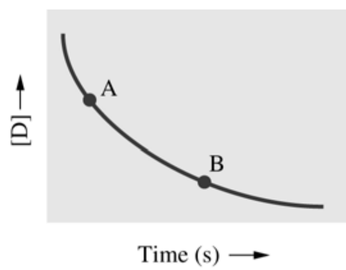
Chapter 14

Rates of Reaction

Concept Check 14.1

Shown here is a plot of the concentration of a reactant D versus time.



a. How do the instantaneous rates at points A and B compare?
b. Is the rate for this reaction constant at all points in time?

Solution

a. Since the slope is steeper at point A, point A must be a faster instantaneous rate.
b. Since the curve is not a flat line, the rate of the reaction must be constantly changing over time. Therefore, the rate for the reaction cannot be constant at all points in time.

Concept Check 14.2

Consider the reaction Q + R $\rightarrow$ S + T and the rate law for the reaction: Rate = $k\,[Q]^0[R]^2$.

a. You run the reaction three times, each time starting with [R] = 2.0 *M*. For each run you change the starting concentration of [Q]: run 1, [Q] = 0.0 *M*; run 2, [Q] = 1.0 *M*; run 3, [Q] = 2.0 *M*. Rank the rates of the three reactions using each of these concentrations.
b. The way the rate law is written in this problem is not typical for expressions containing reactants that are zero order in the rate law. Write the rate law in the more typical fashion.

Solution

a. Keeping in mind that all reactant species must be present in some concentration for a reaction to occur, the reaction with [Q] = 0 is the slowest since no reaction occurs. The other two reactions are equal in rate because the reaction is zero order with respect to [Q]: as long as there is some amount of Q present, the reaction rate depends on the [R] which is constant in this case.
b. Since $[Q]^0 = 1$, you can rewrite the rate law as follows: Rate = $k[R]^2$.

Concept Check 14.3

Rate laws are not restricted to chemical systems; they are used to help describe many “everyday” events. For example, a rate law for tree growth might look something like this:

Rate of Growth = $(\text{soil type})^w(\text{temperature})^x(\text{light})^y(\text{fertilizer})^z$.

In this equation, like chemical rate equations, the exponents need to be determined by experiment. (Can you think of some other factors?)

a. Say you are a famous physician trying to determine the factors that influence the rate of aging in humans. Develop a rate law, like the one above, that would take into account at least four factors that affect the rate of aging.
b. Explain what you would need to do in order to determine the exponents in your rate law.
c. Consider smoking to be one of the factors in your rate law. You conduct an experiment and find that a person smoking two packs of cigarettes a day quadruples (4X) the rate of aging over that of a one-pack-a-day smoker. Assuming that you could hold all other factors in your rate law constant, what will be the exponent of the smoking term in your rate law?

Solution

a. A possible rate law is: Rate of Aging = $(\text{diet})^w(\text{exercise})^x(\text{sex})^y(\text{occupation})^z$. Your rate law probably will be different; however, the general form should be the same.
b. You would need a sample of people that have all of the factors the same except one. For example, using the equation given in part a., you could determine the effect of diet if you had a sample of people that were the same sex, exercised the same amount, and had the same occupation. You would need to isolate each factor in this fashion to determine the exponent on each factor.
c. The exponent on the smoking factor would be 2 since you see a fourfold rate increase: $[2]^2 = 4$.

Concept Check 14.4

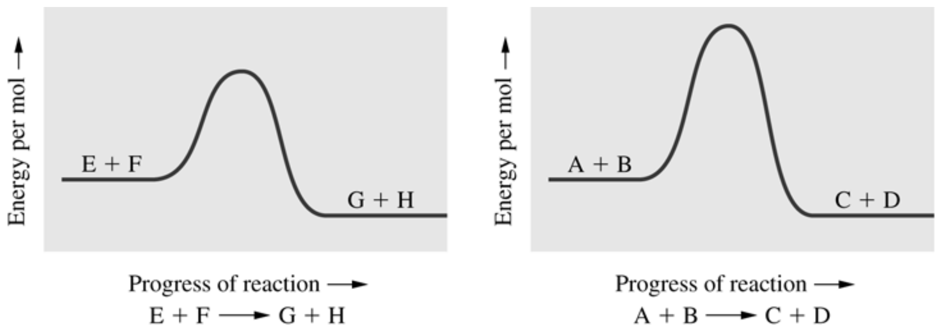
A reaction believed to be either first or second order has a half-life of 20 s at the beginning of the reaction but a half-life of 40 s some time later. What is the order of the reaction?

