, HI, decomposes in the gas phase to produce hydrogen, H_2, and iodine, I_2. The value of the rate constant, k, for the reaction was measured at several different temperatures and the data are shown here:

Temperature (K)	k (L mol^{-1} s^{-1})
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

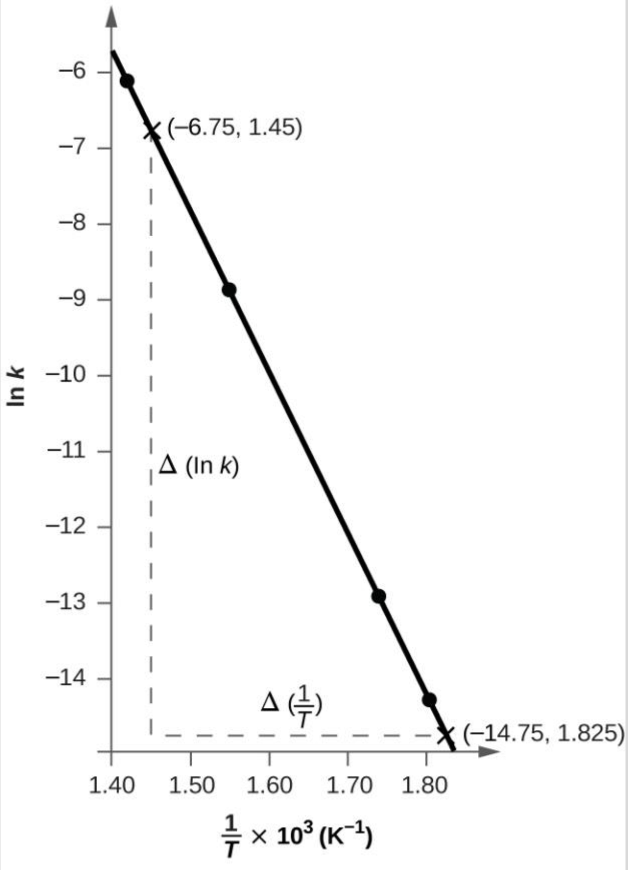
What is the value of the activation energy (in kJ/mol) for this reaction?

Solution

E_a may be determined from a plot of ln k against $\frac{1}{T}$ that gives a straight line whose slope is $\frac{-E_a}{R}$:

T (K)	$\frac{1}{T} \times 10^3$	k (L mol^{-1} s^{-1})	ln k
555	1.802	6.23×10^{-7}	−14.289
575	1.739	2.42×10^{-6}	−12.932
645	1.550	1.44×10^{-4}	−8.846
700	1.429	2.42×10^{-3}	−6.210

A plot of this data shows a straight line. Two points marked by an X are picked for convenience of reading and are used to determine the slope of the line:



$$\text{slope} = \frac{-14.750 - (-6.750)}{1.825 \times 10^{-3} - 1.450 \times 10^{-3}} = \frac{-8.000}{3.75 \times 10^{-4}} = -2.13 \times 10^4$$

$$\frac{-E_a}{R} = -2.13 \times 10^4$$

$E_a = -2.13 \times 10^4 \times 8.314$ J/mol = 177 kJ/mol

64. The hydrolysis of the sugar sucrose to the sugars glucose and fructose,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

follows a first-order rate law for the disappearance of sucrose: rate = $k[C_{12}H_{22}O_{11}]$. (The products of the reaction, glucose and fructose, have the same molecular formulas but differ in the arrangement of the atoms in their molecules.)

(a) In neutral solution, $k = 2.1 \times 10^{-11}$ s^{-1} at 27 °C and 8.5×10^{-11} s^{-1} at 37 °C. Determine the activation energy, the frequency factor, and the rate constant for this equation at 47 °C (assuming the kinetics remain consistent with the Arrhenius equation at this temperature).

(b) When a solution of sucrose with an initial concentration of 0.150 M reaches equilibrium, the concentration of sucrose is 1.65×10^{-7} M. How long will it take the solution to reach equilibrium at 27 °C in the absence of a catalyst? Because the concentration of sucrose at equilibrium is so low, assume that the reaction is irreversible.

(c) Why does assuming that the reaction is irreversible simplify the calculation in part (b)?

