Unit 76 – Chemical Reaction Rates

76-1. 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.

76-2. Ozone decomposes to oxygen according to the equation $2O_3(g) \longrightarrow 3O_2(g).$ Write the equation that relates the rate expressions for this reaction in terms of the disappearance of O_3 and the formation of oxygen.

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:

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

76-3. 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 $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g).$ 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:

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

76-4. A study of the rate of dimerization of C_4H_6 gave the data shown in the table:

$$2C_4H_6 \longrightarrow C_8H_{12}$$

Time (s)	$[C_4H_6]$ (M)
0	1.00×10^{-2}
1600	5.04×10^{-3}
3200	3.37×10^{-3}
4800	2.53×10^{-3}
6200	2.08×10^{-3}

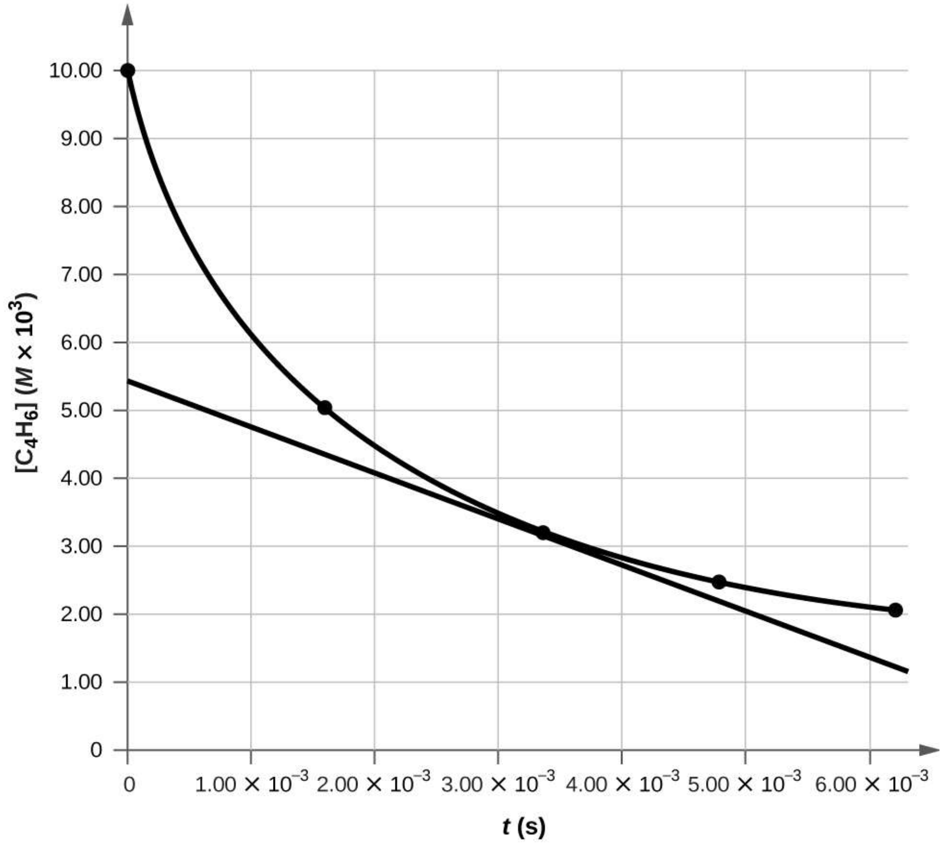
(a) Determine the average rate of dimerization between 0 s and 1600 s, and between 1600 s and 3200 s.

(b) Estimate the instantaneous rate of dimerization at 3200 s from a graph of time versus $[C_4H_6]$. What are the units of this rate?

(c) Determine the average rate of formation of C_8H_{12} at 1600 s and the instantaneous rate of formation at 3200 s from the rates found in parts (a) and (b).

Solution

Plot the concentration of C_4H_6 against time and determine the various slopes required:



$$\text{rate} = -\frac{5.04 \times 10^{-3}\ M - 1.00 \times 10^{-2}\ M}{1600\ \text{s} - 0\ \text{s}} = 3.10 \times 10^{-6}\ M\ \text{s}^{-1}$$

(a)

$$\text{rate} = -\frac{3.37 \times 10^{-3}\ M - 5.04 \times 10^{-3}\ M}{3200\ \text{s} - 1600\ \text{s}} = 1.04 \times 10^{-6}\ M\ \text{s}^{-1};$$

(b) from the approximate points on tangent line in the figure at 3200 s:

$$\text{rate} = -\frac{2.50 \times 10^{-3}\ M - 4.50 \times 10^{-3}\ M}{4.30 \times 10^{3}\ \text{s} - 1.7 \times 10^{3}\ \text{s}} = 7.7 \times 10^{-7}\ M\ \text{s}^{-1};$$

(c) average rate = $\dfrac{3.10 \times 10^{-6}\ M - 0\ M}{2} = 1.55 \times 10^{-6}\ M\ \text{s}^{-1}$

Instantaneous rate = $\dfrac{7.7 \times 10^{-7}}{2} = 3.8 \times 10^{-7}\ M\ \text{s}^{-1}$

somewhat different values may be obtained depending upon the slope of the drawn line.

76-5. 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

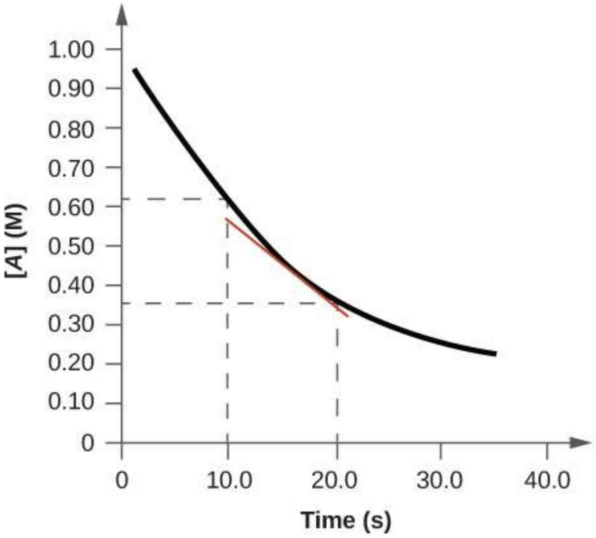
(a) Determine the average rate of disappearance of *A* between 0.0 s and 10.0 s, and between 10.0 s and 20.0 s.