Solution

The half-life of a first-order reaction is constant over the course of the reaction. The half-life of a second-order reaction depends on the initial concentration and becomes larger as time elapses. Thus, the reaction must be second order because the half-life increases from 20 s to 40 s after time has elapsed.

Concept Check 14.5

Considering the following potential energy curves for two different reactions:



a. Which reaction has a higher activation energy for the forward reaction?
b. If both reactions were run at the same temperature and have the same orientation requirements to react, which one would have the larger rate constant?
c. Are these reactions exothermic or endothermic?

Solution

a. Since the "hump" is larger, the A + B reaction has a higher activation energy.
b. Since the activation energy is lower, the E + F reaction would have the larger rate constant. Keep in mind the inverse relationship between the activation energy, E_a, and the rate constant, k.
c. Since in both cases energy per mole of the reactants is greater than the products, both reactions are exothermic.

Concept Check 14.6

You are a chemist in charge of a research laboratory that is trying to increase the reaction rate for the balanced chemical reaction: $X + 2Y \rightarrow Z$.

a. One of your researchers comes into your office and states that she has found a material that significantly lowers the activation energy of the reaction. Explain the effect this will have on the rate of the reaction.
b. Another researcher states that after doing some experiments, he has determined that the rate law is rate = k[X][Y]. Is this possible?
c. Yet another person in the lab reports that the mechanism for the reaction is:
   $2Y \rightarrow I$ (slow)
   $X + I \rightarrow Z$ (fast)
   Is the rate law from part b. consistent with this mechanism? If not, what should the rate law be?

Solution

a. Her finding should increase the rate since the activation energy, E_a, is inversely related to the rate constant, k; a decrease in E_a results in an increase in the value of k.
b. This is possible because the rate law does not have to reflect the overall stoichiometry of the reaction.
c. No. Since the rate law is based on the slow step of the mechanism, it should be Rate = $k[Y]^2$.

Conceptual Problem 14.23

Consider the reaction: $3A \rightarrow 2B + C$.

a. One rate expression for the reaction is: Rate of formation of C = $+\frac{\Delta [C]}{\Delta t}$.
   Write two other rate expressions for this reaction in this form.
b. Using your two rate expressions, if you calculated the average rate of the reaction over the same time interval, would the rates be equal?
c. If your answer to part b. was no, write two rate expressions that would give an equal rate when calculated over the same time interval.

Solution

a. You can write the rate expression in terms of the depletion of A:
   Rate of depletion of A = $-\frac{\Delta[A]}{\Delta t}$.
   Or, you can write the rate expression in terms of the formation of B:

Rate of formation of B= + $\frac{\Delta[B]}{\Delta t}$.

b. No. Consider the stoichiometry of the reaction which indicates that the rate of depletion of A would be faster than the rate of formation of B: for every three moles of A that are consumed, two moles of B would be formed.

c. Taking into account the stoichiometry of the reaction, the two rate expressions that would give an equal rate when calculated over the same time interval are

Rate = - $\frac{\Delta[A]}{3\Delta t}$ = $\frac{\Delta[B]}{2\Delta t}$.

Conceptual Problem 14.24

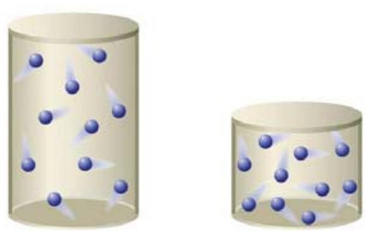
Given the reaction 2A + B → C + 3D, can you write the rate law for this reaction? If so, write the rate law; if not, why?

Solution

You cannot write the rate law for this reaction from the information given. The rate law can only be determined by experiment, not by the stoichiometry of the reaction.

Conceptual Problem 14.25

The reaction 2A(g) →A2(g) is being run in each of the following containers. The reaction is found to be second order with respect to A.



a. Write the rate law for the reaction.
b. Which reaction container will have a faster reaction rate?
c. In which container will the reaction have a shorter half-life?
d. What are the relative rates of the reactions in each container?
e. After a set amount of time has elapsed, which container will contain fewer A atoms?