Solution

(a) The text demonstrates that the value of E_a may be determined from a plot of log k against $\frac{1}{T}$ that gives a straight line whose slope is $\frac{-E_a}{2.303R}$. This relationship is based on the equation $\ln k = \ln A - \frac{E_a}{RT}$ or $\log k = \log A - \frac{E_a}{2.303RT}$ where $\ln k = 2.303 \log k$. Only two data points are given, and these must determine a straight line when log k is plotted against $1/T$. The values needed are:

$k_1 = 2.1 \times 10^{-11}$
$\log k_1 = -10.6778$
$k_2 = 8.5 \times 10^{-11}$
$\log k_2 = -10.0706$
$T_1 = 27\ °\text{C} = 300\ \text{K}$
$\frac{1}{T_1} = 3.3333 \times 10^{-3}$
$T_2 = 37\ °\text{C} = 310\ \text{K}$
$\frac{1}{T_2} = 3.2258 \times 10^{-3}$

The slope of the line determined by these points is given by:

$$\text{Slope} = \frac{\Delta(\log k)}{\Delta \frac{1}{T}} = \frac{(-10.0706) - (-10.6778)}{(3.2258 \times 10^{-3}) - (3.3333 \times 10^{-3})}$$

$$= \frac{0.6072}{-0.1075 \times 10^{-3}} = -5648$$

$E_a = 2.303(8.314\ \text{J/mol})(–5648) = 108{,}100\ \text{J} = 108\ \text{kJ}$

Whenever differences of very small numbers are taken, such as the reciprocals of T provided, an inherent problem occurs. To have accurate differences, a larger number of significant figures than justified by the data must be used. Thus five figures were used to obtain the value $E_a = 108$ kJ. This difficulty may be alleviated by the following approach.

For only two data points, the Arrhenius equation $k = A \times 10^{-E_a/2.303RT}$ may be used in an equally accurate, analytical solution for E_a. This application is possible because the value of A will be the same throughout the course of the reaction. Once the value of E_a is determined, the value of A may be determined from either Equation (1) or (2). Then k at 47 °C may be determined using the value of E_a and A so determined. The procedure is as follows:

$$k = A \times 10^{-E_a/2.303RT}$$

$$2.1 \times 10^{-11}\ \text{s}^{-1} = A \times 10^{-E_a/2.303(8.314\ \text{J K}^{-1})(300\ \text{K})} \qquad \text{(equation 1)}$$

$$8.5 \times 10^{-11}\ \text{s}^{-1} = A \times 10^{-E_a/2.303(8.314\ \text{J K}^{-1})(300\ \text{K})} \qquad \text{(equation 2)}$$

Equating the values of A as solved from equations (1) and (2):

$$2.1 \times 10^{-11}\ \text{s}^{-1} \times 10^{+E_a/2.303(8.314\ \text{J K}^{-1})(300\ \text{K})} = 8.5 \times 10^{-11}\ \text{s}^{-1} \times 10^{+E_a/2.303(8.314\ \text{J K}^{-1})(300\ \text{K})} \text{ or}$$

$$2.1 \times 10^{-11}\ \text{s}^{-1} \times 10^{+E_a/5744} = 8.5 \times 10^{-11}\ \text{s}^{-1} \times 10^{+E_a/5936}.$$

Taking common logs of both sides gives:

$$(\log 2.1 \times 10^{-11}) + \frac{E_a}{5744} = (\log 8.5 \times 10^{-11}) + \frac{E_a}{5936} \;-\; 10.68 + \frac{E_a}{5744} = -10.07 + \frac{E_a}{5936}$$

$$E_a\left(\frac{1}{5744} - \frac{1}{5936}\right) = -10.07 + 10.68$$

$$E_a(1.741 \times 10^{-4} - 1.685 \times 10^{-4}) = 0.61$$

$$E_a = \frac{0.61}{0.056 \times 10^{-4}} = 109 \text{ kJ}$$

The value of *A* may be found from either equation (1) or (2). Using equation (1):

$$2.1 \times 10^{-11} \text{ s}^{-1} = A \times 10^{-109{,}000/2.303(8.314)(300)} = A \times 10^{-18.98}$$

$A = 2.1 \times 10^{-11}$ s$^{-1} \times 10^{+18.91} = 2.1 \times 10^{-11}(9.55 \times 10^{18}$ s$^{-1}) = 2.0 \times 10^{8}$ s^{-1}