(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*:

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

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

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

76-6. Consider the following reaction in aqueous solution:

$$5\text{Br}^-(aq) + \text{BrO}_3^-(aq) + 6\text{H}^+(aq) \longrightarrow 3\text{Br}_2(aq) + 3\text{H}_2\text{O}(l)$$

If the rate of disappearance of $Br^-(aq)$ at a particular moment during the reaction is 3.5×10^{-4} mol L^{-1} s^{-1}, what is the rate of appearance of $Br_2(aq)$ at that moment?

Solution

$$\frac{3}{5}(3.5 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}) = 2.1 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}$$

Unit 77 – Factors Affecting Reaction Rates

77-1. 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.

77-2. Explain why an egg cooks more slowly in boiling water in Denver than in New York City. (Hint: Consider the effect of temperature on reaction rate and the effect of pressure on boiling point.)

Solution

Water boils at a lower temperature at higher elevations. The higher cooking temperature at sea level makes the rate of cooking faster and the time to completion shorter.

Unit 78 – Rate Laws

78-1. How do the rate of a reaction and its rate constant differ?

Solution

A rate of reaction is a change in concentration per unit time; the rate of a reaction is proportional to its rate constant, and it typically increases with concentration of reactants. A rate constant is a characteristic property of a reaction that indicates its intrinsic speed; a large rate constant is characteristic of a rapid reaction. The rate constant for a given reaction does not change (it is *constant*) unless the temperature changes.

78-2. 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 $2^2 = 4$.

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

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

(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.

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

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

78-3. Tripling the concentration of a reactant increases the rate of a reaction nine-fold. With this knowledge, answer the following questions:

(a) What is the order of the reaction with respect to that reactant?

(b) Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four-fold. What is the order of the reaction with respect to that reactant?

Solution

(a) Since the concentration of the reactant tripled and the rate increased nine fold, we can conclude that the order with respect to the reactant is 2, since $3^2 = 9$.

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

$$9(\text{rate}) = k[3(\text{reactant})]^2;$$

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

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

$$4(\text{rate}) = k[4(\text{reactant})]^1$$

78-4. 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 $\text{rate } = k[\text{NO}_2]^2$?

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

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.

78-5. How will each of the following affect the rate of the reaction:

$\text{CO}(g) + \text{NO}_2(g) \longrightarrow \text{CO}_2(g) + \text{NO}(g)$ if the rate law for the reaction is

$\text{rate } = k[\text{NO}_2][\text{CO}]$?

(a) Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm

(b) Increasing the concentration of CO from 0.02 *M* to 0.06 *M*

Solution

(a) $$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[0.3\,\text{atm}][\text{CO}]}{k[0.1\,\text{atm}][\text{CO}]} = 3$$

The rate increases by a factor of 3.

(b) Concentration increases by a factor of 3; the rate increases by a factor of 3.

78-6. 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 $NO + O_3 \longrightarrow NO_2 + O_2$ 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 $[NO] = 3.3 \times 10^{-6}$ *M* and $[O_3] = 5.9 \times 10^{-7}$ *M*?

Solution

Rate = $k[NO][O_3] = 2.20 \times 10^7$ L/mol/s$[3.3 \times 10^{-6}\,M][5.9 \times 10^{-7}\,M] = 4.3 \times 10^{-5}$ mol/L/s

78-7. Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

$${}^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-$$

rate = 4.85×10^{-2} day$^{-1}\left[{}^{32}P\right]$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

Solution

Rate = 4.85×10^{-2} day$^{-1}[0.0033\,M] = 1.6 \times 10^{-4}$ mol/L/d

78-8. 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):

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

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

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

Solution

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

78-9. The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71×10^{-8} L mol^{-1} s^{-1}. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of 5.55×10^{-4} *M*?

Solution

rate = $k[\text{acetaldehyde}]^2 = 4.71 \times 10^{-7}$ L/mol/s $[5.55 \times 10^{-4}$ mol/L$]^2 = 1.45 \times 10^{-13}$ mol/L/s

CORRECTION by DV:

rate = k[acetaldehyde]^2 = 4.71×10^{-8} L/mol/s [5.55×10^{-4} mol/L]^2 = 1.45×10^{-14} mol/L/s

78-10. 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; $k = 2.0 \times 10^{-2}$ 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.

78-11. Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

[NH_3] (M)	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (mol L^{-1} h^{-1})	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

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

Solution

The rate does not change as the concentration changes. The reaction is zero order because it is independent of the concentration: rate = k; $k = 1.5 \times 10^{-6}$

78-12. Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$$

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 = $k[\text{NOCl}]^2$; $k = 8.0 \times 10^{-8}$ L/mol/h; second order

78-13. From the following data, determine the rate law, the rate constant, and the order with respect to *A* for the reaction $A \longrightarrow 2C$.

$[A]$ (M)	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (mol L^{-1} h^{-1})	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

Solution

Use the general rate expression, rate = $k[A]^m$, 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 are substituted into three rate laws, all of which apply to the same system:

Experiment 1: 3.80×10^{-7} mol/L/h = $k[1.33 \times 10^{-2}]^m$
Experiment 2: 1.52×10^{-6} mol/L/h = $k[2.66 \times 10^{-2}]^m$
Experiment 3: 3.42×10^{-6} mol/L/h = $k[3.99 \times 10^{-2}]^m$

Find the value of *m* by inspection. From Experiments 1 and 2, the rate increases by a factor of four as the concentration doubles. Comparing Experiments 1 and 3, the rate increases by a factor of nine as the concentration increases by a factor of three. This situation can occur only if the value of *m* is 2. The rate law is $\text{Rate} = k[A]^2$ and the reaction is second order. The value of *k* as calculated from the first set of data is:

$$k = \frac{3.80 \times 10^{-7}\ \text{mol L}^{-1}\ \text{h}^{-1}}{[1.33 \times 10^{-2}\ \text{mol L}^{-1}]^2} = 2.15 \times 10^{-3}\ \text{mol L}^{-1}\ \text{h}^{-1}$$

78-14. 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:

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

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:

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

Data from row 1 are used to determine k.

