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Rate of Decomposition of Calcium Carbonate

AP* Chemistry Big Idea 4, Investigation 10

An Advanced Inquiry Lab

Introduction

What factors determine how fast a chemical reaction will occur? The answer has applications not just in chemistry, but also in food science, geology, ecology, and even art and architecture. Consider the weathering of beautiful marble statues from antiquity. The history of our civilization is gradually being eroded as acid in the environment dissolves the calcium carbonate in marble. Investigate the rate of decomposition of calcium carbonate with different concentrations of hydrochloric acid to learn more about kinetics and the rates of chemical reactions.

Concepts

- Kinetics
- Rate law
- Acids and bases
- Rate of reaction
- Order of reaction
- Neutralization
- Collision theory
- Gas laws
- Environmental chemistry

Background

Calcium carbonate, $CaCO_3$, is one of the most abundant minerals on the Earth. More than 4% of the Earth's crust is composed of calcium carbonate. It is a major component in limestone, marble, seashells, bedrock, etc. Limestone and marble have been among the most widely used building materials for more than 5000 years, from the pyramids in Egypt to the Parthenon in Greece and the Taj Mahal in India. In many places, limestone is also the foundation of our Earth—literally, since it is forms both bedrock and mountain ranges. Calcium carbonate dissolves in water to only a limited extent, but its solubility is greatly enhanced when the water is acidic. The gradual dissolution of marble and limestone, as well as coral and seashells, in acids is due to acid–base neutralization. The products of the neutralization reaction between calcium carbonate and hydrochloric acid, for example, are calcium chloride and carbonic acid, or H_2CO_3. Carbonic acid is unstable, decomposing to give carbon dioxide gas and water.

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2CO_3(aq) \qquad \textit{Equation 1}$$

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O(l) \qquad \textit{Equation 2}$$

The rate of the overall reaction (Equation 3) and, in particular, its dependence on the concentration of HCl, is an important concern in environmental chemistry due to the combined effects of acid rain and ocean acidification.

$$CaCO_3(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l) \qquad \textit{Equation 3}$$

Kinetics is the study of the rates of chemical reactions. As reactants are transformed into products in a chemical reaction, the amount of reactants will decrease and the amount of products will increase. The rate of the reaction can be determined by measuring the amounts or concentrations of reactants or products as a function of time. In some cases, it is possible to use a simple visual clue to determine a reaction rate. Some of the "clues" that may be followed to measure a reaction rate include appearance or disappearance of a color, amount of precipitate that forms, or amount of gas generated. In the case of the reaction of $CaCO_3$ with HCl, one of the products is a gas. Since either volume or mass of the gas is proportional to moles, the rate can be followed by measuring the time it takes for a specific volume or mass of carbon dioxide to be released. The reaction rate is calculated by dividing the moles of carbon dioxide produced by the time. The rate of a reaction describes how fast the reaction occurs—the faster the rate, the less time that is needed for a specific amount of reactants to be converted to products.

$$\text{Rate} = \frac{\text{Change in the number of moles of } CO_2}{\text{Time}}$$

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Some factors that affect the rates of chemical reactions include the nature of the reactants, their concentration, the reaction temperature, the surface area of solids, and the presence of catalysts. The relationship between the rate of a reaction and the concentration of reactants is expressed in a mathematical equation called a rate law. For a general reaction of the form

$$A + B \rightarrow C$$

the rate law can be written as

$$\text{Rate} = k[A]^n[B]^m$$

where k is the rate constant, [A] and [B] are the molar concentrations of the reactants, and n and m are exponents that define how the rate depends on the individual reactant concentrations. The rate of a reaction decreases over the course of the reaction as the concentrations of reactants decreases. For this reason, rate laws are usually determined by analyzing the rate after approximately 10–20% of reactant(s) have been converted to product.

The exponents n and m are also referred to as the *order of reaction* with respect to each reactant. In the above example, the reaction is said to be nth order in A and mth order in B. In general, n and m will be positive whole numbers—typical values of n and m are 0, 1, and 2. Note that when $n = 0$, the rate does not depend on the concentration of the reactant. When $n = 1$, the reaction will occur twice as fast when the reactant concentration is doubled, and when $n = 2$, the rate will increase by a factor of four when the reactant concentration is doubled. The values of the exponents must be determined by experiment—they cannot be predicted simply by looking at the balanced chemical equation.

Experiment Overview

The purpose of this advanced inquiry lab is to learn how reaction rates are measured and to design a kinetics experiment for the heterogeneous reaction of calcium carbonate with hydrochloric acid. The investigation begins with an introductory activity to observe the gradual evolution of carbon dioxide gas from the decomposition of calcium carbonate with acid. Special equipment is provided to collect and measure the volume of gas generated. The procedure provides a model for guided-inquiry design of kinetics experiments to determine the rate of reaction with different concentrations of acid. Using a cooperative classroom approach, different groups will compare data for mass loss and volume of gas generation versus time. Initial rates and the rate law for the reaction are determined by graphical analysis of the results. Other factors, such as the effect of temperature and particle size or surface area on the reaction rate, provide additional opportunities for inquiry.