The value of *k* at 47°C may be determined from the Arrhenius equation now that the values of E_a and *A* have been calculated:

$$k = A \times 10^{-E_a/2.303RT}$$

$$= 2.0 \times 10^{8} \text{ s}^{-1} \times 10^{-109{,}000 \text{ J}/2.303(8.314 \text{ J K}^{-1})(320 \text{ K})}$$

$= 2.0 \times 10^{8}$ s$^{-1} \times 10^{-17.79} = 2.0 \times 10^{8}$ s$^{-1}(1.62 \times 10^{-18}) = 3.2 \times 10^{-10}$ s^{-1}

Using the earlier value of E_a = 108 kJ, the calculated value of *A* is 1.3×10^{8} s^{-1}, and $k = 3.1 \times 10^{-10}$ s^{-1}. Either answer is acceptable.

(b) Since this is a first-order reaction we can use the integrated form of the rate law to calculate the time that it takes for a reactant to fall from an initial concentration $[A]_0$ to some final concentration [*A*]:

$$\ln \frac{[\text{A}]_0}{[\text{A}]} - kt$$

At 27 °C.

$k = 2.1 \times 10^{-11}$ s^{-1}.

In this case, the initial concentration is 0.150 *M* and the final concentration is $1.65 \times 10^{-7}M$. We can now solve for the time *t*:

$$\ln \frac{[0.150\ M]}{[1.65 \times 10^{-7}\ M]} = (2.1 \times 10^{-11} \text{ s}^{-1})(t)$$

$$t = \frac{13.720}{2.1 \times 10^{-11} \text{ s}^{-1}} = 6.5 \times 10^{11} \text{ s}$$

or 1.81×10^{8} h or 7.6×10^{6} day. (c) Assuming that the reaction is irreversible simplifies the calculation because we do not have to account for any reactant that, having been converted to product, returns to the original state.

66. Use the PhET Reactions & Rates interactive simulation(http://openstaxcollege.org/l/16PHETreaction) to simulate a system. On the “Single collision” tab of the simulation applet, enable the “Energy view” by clicking the “+” icon. Select the first $A + BC \longrightarrow AB + C$ reaction (A is yellow, B is purple, and C is navy blue). Using the “angled shot” option, try launching the *A* atom with varying angles, but with more Total energy than the transition state. What happens when the *A* atom hits the *BC* molecule from different directions? Why?

Solution

The *A* atom has enough energy to react with *BC*; however, the different angles at which it bounces off of *BC* without reacting indicate that the orientation of the molecule is an important part of the reaction kinetics and determines whether a reaction will occur.

Chemistry 2e
12: Kinetics
12.6: Reaction Mechanisms

68. In general, can we predict the effect of doubling the concentration of *A* on the rate of the overall reaction $A + B \longrightarrow C$? Can we predict the effect if the reaction is known to be an elementary reaction?

Solution

No. In general, for the overall reaction, we cannot predict the effect of changing the concentration without knowing the rate law. Yes if the reaction is an elementary reaction, then doubling the concentration of *A* doubles the rate.

70. What is the rate law for the elementary termolecular reaction $A + 2B \longrightarrow \text{products}$? For $3A \longrightarrow \text{products}$?

Solution

In an elementary reaction, the rate constant is multiplied by the concentration of the reactant raised to the power of its stoichiometric coefficient. Rate = $k[A][B]^2$; Rate = $k[A]^3$

72. Write the rate law for each of the following elementary reactions:

(a) $O_3 \xrightarrow{\text{sunlight}} O_2 + O$

(b) $O_3 + Cl \longrightarrow O_2 + ClO$

(c) $ClO + O \longrightarrow Cl + O_2$

(d) $O_3 + NO \longrightarrow NO_2 + O_2$

(e) $NO_2 + O \longrightarrow NO + O_2$

Solution

(a) $\text{Rate}_1 = k[O_3]$; (b) $\text{Rate}_2 = k[O_3][Cl]$; (c) $\text{Rate}_3 = k[ClO][O]$; (d) $\text{Rate}_2 = k[O_3][NO]$; (e) $\text{Rate}_3 = k[NO_2][O]$

74. Experiments were conducted to study the rate of the reaction represented by this equation.[1]

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

Initial concentrations and rates of reaction are given here.