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

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

78-15. Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation: $H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$

Determine the rate law, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (M)	0.30	0.60	0.60
[H_2] (M)	0.35	0.35	0.70
Rate (mol L^{-1} s^{-1})	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

Solution

Use the algebraic method to determine the rate law expression:

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.01134}{0.002835} = \frac{k(0.60)^m(0.35)^n}{k(0.30)^m(0.35)^n}$$

$4.00 = 2.0^m$, $m = 2$

$$\frac{\text{rate 3}}{\text{rate 2}} = \frac{0.02268}{0.01134} = \frac{k(0.60)^m(0.70)^n}{k(0.60)^m(0.35)^n}$$

$2.00 = 2^n$, $n = 1$

To determine the value of the rate constant, data from any one of the three experiments could be substituted into the rate law to solve for k. Using data from Experiment 1 gives:

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

$$2.835 \times 10^{-3} \text{mol/L/s } = k[0.30\, M]^2[0.35\, M]$$

$$k = \frac{2.835 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{[0.30\, m]^2[0.35\, M]} = 9.0 \times 10^{-2} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

78-16. 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 = $k[\mathrm{A}]^m$ 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):

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

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

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 = $k[0.230\ M]^2$

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

78-17. For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

$[Q]_{\text{initial}}$ (M)	0.170	0.212	0.357
Rate (mol $\mathrm{L^{-1}\ s^{-1}}$)	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

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

Solution

(a) Write the rate law using the first two sets of data:

$6.68 \times 10^{-3} = k[0.170]^n$
$1.04 \times 10^{-2} = k[0.212]^n$

Eliminate k:

$$\begin{aligned}6.68 \times 10^{-3} &= \frac{1.04 \times 10^{-2}}{[0.212]^n}[0.170]^n \\ 0.6423 &= [0.8019]^n \\ \ln 0.6423 &= n(\ln 0.8019) \\ -0.4427 &= n(-0.2208) \\ n &= 2\end{aligned}$$

;

(b) Using the first set of data and $n = 2$, 6.68×10^{-3} mol/L/s = $k[0.170 \text{ mol/L}]^2$; $k = 0.231$ L/mol/s

78-18. 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 6.2×10^{-4} min^{-1}. When $[N_2O_5] = 0.40$ *M*,
rate = 6.2×10^{-4} min^{-1} (0.40 mol/L) = 2.5×10^{-4} mol/L/min

30. The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

(a) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(c) $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8×10^{-6} $\text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$.

Solution

The rate law governing the formation of HNO_3 is:

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

From the data given:

rate = $k[0.75 \text{ mol L}^{-1}]^2[0.50 \text{ mol/L}]$
= $(5.8 \times 10^{-6} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1})(0.75 \text{ mol L}^{-1})^2(0.50 \text{ mol/L})$
= 1.631×10^{-6} mol/L/s
= 1.6×10^{-6} mol/L/s

78-19. The following data have been determined for the reaction:

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

	1	2	3
$[I^-]_{initial}$ (M)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (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:

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

Unit 79 – Integrated Rate Laws

79-1. Describe how graphical methods can be used to determine the order of a reaction and its rate constant from a series of data that includes the concentration of A at varying times.

Solution

Plot $[A]$, $\ln[A]$, and $\frac{1}{[A]}$ versus time, t. A linear plot of $[A]$ versus t indicates a zero-order reaction with slope = $-k$. A linear plot of $\ln[A]$ versus t indicates a first-order reaction with $k = -$slope. A linear plot of $\frac{1}{[A]}$ versus t indicates a second-order reaction with k = slope.

79-2. What is the half-life for the first-order decay of phosphorus–32? ($^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-$) The rate constant for the decay is $4.85 \times 10^{-2}\ day^{-1}$.

Solution

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

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

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

79-3. What is the half-life for the first-order decay of carbon–14? ($^{14}_{6}\text{C} \longrightarrow {}^{14}_{7}\text{N} + \text{e}^{-}$) The rate constant for the decay is 1.21×10^{-4} year^{-1}.

Solution

The half-life of a first-order reaction is $t_{1/2} = \dfrac{0.693}{k}$ is the rate constant:

$$t_{1/2} = \frac{1}{1.21 \times 10^{-4}\ \text{y}^{-1}} = 5.73 \times 10^{3}\ \text{y}$$

79-4. 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,

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

79-5. Both technetium–99 and thallium–201 are used to image heart muscle in patients with suspected heart problems. The half-lives are 6 h and 73 h, respectively. What percent of the radioactivity would remain for each of the isotopes after 2 days (48 h)?

Solution

The half-life of a first-order reaction is determined from the expression:

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

Tc, $k = \frac{0.693}{6\text{ h}} = 0.116\text{ h}^{-1}$

Tl, $k = \frac{0.693}{73\text{ h}} = 0.00949\text{ h}^{-1}$;

for a first-order reaction:

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

Let $[A_0]$ = unity, then

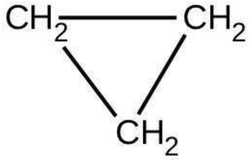
for Tc: $\ln\frac{1}{[A]} = 0.116\text{ h}^{-1} \times 48\text{ h} = 5.568$

Convert 5.568, a natural log, to the corresponding number by taking the *e*s of both sides:

$\frac{1}{[A]} = 261.9$; $[A] = 0.004$ or 0.4% after multiplying by 100%;

for Tl: $\ln\frac{1}{[A]} = 0.00949\text{ h}^{-1} \times 48\text{ h} = 0.4555$; convert 0.4555, a natural log, to the corresponding number by taking the *e*s of both sides: $\frac{1}{[A]} = 1.577$; $[A] = 0.63$ or 63% after multiplying by 100%.

79-6. 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 $5.95 \times 10^{-4}\text{ s}^{-1}$. 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

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{5.95 \times 10^{-4}\text{ s}^{-1}} = 1.16 \times 10^{3}\text{ s}$$

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

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

And so, 20% of the reactant remains.