Pre-Lab Questions

1. Collision theory states that the rate of a reaction depends on the number of collisions between molecules or ions, the average energy of the collisions, and their effectiveness. Does the general effect of concentration on reaction rate support the collision theory? Explain.
2. The reaction of solid calcium carbonate with hydrochloric acid is a heterogeneous reaction (a solid with a liquid). The rate law for this reaction will have the following form: rate = $k[HCl]^n$. Explain why the concentration of calcium carbonate does not appear in the rate law.
3. Read the entire procedure for the *Introductory Activity*. In step 5, why is it necessary to make sure the stopcock is in the open position and then immediately replace the stopper and syringe assembly in the Erlenmeyer flask after adding the hydrochloric acid to the marble chips?
4. The average rate of reaction of hydrogen peroxide with iodide ions to produce iodine was determined for three initial concentrations of hydrogen peroxide as shown in the table below. What is the order of the reaction with respect to hydrogen peroxide? Explain your reasoning.

Concentration of H_2O_2	Average initial rate (M/sec)
0.089 M	1.6×10^{-5}
0.044 M	7.2×10^{-6}
0.022 M	3.5×10^{-6}

Materials

Calcium carbonate (marble chips), $CaCO_3$, 3–5 g
Hydrochloric acid solution, 6 M, 10–20 mL
Hydrochloric acid solution, 4 M, 10–20 mL
Hydrochloric acid solution, 2 M, 10–20 mL
Hydrochloric acid solution, 1 M, 10–20 mL
Silicone grease or petroleum jelly (optional)
Water, distilled
Balance, 0.001-g precision (shared)
Beakers, 100- or 150-mL, 3
Clamp, single, buret
Erlenmeyer flasks, 125-mL, 3
Gas collection apparatus
  Syringe, 140-mL
  Syringe, adapter
  Stopcock
  Stopper
Graduated cylinders, 10- and 25-mL
Mortar and pestle
Support stand
Timer or stopwatch
Wash bottle

Safety Precautions

Hydrochloric acid is corrosive to skin and eyes and toxic by inhalation or skin absorption. Avoid contact with eyes and skin and clean up all spills immediately. Wear chemical splash goggles, chemical-resistant gloves, and a chemical-resistant apron. For the gas collection experiment, do not use more than 0.5 g of calcium carbonate. The concentration of hydrochloric acid must not exceed 6 M in any experiment. Wash hands thoroughly with soap and water before leaving the laboratory. Please follow all laboratory safety guidelines.

Introductory Activity

1. Read the entire procedure before beginning. This activity may be done as an individual experiment or an interactive classroom demonstration to encourage participation and discussion.
2. Obtain about 0.5 g of calcium carbonate (marble chips) and measure the precise mass. Place the marble chips (about 3 pieces) into a 125-mL Erlenmeyer flask.
3. Set up the gas-collection apparatus as shown in Figure 1. Make sure the rubber stopper fits securely in the flask and that the stopcock is open.
4. Carefully measure 10 mL of 6 M hydrochloric acid in a 10-mL graduated cylinder.
5. Remove the stopper and syringe assembly from the Erlenmeyer flask and *quickly but carefully* add the acid to the flask. **Immediately replace the stopper and syringe assembly in the flask and start timing.**
6. The syringe plunger will gradually expand out or lift up as gas is generated and collected in the syringe.
7. Measure the volume of gas in the syringe after one minute and again at 1-minute intervals for 10 minutes. To overcome friction or resistance in the syringe, it may be helpful to gently depress the plunger and then release it just before measuring the volume every minute.
8. Graph the volume (mL) of gas produced on the y-axis versus time (minutes) on the x-axis.

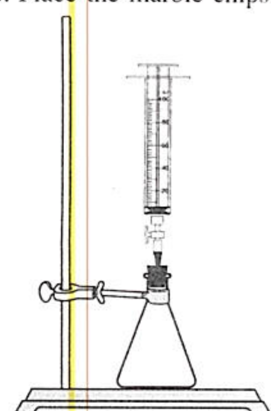


Figure 1.

Guided-Inquiry Design and Procedure

Form a working group with other students and discuss the following questions.