Experiment	Initial Concentration [NO] (mol L^{-1})	Initial Concentration, $[H_2]$ (mol L^{-1})	Initial Rate of Formation of N_2 (mol L^{-1} min^{-1})
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

Consider the following questions:

(a) Determine the order for each of the reactants, NO and H_2, from the data given and show your reasoning.

(b) Write the overall rate law for the reaction.

(c) Calculate the value of the rate constant, *k*, for the reaction. Include units.

---

[1] This question is taken from the Chemistry Advanced Placement Examination and is used with the permission of the Educational Testing Service.

(d) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.

(e) The following sequence of elementary steps is a proposed mechanism for the reaction.

Step 1: $NO + NO \longrightarrow N_2O_2$

Step 2: $N_2O_2 + H_2 \longrightarrow H_2O + N_2O$

Step 3: $N_2O + H_2 \longrightarrow N_2 + H_2O$

Based on the data presented, which of these is the rate determining step? Show that the mechanism is consistent with the observed rate law for the reaction and the overall stoichiometry of the reaction.

Solution

(a) Doubling [H_2] doubles the rate. [H_2] must enter the rate law to the first power. Doubling [NO] increases the rate by a factor of 4. [NO] must enter the rate law to the second power. (b) The rate law is Rate = $k[NO]^2[H_2]$. (c) 1.8×10^{-4} mol L^{-1} min^{-1} = $k[0.0060 \text{ mol/L}]^2[0.0010 \text{ mol/L}]$, $k = 5.0 \times 10^3$ mol^{-2} L^2 min^{-1}; (d) The reaction has consumed 0.0010 mol/L of H_2. The amount of NO consumed is the same, 0.0010 mol/L of NO. Thus 0.0060 – 0.0010 = 0.0050 mol/L remains. (e) Step II is the rate-determining step. If step I gives N_2O_2 in adequate amount, steps 1 and 2 combine to give $2NO + H_2 \longrightarrow H_2O + N_2O$. This reaction corresponds to the observed rate law. Combine steps 1 and 2 with step 3, which occurs by supposition in a rapid fashion, to give the appropriate stoichiometry.

Chemistry 2e
12: Kinetics
12.7: Catalysis

76. Account for the increase in reaction rate brought about by a catalyst.

Solution

The general mode of action for a catalyst is to provide a mechanism by which the reactants can unite more readily by taking a path with a lower reaction energy. The rates of both the forward and the reverse reactions are increased, leading to a faster achievement of equilibrium.

78. Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as CCl_2F_2, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$
$$O_3 + Cl \longrightarrow O_2 + ClO$$
$$ClO + O \longrightarrow Cl + O_2$$

(a) Explain why chlorine atoms are catalysts in the gas-phase transformation:

$$2O_3 \longrightarrow 3O_2$$

(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:

$$O_3 \xrightarrow{\text{sunlight}} O_2 + O$$
$$O_3 + NO \longrightarrow NO_2 + O_2$$
$$NO_2 + O \longrightarrow NO + O_2$$

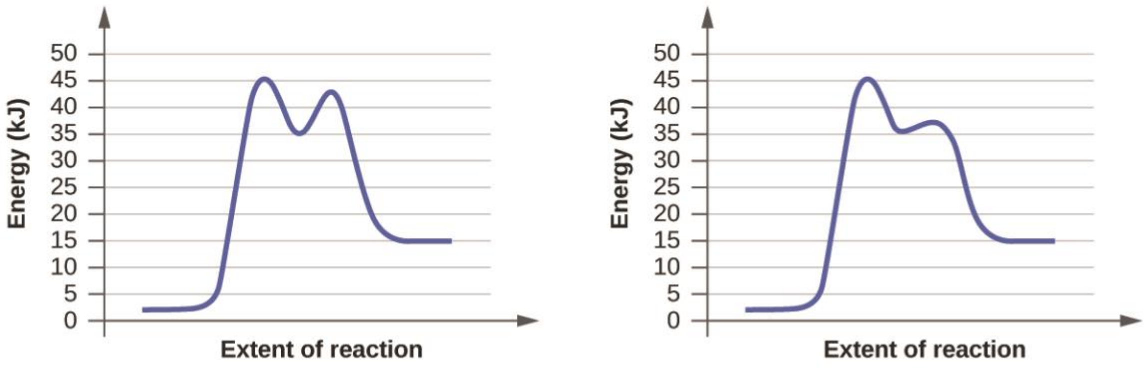
Is NO a catalyst for the decomposition? Explain your answer.

