

- Hydrochloric acid has a much higher concentration of reactive hydrogen ions in solution than carbonic acid. Most of the carbonic acid remains in solution undissociated.

Making Connections

- To be suitable for starting a campfire, fuel should be flammable (chemical nature), and have a high surface area (more subdivided if a solid).
- Heterogeneous catalysts are easier to separate from the products and reuse. Since many catalysts are very expensive, reuse is very important economically. For example, vanadium(V) oxide is a solid catalyst used in the industrial production of millions of tonnes of sulfuric acid; platinum is used in the manufacture of nitrogen dioxide, and so on.
- Catalytic converters are used to remove carbon monoxide, VOCs (volatile organic compounds), and NO_x (nitrogen oxides) from exhaust. Two separate types of catalysts, reduction and oxidation catalysts, are arranged in a honeycomb pattern. Nitrogen oxides are reduced to nitrogen and oxygen by the reduction catalyst. The oxidation catalyst changes carbon monoxide and unburned hydrocarbons (VOCs) into carbon dioxide and water.

6.3 RATE LAWS AND ORDER OF REACTION

PRACTICE

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Understanding Concepts

- Order of reaction refers to the rate dependence or exponential index of one species in the rate law, whereas overall order is the sum of all the indices. If a rate law were $r = k[A][B]^2$, the order of reaction with respect to A would be 1, the order of reaction with respect to B would be 2, and the overall order would be 3.
- This is a first-order reaction, so doubling the initial concentration should double the initial rate.
- $$k = \frac{r}{([\text{NH}_4^+]_{\text{(aq)}} [\text{NO}_2^-]_{\text{(aq)}})}$$

$$= \frac{2.40 \times 10^{-7} \text{ mol/(L}\cdot\text{s)}}{(0.200 \text{ mol/L} \times 0.00500 \text{ mol/L})}$$

$$k = 2.4 \times 10^{-4} \text{ L/(mol}\cdot\text{s)}$$
 - $$r = k[\text{NH}_4^+]_{\text{(aq)}}[\text{NO}_2^-]_{\text{(aq)}}$$

$$= 3.20 \times 10^{-4} \text{ L/(mol}\cdot\text{s)} \times 0.100 \text{ mol/L} \times 0.0150 \text{ mol/L}$$

$$r = 4.8 \times 10^{-7} \text{ mol/(L}\cdot\text{s)}$$
- Rate is second order with respect to A, first order with respect to B, zeroth order with respect to C.
 - $r = k[A]^2[B]$
- The reaction rate constant increases.
 - The reaction rate constant is unchanged.
- When we compare Trials 1 and 2, we see that as [A] is doubled, rate is multiplied by 4; therefore, rate depends on [A]².
When we compare Trials 1 and 3, we see that as [B] is tripled, rate is multiplied by 1; therefore, rate depends on [B]⁰.
When we compare Trials 2 and 4, we see that as [C] is doubled, rate is multiplied by 2; therefore, rate depends on [C]¹.
 - $r = k[A]^2[C]^1$
 - When we use data from Trial 1,

$$k = \frac{r}{[A]^2[C]}$$

$$= \frac{3.0 \times 10^{-4} \text{ mol/(L}\cdot\text{s)}}{(0.10 \text{ mol/L})^2 \times 0.10 \text{ mol/L}}$$

$$k = 0.30 \text{ L}^2\text{/(mol}^2\cdot\text{s)}$$

$$\begin{aligned}
 \text{(d) } r &= k [A]^2 [C]^1 \\
 &= 0.30 \text{ L}^2/(\text{mol}^2 \cdot \text{s}) \times (0.40 \text{ mol/L})^2 \times 0.40 \text{ mol/L} \\
 r &= 1.9 \times 10^{-2} \text{ mol}/(\text{L} \cdot \text{s})
 \end{aligned}$$

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Understanding Concepts

7. (a) 72 a is three half-lives.

$$\text{Remaining mass, } m = 0.084 \text{ g} \times \frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$$

$$m = 0.0105 \text{ g}$$

- (b) 192 a is eight half-lives.

$$\text{Remaining mass, } m = 0.084 \times \left(\frac{1}{2}\right)^8$$

$$= \frac{0.084 \text{ g}}{256}$$

$$m = 3.3 \times 10^{-4} \text{ g}$$

$$8. \text{ (a) } t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{2.34 \times 10^{-3} \text{ s}^{-1}}$$

$$t_{1/2} = 296 \text{ s}$$

- (b) 12.5% is $1/8$ or $(1/2)^3$, which suggests three half-lives have passed.

$$\text{The time elapsed will be } 3 \times 296 \text{ s} = 888 \text{ s}.$$

Making Connections

9. Radioisotopes in such patients emit dangerous radioactive particles within the body and to the surroundings, but this emission declines over time. The most appropriate isotopes are those with a short half-life.