Solution

a. The rate law for a second-order reaction is Rate = $k[A]^2$.
b. The faster reaction rate will correspond to the container with the higher concentration of A. Both containers contain the same number of A particles, but the volume of container B is only one-half the volume of container A. Therefore, the initial concentration of A in container B is double the initial concentration of A in container A. Thus, the reaction will be faster in container B.
c. For a second-order reaction, the relationship between the half-life, rate constant, and initial concentration of A is

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

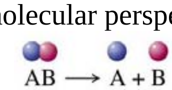
Since the half-life is inversely proportional to the initial concentration, the shorter half-life will correspond to the higher initial concentration of A, which is container B.
d. The relative rates of the reactions can be determined as follows. Since the initial concentration of A in container B is double the initial concentration of A in container A, the ratio of the rate in container B to that in container A is

$$\frac{\text{Rate}_B}{\text{Rate}_A} = \frac{k[A]^2_{o,B}}{k[A]^2_{o,A}} = \left(\frac{[A]_{o,B}}{[A]_{o,A}}\right)^2 = \left(\frac{2[A]_{o,A}}{[A]_{o,A}}\right)^2 = 2^2 = 4$$

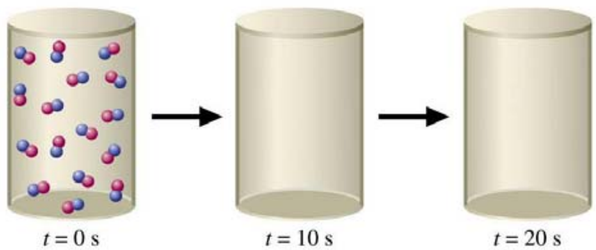
Thus, the reaction rate in container B is four times the reaction rate in container A.
e. Since both containers start with the same number of A particles, and the reaction rate is faster in container B, more A particles will have reacted in container B than in container A, so container B will contain fewer atoms.

Conceptual Problem 14.26

When viewed from a molecular perspective, a particular reaction is written as:



a. If the reaction is first-order with a half-life of 10 seconds, complete the following pictures after 10 and 20 seconds have elapsed.



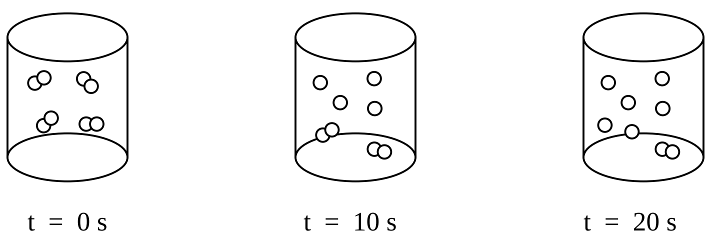
b. How would the pictures from part a change if the reaction were second-order with the same half-life?

c. For the first-order case, what are the relative reaction rates at the start of the reaction and after 10 seconds have elapsed?

d. For the second-order case, what are the relative reaction rates at the start of the reaction and after 10 seconds have elapsed?

Solution

a. The reaction is first-order with a half-life of 10 seconds. Starting with four particles in the container, after 10 seconds (one half-life), two of the particles will have reacted and two will remain unreacted. After 20 seconds (two half-lives), three of the particles will have reacted and one will remain unreacted. The pictures are



b. If the half-life is the same for the second-order reaction, the pictures will be the same.

c. After 10 seconds (one half-life), the concentration of the particles is one-half their initial value. If we call the particles A, then for the first-order case the relative reaction rates at the start and after 10 seconds are

$$\frac{\text{Rate}_0}{\text{Rate}_{10}} = \frac{k[A]_{o,0}}{k[A]_{o,10}} = \frac{[A]_{o,0}}{[A]_{o,10}} = \frac{[A]_o}{1/2[A]_o} = 2$$

Thus, for the first-order case, after 10 seconds, the rate is one-half the initial rate.

d. After 10 seconds (one half-life), the concentration of the particles is one-half their initial value. If we call the particles A, then for the second-order case the relative reaction rates at the start and after 10 seconds are

$$\frac{\text{Rate}_0}{\text{Rate}_{10}} = \frac{k[A]^2_{o,0}}{k[A]^2_{o,10}} = \left(\frac{[A]_{o,0}}{[A]_{o,10}}\right)^2 = \left(\frac{[A]_o}{1/2[A]_o}\right)^2 = 2^2 = 4$$

Thus, for the second-order case, after 10 seconds, the rate is four times the initial rate.