78-7. 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

This problem can be solved "on your fingers", by working out the half-lives to get to 1/64 of the original does (i.e., after one half-life there would be ½ left; after two half-lives there would be ½ x ½ = ¼ left; after three half-lives there would be ½ x 1/4 = 1/8 left; after four half-lives there would be ½ x 1/8 = 1/16 left; after five half-lives there would be ½ x 1/16 = 1/32 left; and after six half-lives there would be ½ x 1/32 = 1/64 left. The six half-lives = 6 x 42 days = 252 days. OR you can calculate the time as follows:

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

78-8. In 2012, the skeleton of King Richard III was found under a parking lot in England. If tissue samples from the skeleton contain about 93.79% of the carbon-14 expected in living tissue, what year did King Richard III die? The half-life for carbon-14 is 5730 years.

Solution

Use the half-life equation for a first order process: $t_{1/2} = \frac{0.693}{k}$. $5730 = \frac{0.693}{k}$. So $k = 1.21 \times 10^{-4}\ \mathrm{y}^{-1}$. Next plug into the integrated rate law for a first order reaction: $\ln(0.9379) = -(1.21 \times 10^{-4})t + \ln(1.00)$ where 1.00 represents 100% of the carbon-14;
t = 530 years. 2015 – 530 = 1485, the year that King Richard III died.

78-9. 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:

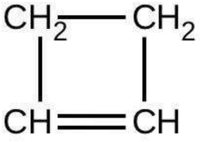
Initial $[C_3H_5N_3O_9]$ (M)	4.88	3.52	2.29	1.81	5.33	4.05	2.95	1.72
t (s)	300	300	300	300	180	180	180	180
% Decomposed	52.0	52.9	53.2	53.9	34.6	35.9	36.0	35.4

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

78-10. For the past 10 years, the unsaturated hydrocarbon 1,3-butadiene $(CH_2=CH-CH=CH_2)$ has ranked 38th among the top 50 industrial chemicals. It is used primarily for the manufacture of synthetic rubber. An isomer exists also as cyclobutene:



The isomerization of cyclobutene to butadiene is first-order and the rate constant has been measured as 2.0 × 10^{-4} s^{-1} at 150 °C in a 0.53-L flask. Determine the partial pressure of cyclobutene and its concentration after 30.0 minutes if an isomerization reaction is carried out at 150 °C with an initial pressure of 55 torr.

Solution

For a first-order reaction:

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

$$\ln\frac{[55\text{ torr}]}{[P\text{ torr}]} = 2.0 \times 10^{-4}\text{ s}^{-1} \times 30.0\text{ min} \times 60\text{ s min}^{-1}$$

$$\ln 55 - \ln P = 0.36$$

$$\ln P = \ln 55 - 0.36 = 4.01 - 0.36 = 3.65$$

$$P = 38\text{ torr}$$

As both reactants are gases, the pressure remains constant at 55 torr. The concentration of cyclobutene is found from the ideal gas law, $PV = nRT$:

$$n = \frac{PV}{RT} = \frac{\frac{38\text{ torr}}{760\text{ torr}} \times 0.53\text{ L}}{0.08206\text{ L atm K}^{-1}\text{ mol}^{-1} \times 423\text{ K}}$$

$$n = 7.6 \times 10^{-4}$$

$$;\ \text{molarity} = \frac{n}{0.53\text{ L}} = 1.4 \times 10^{-3}\ M$$

79-11. 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, $t_{1/2} = \frac{1}{k[A]_0}$.

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

79-12. What is the half-life for the decomposition of O_3 when the concentration of O_3 is 2.35×10^{-6} *M*? The rate constant for this second-order reaction is 50.4 L mol^{-1} h^{-1}.

Solution

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

$$t_{1/2} = \frac{1}{k[\mathrm{A}]_0} = \frac{1}{50.4\ \text{L mol}^{-1}\ \text{h}^{-1}[2.35 \times 10^{-6}\ M]} = 8.44 \times 10^{3}\ \text{h}$$

79-13. 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:

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

79-14. The half–life of a reaction of compound *A* to give compounds *D* and *E* is 8.50 min when the initial concentration of *A* is 0.150 *M*. How long will it take for the concentration to drop to 0.0300 *M* if the reaction is (a) first order with respect to *A* or (b) second order with respect to *A*?

Solution

(a) In a first-order reaction, the half-life is given by $t_{1/2} = 0.693/k$. Knowing $t_{1/2}$, the value of *k* can be determined:

$$k = \frac{0.693}{8.50\ \text{min}} = 0.0815\ \text{min}^{-1}$$

Then, from:

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

$$t = \ln\left[\frac{0.150\ \cancel{\text{mol}}\ \cancel{\text{L}^{-1}}}{0.0300\ \cancel{\text{mol}}\ \cancel{\text{L}^{-1}}}\right] \times \frac{1}{0.0815\ \text{min}^{-1}} = 1.60944 \times 12.27\ \text{min} = 19.7\ \text{min};$$

(b) In a second-order reaction, the rate is concentration-dependent:

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

$$k = \frac{1}{t_{1/2}[A]_0} = \frac{1}{8.50\text{ min }[0.150\text{ mol L}^{-1}]} = 0.784\text{ L mol}^{-1}\text{ min}^{-1}$$

Then substitution into:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

Gives:

$$t = \frac{\dfrac{1}{0.0300\text{ mol L}^{-1}} - \dfrac{1}{0.150\text{ mol L}^{-1}}}{0.784\text{ L mol}^{-1}\text{ min}^{-1}} = \frac{33.333\ \cancel{\text{L}}\ \cancel{\text{mol}^{-1}} - 6.667\cancel{\text{L}}\ \cancel{\text{mol}^{-1}}}{0.784\ \cancel{\text{L}}\ \cancel{\text{mol}^{-1}}\text{ min}^{-1}} = 34.0\text{ min}$$

79-15. From the given data, use a graphical method to determine the order and rate constant of the following reaction:

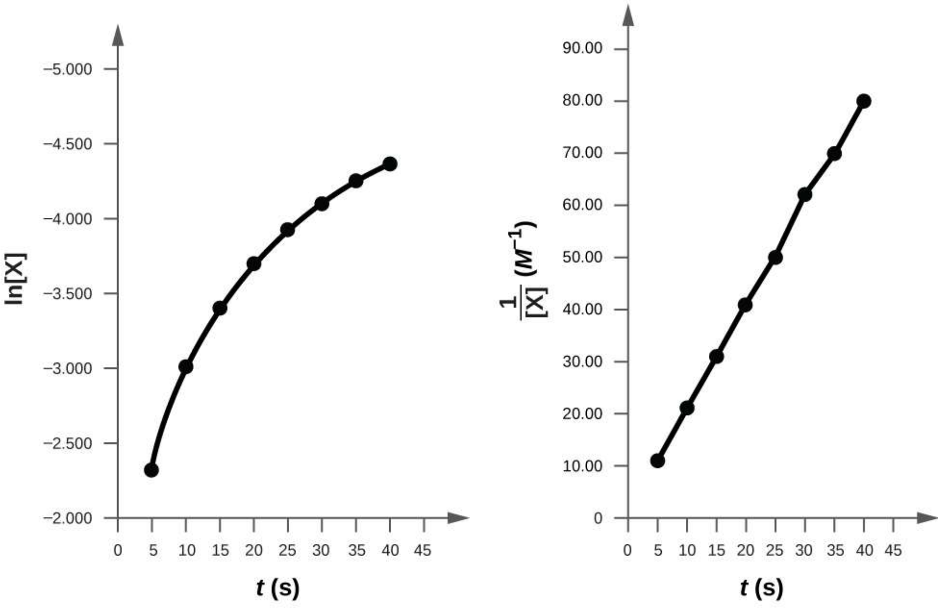
$$2X \longrightarrow Y + Z$$

Time (s)	5.0	10.0	15.0	20.0	25.0	30.0	35.0	40.0
$[X]$ (M)	0.0990	0.0497	0.0332	0.0249	0.0200	0.0166	0.0143	0.0125

Solution

To distinguish a first-order reaction from the second-order reaction, we plot ln[X] against t and compare that plot with a plot of $\frac{1}{[X]}$ versus t. The necessary data are as follows:

Time (s)	5.0	10.0	15.00	20.00	25.00	30.00	35.00	40.00
$\frac{1}{[X]}$	10.10	20.12	30.12	40.16	50.00	60.24	69.93	80.00
ln[X]	−2.313	−3.002	−3.405	−3.693	−2.313	−4.098	−4.247	−4.382



(a) (b)

The plot shows that the reaction data are constant with second-order kinetics, as $\frac{1}{[X]}$ versus *t* is a straight line.

Unit 80 – Collision Theory

80-1. 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.

80-2. When every collision between reactants leads to a reaction, what determines the rate at which the reaction occurs?

Solution

diffusion; in this example, since every collision between reactants leads to a reaction, the activation energy has been exceeded

80-3. 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.

80-4. Account for the relationship between the rate of a reaction and its activation energy.

Solution

The rate of reaction will increase as the activation energy decreases. This relationship is reasonable because a large activation energy that requires a large amount of energy is a hindrance to reaction.

80-5. In terms of collision theory, to which of the following is the rate of a chemical reaction proportional?

(a) the change in free energy per second

(b) the change in temperature per second

(c) the number of collisions per second
(d) the number of product molecules

Solution

(c) the number of collisions per second

80-6. How does an increase in temperature affect rate of reaction? Explain this effect in terms of the collision theory of the reaction rate.

Solution

It increases the rate of reaction by increasing the average kinetic energy of the molecules involved. This results in a larger fraction of collisions resulting in the molecules having the energy to overcome the activation energy barrier to form activated complexes.

80-7. 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.

80-8. 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 $\frac{-E_\text{a}}{R}$, from which E_a may be determined.

80-9. In an experiment, a sample of $NaClO_3$ was 90% decomposed in 48 min. Approximately how long would this decomposition have taken if the sample had been heated 20 °C higher? (Hint: Assume the rate doubles for each 10 °C rise in temperature.)

Solution

The rate doubles for each 10 °C rise in temperature. Thus, an increase of 20 °C would increase the rate four times, thereby decreasing the time required to one-fourth its original value:

$$\frac{48\text{ min}}{4} = 12\text{ min}.$$

80-10. 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:

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

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

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

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

80-11. The rate constant for the decomposition of acetaldehyde, CH_3CHO, to methane, CH_4, and carbon monoxide, CO, in the gas phase is 1.1×10^{-2} L mol^{-1} s^{-1} at 703 K and 4.95 L mol^{-1} s^{-1} at 865 K. Determine the activation energy for this decomposition.

Solution

In the text, a graphical method was used to determine activation energies, but we are only given two data points in this problem. With only two data points available, it is not necessary to plot the points to calculate the slope of the line that would be generated if more points were plotted:

T (K)	$\frac{1}{T}$ (K^{-1})	k (L mol^{-1} s^{-1})	Lnk
703	1.422×10^{-3}	1.1×10^{-2}	–4.50986
865	1.156×10^{-3}	4.95	1.59939

$$\text{Slope} = \frac{\Delta(\ln\ k)}{\Delta\left(\frac{1}{T}\right)}$$
$$= \frac{(-4.50986) - (1.599388)}{(1.422 \times 10^{-3}\ \text{K}^{-1}) - (1.156 \times 16^{-3}\ \text{K}^{-1})}$$
$$= \frac{-6.109248}{0.266 \times 10^{-3}\ \text{K}^{-1}}$$
$$= -2.297 \times 10^{4}\ \text{K}$$

Also, the $\text{slope} = \frac{-E_a}{R}$, so

E_a = slope × RE_a = slope R

$= -(-2.297 \times 10^4\ \text{K})(8.314\ \text{J/mol/K})$

$= 1.91 \times 10^5\ \text{J/mol} \longrightarrow 1.91 \times 10^2\ \text{kJ/mol}$

80-12. 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

80-13. 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* ($\text{L mol}^{-1}\text{ s}^{-1}$)
555	6.23×10^{-7}
575	2.42×10^{-6}
645	1.44×10^{-4}
700	2.01×10^{-3}