SECTION 6.3 QUESTIONS

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Understanding Concepts

1. First-order reaction implies a rate law in which only one species is present, with a rate dependence of one (e.g., $r = k[A]^1$).

Second-order reaction implies a rate law in which two molecules are present, with a total rate dependence of two (e.g., $r = k[A]^2$ or $r = k[A][B]$).

2. (a) The orders of reaction are: 1 with respect to $\text{Cl}_{2(g)}$, and 2 with respect to $\text{NO}_{(g)}$.

- (b) The rate would double.

- (c) The rate would multiply by 9.

$$\text{(d) } k = \frac{r}{[\text{Cl}_2] [\text{NO}]^2}$$

$$= \frac{0.0242 \text{ mol}/(\text{L} \cdot \text{s})}{0.20 \text{ mol/L} \times (0.20 \text{ mol/L})^2}$$

$$k = 3.0 \text{ L}/(\text{mol} \cdot \text{s})$$

$$\text{(e) } r = k [\text{Cl}_2] [\text{NO}]^2$$

$$= 3.00 \text{ L}/(\text{mol} \cdot \text{s}) \times 0.44 \text{ mol/L} \times (0.025 \text{ mol/L})^2$$

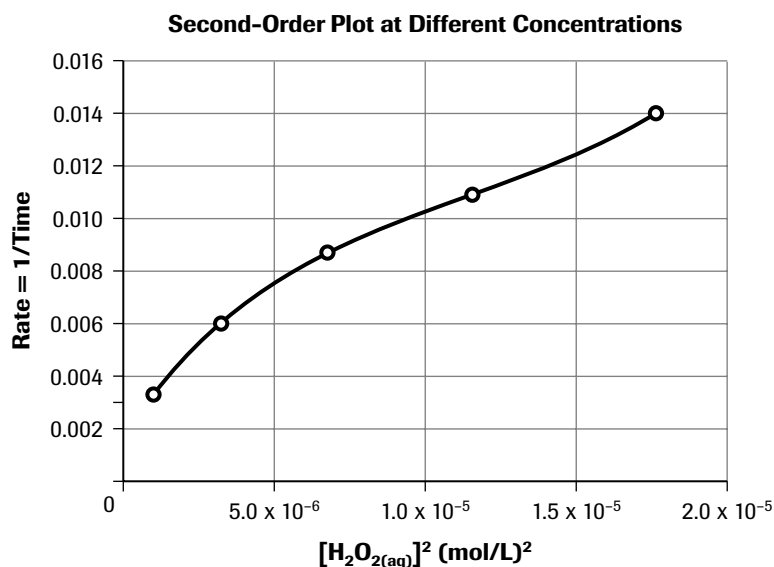
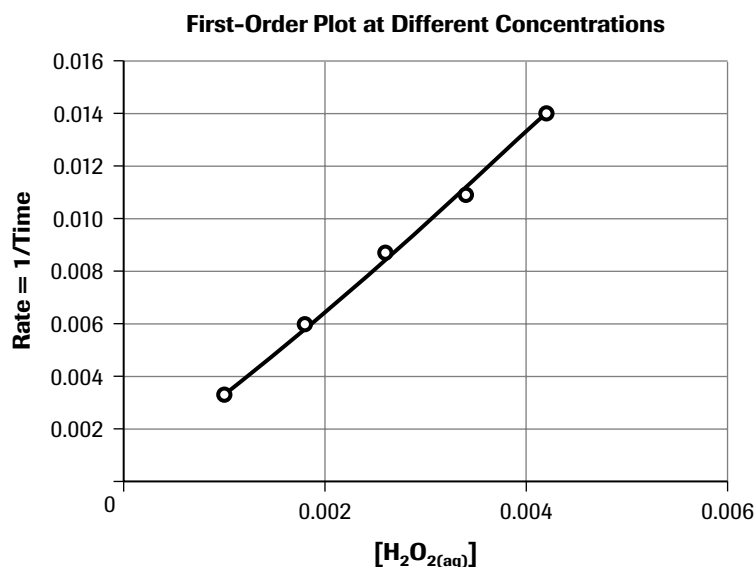
$$r = 8.2(5) \times 10^{-4} \text{ mol}/(\text{L} \cdot \text{s})$$