Conceptual Problem 14.28

You perform some experiments for the reaction A → B + C and determine the rate law has the form: Rate = $k[A]^x$. Calculate the value of the exponent x for each of the following cases.

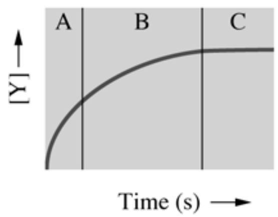
a. [A] is tripled and you observe no rate change.
b. [A] is doubled and the rate doubles.
c. [A] is tripled and the rate goes up by a factor of 27.

Solution

a. If the concentration is tripled but there is no effect on the rate, the order of the reaction must be zero. Thus, $x = 0$.
b. If the concentration is doubled and the rate doubles, it is a first order reaction. Thus, $x = 1$.
c. If the concentration is tripled and the rate goes up by a factor of 27, it is a third order reaction. Thus, $x = 3$.

Conceptual Problem 14.29

Given the hypothetical plot shown here for the concentration of compound Y versus time, answer the following questions.



a. In which region of the curve does the rate have a constant value (A, B, or C)?
b. In which region of the curve is the rate the fastest (A, B, or C)?

Concept Target

• Illustrate that rate information can be extracted from an experimental concentration versus time plot.

Solution

a. The rate has a constant value in region C, since the slope of the curve is constant (flat) in this region.
b. The rate is the fastest in region A, since the slope of the curve is steepest in this region.

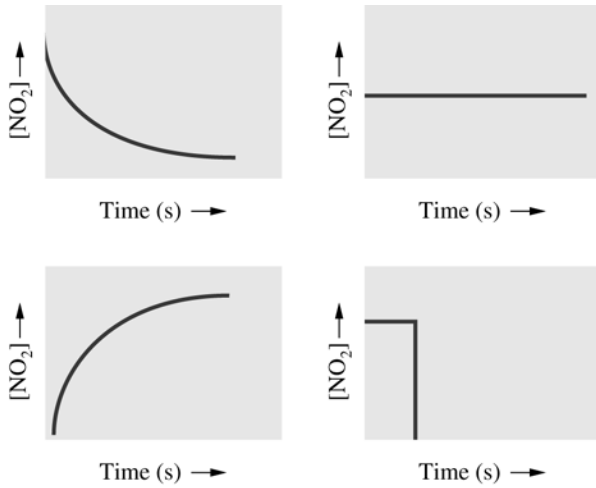
Conceptual Problem 14.30

You carry out the following reaction by introducing N_2O_4 into an evacuated flask and observing the concentration change of the product over time.

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

Which one of the curves shown here reflects the data collected for this reaction?

Curve A Curve B



Curve C Curve D

Solution

Since NO_2 is a product in the reaction, its concentration must increase with time. The only graph that has $[NO_2]$ increasing with time is curve C.

Conceptual Problem 14.31

You are running the reaction $2A + B \rightarrow C + 3D$. Your lab partner has conducted the first two experiments to determine the rate law for the reaction. He has recorded the initial rates for these experiments in another data table. Come up with some reactant concentrations for Experiment 3 that will allow you to determine the rate law by measuring the initial rate.

Experiment Number	Concentration of A (*M*)	Concentration of B (*M*)
1	1.0	1.0
2	2.0	1.0
3		

Solution

A number of answers will work as long as you match one of the existing concentrations of A or B. For example: [A] = 2.0 *M* with [B] = 2.0 *M*, or [A] = 1.0 *M* with [B] = 2.0 *M*.

Conceptual Problem 14.31

The chemical reaction A $\rightarrow$ B + C has a rate constant that obeys the Arrhenius equation. Predict what happens to both the rate constant *k* and the rate of the reaction if the following were to occur:

a. a decrease in temperature.
b. an increase in the activation energy of the forward and reverse reactions.
c. an increase in both activation energy and temperature.

Solution

The Arrhenius equation is $k = Ae^{-E_a/RT}$

a. When the temperature is decreased, the rate constant, *k*, will also decrease. When *k* decreases, the rate also decreases.
b. When the activation energy is increased, the rate constant, *k*, also decreases. When *k* decreases, the rate also decreases.
c. Since the activation energy is in the numerator and the temperature is in the denominator, you cannot predict the effect without knowing the magnitude of the changes.