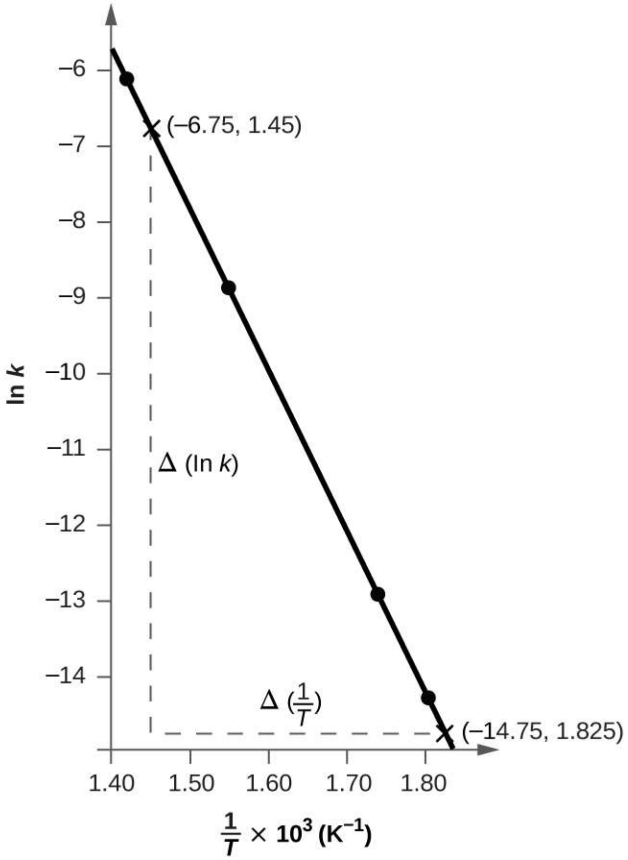
What is the value of the activation energy (in kJ/mol) for this reaction?

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

80-14. The element Co exists in two oxidation states, Co(II) and Co(III), and the ions form many complexes. The rate at which one of the complexes of Co(III) was reduced by Fe(II) in water was measured. Determine the activation energy of the reaction from the following data:

T (K)	k (s^{-1})
293	0.054
298	0.100

Solution

For only two data points, the Arrhenius equation:

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

may be used in an analytical solution for E_a. This approach is possible because the value of A will be constant 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). At 293 K or 298 K, the value of k may be determined using the value of E_a and A so determined. The procedure is as follows:

At 293 K:

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

$$0.054\ \text{s}^{-1} = A \times e^{-E_a(8.314\ \text{J K}^{-1})(293\ \text{K})} \qquad \text{(equation 1)}$$

$$0.100\ \text{s}^{-1} = A \times e^{-E_a(8.314\ \text{J K}^{-1})(293\ \text{K})} \qquad \text{(equation 2)}$$

Equating the values of A as calculated from equations (1) and (2), we have:

$$0.054 \times e^{E_a/(8.314\ \text{J})(293)} = 0.100 \times e^{E_a/(8.314\ \text{J})(298)} \text{ or } 0.054 \times e^{E_a/2436} = 0.100 \times e^{E_a/2478}.$$

Taking natural logarithms of both sides gives:

$$\begin{aligned}
\ln 0.054 + \frac{E_a}{2436} &= \ln 0.100 + \frac{E_a}{2478} \\
-2919 + \frac{E_a}{2436} &= -\ 2.303 + \frac{E_a}{2478} \\
-0.616 &= E_a\left(\frac{1}{2478} - \frac{1}{2436}\right) \\
&= E_a(4.0355 \times 10^{-4} - 4.1051 \times 10^{-4}) \\
&= E_a(-6.96 \times 10^{-6}) \\
E_a &= 89 \times 10^{4}\ \text{J or } 8.9 \times 10^{1}\ \text{kJ}
\end{aligned}$$

80-15. 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:

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

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

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

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

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

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

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

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:

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

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

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

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

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.

Unit 81 – Reaction Mechanisms

81-1. Why are elementary reactions involving three or more reactants very uncommon?

Solution

Although some termolecular reactions are known, it is very rare for three or more molecules come together at exactly the same instant and with the proper orientation required for a reaction to occur.

81-2. 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.

81-3. Define these terms:
(a) unimolecular reaction
(b) bimolecular reaction
(c) elementary reaction
(d) overall reaction

Solution

(a) Unimolecular reaction: A reaction in which a single molecule or ion produces one or more molecules or ions of product. (b) Bimolecular reaction: A collision and combination of two reactants to give an activated complex in an elementary reaction. (c) Elementary reaction: A reaction that occurs in a single step. One or more elementary reactions combine to form a reaction mechanism. (d) Overall reaction: An addition of all steps that excludes the intermediates. It indicates the stoichiometry of the reactants and the products, but not the mechanism.

81-4. 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 = $k[A]^3$

81-5. Given the following reactions and the corresponding rate laws, in which of the reactions might the elementary reaction and the overall reaction be the same?

(a)

$$\mathrm{Cl_2 + CO \longrightarrow Cl_2CO}$$

$$\text{rate} = k[\mathrm{Cl_2}]^{3/2}[\mathrm{CO}]$$

(b)

$$\mathrm{PCl_3 + Cl_2 \longrightarrow PCl_5}$$

$$\text{rate} = k[\mathrm{PCl_3}][\mathrm{Cl_2}]$$

(c)

$$\mathrm{2NO + H_2 \longrightarrow N_2 + H_2O_2}$$

$$\text{rate} = k[\mathrm{NO}][\mathrm{H_2}]$$

(d)

$$\mathrm{2NO + O_2 \longrightarrow 2NO_2}$$

$$\text{rate} = k[\mathrm{NO}]^2[\mathrm{O_2}]$$

(e)

$$\mathrm{NO + O_3 \longrightarrow NO_2 + O_2}$$

$$\text{rate} = k[\mathrm{NO}][\mathrm{O_3}]$$

Solution

In (b), (d), and (e), the elementary and overall reactions are likely to be the same. (a) An elementary reaction is unlikely to have a collision involving more than two reactants. Thus, it would be improbable to find the concentration in the rate law raised to a power other than 1 or 2. (b) The rate expression indicates that both reactants are involved in the reaction. A binary collision is likely, leading to the possibility of an elementary reaction. (c) The rate law does not correspond to the stoichiometry of the overall equation and therefore the reaction cannot be elementary. (d) This equation could correspond to a termolecular collision process, one not highly likely, but possible as an elementary process. (e) This equation corresponds to a simple bimolecular collision and could be an elementary reaction.