3. (a) $r = k [\text{antibiotic}]$
- (b) $t_{1/2} = 0.693/k$
 $= \frac{0.693}{1.40 \text{ a}^{-1}}$
 $t_{1/2} = 0.495 \text{ a}$
- (c) 2.0 a is about 4 half-lives.
- $$m = 20 \text{ g} \times (1/2)^4$$
- $$m = 2.5 \text{ g}$$
4. $1.84 \times 10^6 \text{ a}$ is $\frac{1.84 \times 10^6 \text{ a}}{2.3 \times 10^8 \text{ a}} = 8$ half-lives
- $$m = 10.0 \text{ g} \times \left(\frac{1}{2}\right)^8$$
- $$m = 0.039 \text{ g}$$

Applying Inquiry Skills

5. Analysis

- (a) The order of reaction can be determined by plotting 1/time vs. $[\text{H}_2\text{O}_2]$.



6. Question

What is the effect on rate of reaction on the iodine clock reaction?

Prediction

Predict qualitatively what will happen to the time of reaction as the temperature is increased. What will happen to the rate of reaction?

Experimental Design

A series of solutions will be prepared in which the only variable is the temperature. Equal amounts of starch, sodium bisulfite, and hydrochloric acid will be mixed with each of these solutions, so that the time from mixing to formation of a blue-black product can be recorded. The evidence will be analyzed graphically.

Materials

lab apron

eye protection

0.020 mol/L potassium iodate solution (Solution A)

0.001 00 mol/L sodium bisulfite/hydrochloric acid/starch solution (Solution B)

distilled water

3 plastic micropipets, labelled A, B, and H₂O

3 100-mL beakers, labelled A, B, and H₂O

2 large-well microtrays or spot plates, labelled A and B

stopwatch

hot plate

CAUTION:

There are no major safety concerns with this investigation. Follow general lab safety procedures.

Procedure

1. Place a test tube of Solution A and a test tube of Solution B in each of five water baths at different temperatures.
2. Place the two microtrays on clean sheets of white paper. For microtray A, using the appropriate micropipets, place 10 drops of Solution A (at different temperatures) in Wells 1–5. For microtray B, using the appropriate micropipets, place 10 drops of Solution B (at corresponding temperatures) in Wells 1–5.
3. With stopwatch ready, and using the water pipet, transfer the contents of Plate A Well 1 into Plate B Well 1. In doing so, insert the tip of the pipet below the surface of the liquid in Plate B to ensure that the solutions mix thoroughly and keep stirring. Start timing at the moment the pipet is squeezed and stop when the colour first appears. Record your observations.
4. Repeat this process for the other four temperatures of solutions.
5. Dispose of solutions down the drain with lots of running water.

Making Connections

7. (Answers will vary.) Most carbon on Earth is carbon-12. However, the atmosphere contains a small constant percentage of carbon-14, because there is an equilibrium between the rate of its production and its decay. Living animals and plants also contain a constant level of C-14, but at death the organism becomes isolated from the atmosphere and the C-14 starts to decay at a known rate of about 1.2% every century. The remaining percentage of C-14 in artifacts can be used to determine their age. Other radioisotopes used in dating artifacts and soil samples include U-238, Th-232, and K-40.
8. (a) (Answers will vary.) Types of nuclear wastes produced from electricity generation activities can be categorized as low-level wastes and high-level wastes. Low-level wastes are mostly items related to operations, such as mops, plastic sheeting, protective clothing, and paper products. These make up around 1% of the waste and are easily stored in monitored facilities. High-level waste is the used nuclear fuel removed from the reactors. This fuel is in the form of solid ceramic pellets, which must be stored in shielded facilities.
(b) AECL stores some solid low-level radioactive wastes at its Chalk River Laboratories in Ontario, in above-ground storage buildings. Since used reactor fuel is compact, solid, low in volume, and stable in a water environment, it is initially stored in deep-water pools used for cooling and shielding. After a few years, the used fuel may be moved to above-ground dry storage in concrete canisters.
(c) Proposed methods include storage deep underground in unused mines.
(d) Opposition could be based on environmental concerns. Support could be based on economic benefits to the community.