Solution

a) Chlorine atoms are a catalyst because they react in the second step but are regenerated in the third step. Thus, they are not used up, which is a characteristic of catalysts. (b) NO is a catalyst for the same reason as in part (a).

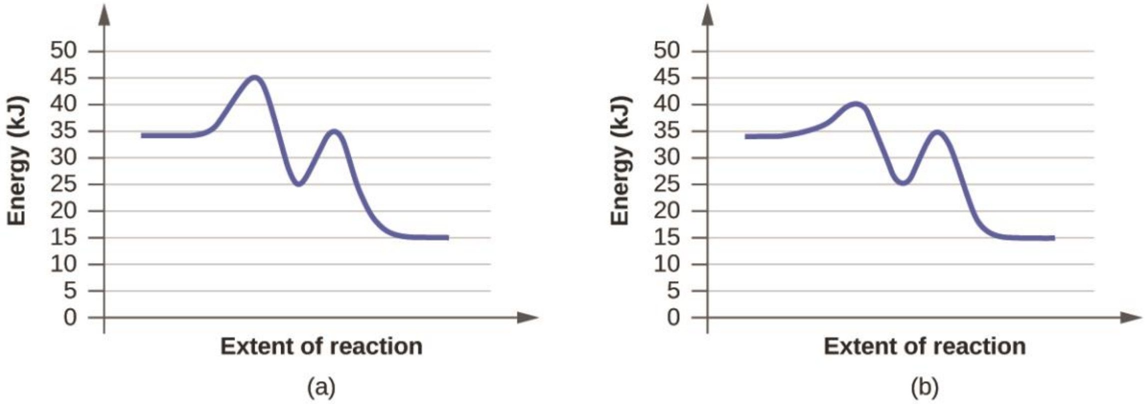
80. For each of the following pairs of reaction diagrams, identify which of the pairs is catalyzed:

(a)



(a) (b)

(b)

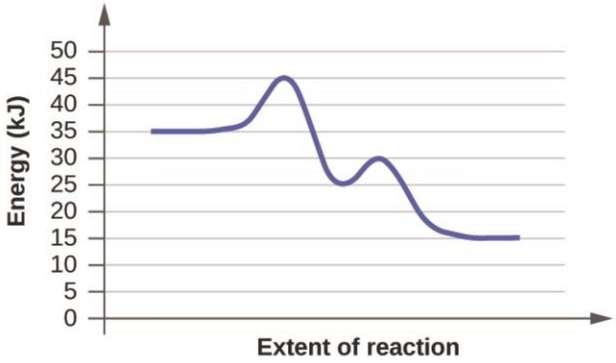


(a) (b)

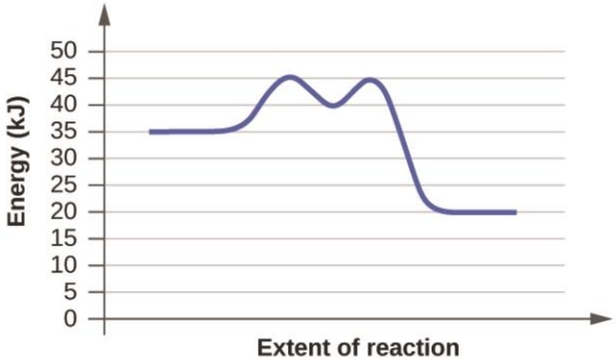
Solution
The lowering of the transition state energy indicates the effect of a catalyst. (a) b; (b) b

82. For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)



Solution
The energy needed to go from the initial state to the transition state is (a) 10 kJ; (b) 10kJ.

84. Consider the similarities and differences in the two reaction diagrams shown in Exercise 12.82. Do these diagrams represent two different overall reactions, or do they represent the same overall reaction taking place by two different mechanisms? Explain your answer.

Solution

Both diagrams describe two-step, exothermic reactions, but with different changes in enthalpy. For reaction (a), the enthalpy change is 15 kJ – 35 kJ = –20 kJ, whereas for reaction (b) it's 20 kJ – 35 kJ = –15 kJ, suggesting the diagrams depict two different overall reactions.