81-6. Write the rate law for each of the following elementary reactions:

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

(b) $\mathrm{O_3 + Cl \longrightarrow O_2 + ClO}$

(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) $\text{Rate}_3 = k[NO_2][O]$

81-7. Nitrogen monoxide, NO, reacts with hydrogen, H_2, according to the following equation:

$$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$$

What would the rate law be if the mechanism for this reaction were:

$$2NO + H_2 \longrightarrow N_2 + H_2O_2 \left(\text{slow}\right)$$

$$H_2O_2 + H_2 \longrightarrow 2H_2O \left(\text{fast}\right)$$

Solution

The slow reaction is the rate-determining step:

$$2NO + H_2 \longrightarrow N_2 + H_2O_2$$

Therefore, the rate must be based on this equation.

$$\text{Rate } = k\left[NO\right]^2\left[H_2\right]$$

81-8. `The reaction of CO with Cl_2 gives phosgene ($COCl_2$), a nerve gas that was used in World War I. Use the mechanism shown here to complete the following exercises:

$Cl_2(g) \longrightarrow 2Cl(g)$ (fast, k_1 represents the forward rate constant, k_{-1} the reverse rate constant)

$CO(g) + Cl(g) \longrightarrow COCl(g)$ (slow, k_2 the rate constant)

$COCl(g) + Cl(g) \longrightarrow COCl_2(g)$ (fast, k_3 the rate constant)

(a) Write the overall reaction.
(b) Identify all intermediates.
(c) Write the rate law for each elementary reaction.
(d) Write the overall rate law expression.

Solution

(a) overall reaction: $CO\ (g) + Cl_2(g) \longrightarrow COCl_2(g)$; (b) identify all intermediates—Cl(g), COCl(g); (c) write the rate law for each elementary reaction: $k_1[Cl_2] = k_{-1}[Cl]^2$, Rate = $k_2[CO][Cl]$, Rate = $k_3[COCl][Cl]$; (d) Write the overall rate law expression: The overall rate law expression is derived from the slow step, which is the rate-determining step. In this case Rate = $k_2[CO][Cl]$. Since Cl is an intermediate, algebraic manipulation is required to eliminate [Cl] from the rate law expression. Use the first equilibrium reaction to derive an expression that represents

[Cl]: $k_1[\mathrm{Cl_2}] = k_{-1}[\mathrm{Cl}]^2$; now divide each side by k_{-1}: $\left(\frac{k_1[\mathrm{Cl_2}]}{k_{-1}}\right) = [\mathrm{Cl}]^2$; then take the square root of each side: $\left(\frac{k_1[\mathrm{Cl_2}]}{k_{-1}}\right)^{1/2} = [\mathrm{Cl}]$. Now substitute into— Rate $= k_2[\mathrm{CO}][\mathrm{Cl}]$.

$$\text{Rate} = k_2[\mathrm{CO}]\left(\frac{k_1[\mathrm{Cl_2}]}{k_{-1}}\right)^{1/2}$$

Unit 82 – Catalysis

82-1. 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.

82-2. Compare the functions of homogeneous and heterogeneous catalysts.

Solution

Both change the mechanism to one with a lower activation energy, thus producing a faster reaction. Homogeneous catalysts work in the same phase as the reactants; heterogeneous catalysts work in a different phase than the reactants, generally providing a surface upon which the reaction takes place.

82-3. Consider this scenario and answer the following questions: Chlorine atoms resulting from decomposition of chlorofluoromethanes, such as $\mathrm{CCl_2F_2}$, catalyze the decomposition of ozone in the atmosphere. One simplified mechanism for the decomposition is:

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

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

$$\mathrm{2O_3 \longrightarrow 3O_2}$$

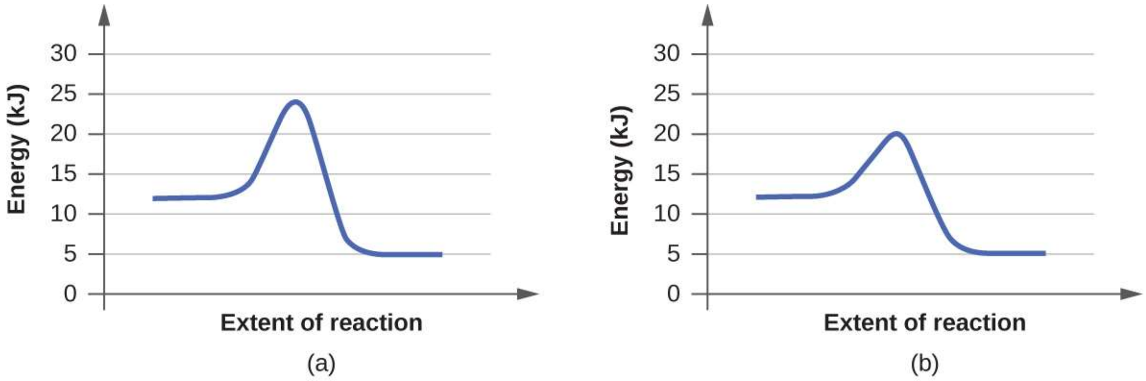
(b) Nitric oxide is also involved in the decomposition of ozone by the mechanism:

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

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

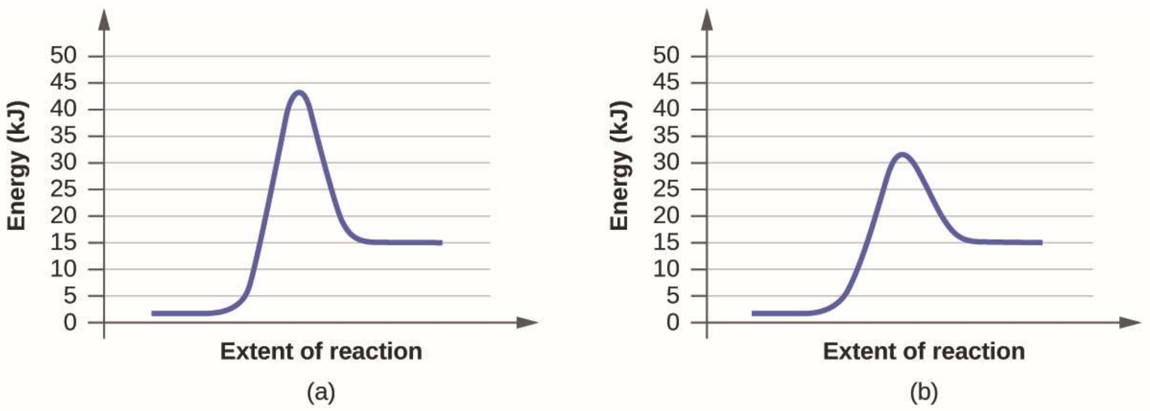
Solution
a) Chlorine atoms are a catalyst because they react in the second step but are regenerated in the third step. Thus, they are not used up, which is a characteristic of catalysts. (b) NO is a catalyst for the same reason as in part (a).