1. Analyze the graph generated in the *Introductory Activity*. Does the amount of CO_2 produced increase linearly with time, or does it begin to level off as the reaction proceeds? Explain the shape of the curve based on the rate of the reaction and changes in the concentration of HCl versus time.
2. Initial rates are generally used to compare reaction rates for different concentrations of reactants. The initial rate is calculated from the slope or linear portion of the graph of the amount of product versus time. Estimate the initial rate for the reaction of $CaCO_3$ with HCl, and express in units of volume of CO_2 per minute.
3. Calculate the number of moles of $CaCO_3$ and HCl, respectively, used in the *Introductory Activity*. Determine the limiting reactant and use the ideal gas law to estimate the maximum volume of CO_2 that could be produced in this reaction. Use the average room temperature and barometric pressure in the calculations.
4. Is the volume of the syringe sufficient to contain all of the CO_2 that could be produced? What was the average percent of reaction completion after 10 minutes? Explain in terms of potential sources of error in the experiment.
5. As mentioned in the *Experiment Overview*, two alternative procedures may be used to compare the effect of concentration on reaction rate. The first was demonstrated in the *Introductory Activity*. The second procedure involves the change in mass of the reaction mixture versus time. How would you expect the mass of the system to change as the reaction proceeds? What quantity would be proportional to the amount of CO_2 produced?
6. What is the theoretical mass of CO_2 that could be produced from (a) 0.50 g of $CaCO_3$ in the *Introductory Activity*, and (b) 1.00 g of $CaCO_3$? Which reactant quantity would be more suitable for the alternative procedure? Explain based on the precision of the balance and other factors, and also discuss how this choice would affect the volume of HCl that is used.
7. Identify the measurements that must be made for both procedures to investigate the effect of HCl concentration on the reaction rate and to determine the reaction order with respect to HCl. Name the independent and dependent variables for each series of experiments, and choose some suitable values for the independent variable.
8. Discuss how the size or surface area of the marble chips might affect the purpose or design of the experiments. What would be the best way to control this variable so that it remains constant throughout and does not affect the analysis?
9. Write a detailed step-by-step procedure for two alternative series of kinetics experiments to investigate the effect of HCl concentration on the reaction of $CaCO_3$ with HCl. Include all the materials, glassware and equipment that will be needed, safety precautions that must be followed, concentrations and amounts of reactants, etc.
10. Review additional variables that may affect the accuracy or reproducibility of the experiments and how these variables will be controlled.
11. Carry out the experiment and record results in an appropriate data table.

Analyze the results:

Graph the results obtained for each trial and calculate the average or initial rate for each concentration of HCl. Plot or analyze the rate versus HCl concentration to determine the reaction order. Compare and contrast the results obtained using the two alternative procedures and discuss any discrepancies. Review potential sources of experimental error in each procedure and how they would have affected the results.

Opportunities for Inquiry

Investigate the effect of other variables, such as temperature, particle size or surface area, and the presence of a catalyst, on the rate of decomposition of calcium carbonate with hydrochloric acid.

AP Chemistry Review Questions

Integrating Content, Inquiry and Reasoning

1. An unknown Group 1 metal carbonate M_2CO_3 (M = Li, Na or K) was reacted with excess 2 M HCl and the mass of CO_2 released was determined by mass difference. The initial mass of solid M_2CO_3 was 2.002 g and the mass of CO_2 released was 1.206 g.

   a. Write the balanced chemical equation for the reaction of M_2CO_3 with HCl.

   b. What is the mole ratio of CO_2 to M_2CO_3?

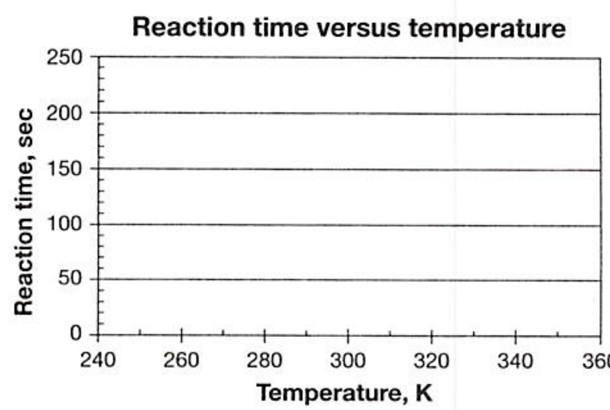
   c. Calculate the molar mass of the unknown metal carbonate and identify the Group 1 metal.

2. The rate of reaction of 0.030 g of magnesium ribbon with 1 M hydrochloric acid was studied at four different temperatures by measuring the time required for the magnesium metal to disappear. The following data was recorded:

Temperature	2 °C	23 °C	40 °C	53 °C
Average Reaction Time (sec)	204	73	56	41
Average Reaction Rate (moles/sec)				

   a. Calculate the number of moles of magnesium that reacted and the average reaction rate for each temperature.

   b. Convert each temperature to kelvins and plot the average reaction time versus temperature in the graph below. Predict how long the reaction would take at 75 °C.



   c. Using kinetic molecular theory and collision theory, explain why the absolute temperature scale (kelvins) is more appropriate than Celsius for explaining the effect of temperature on reaction rate. Does the effect of temperature on reaction rate support the collision theory of chemical reactions?