82-4. For each of the following pairs of reaction diagrams, identify which of the pair is catalyzed:
(a)



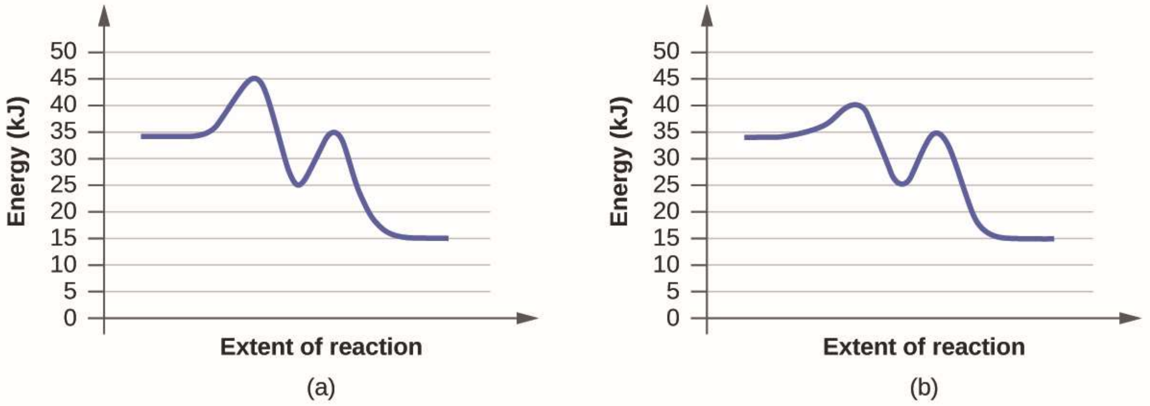
(a) (b)

(b)



(a) (b)

(c)

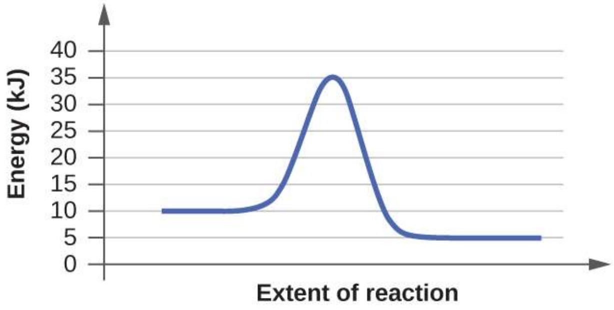


(a) (b)

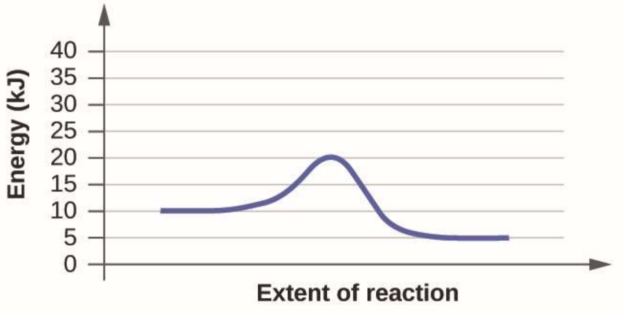
Solution
The lowering of the transition state energy indicates the effect of a catalyst. (a) b; (b) b; (c) b.

82-5. For each of the following reaction diagrams, estimate the activation energy (E_a) of the reaction:

(a)



(b)

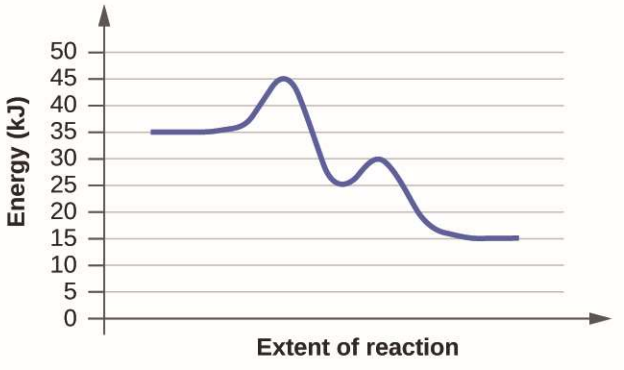


Solution

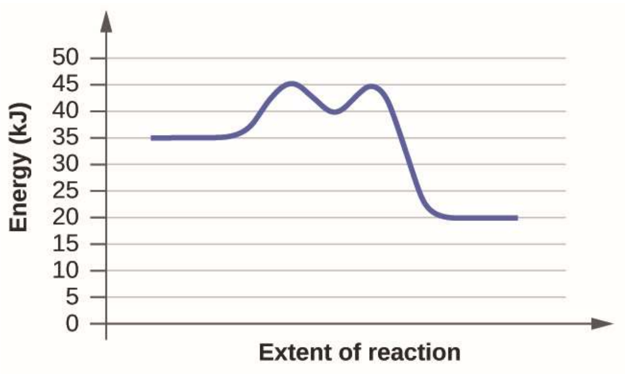
The energy needed to go from the initial state to the transition state is (a) 25 kJ; (b) 10 kJ.

82-6. 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.

82-7. Assuming the diagrams in Exercise 12.81 represent different mechanisms for the same reaction, which of the reactions has the faster rate?

Solution

The rate of a reaction increases as activation energy decreases. Reaction (b) exhibits a lesser activation energy and will be the faster reaction under a given set of conditions.