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# AP<sup>®</sup> Chemistry 2







# AP Chemistry 2

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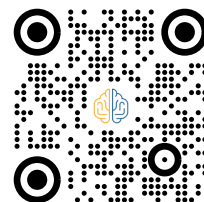
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# 1 Reaction Kinetics

This chapter focuses on the following AP Unit from the College Board:

## Unit 5: Kinetics

By the end of this chapter, you should be able to do the following:

- Demonstrate awareness that reactions occur at differing rates
- Experimentally determine rate of a reaction
- Demonstrate knowledge of collision theory
- Describe the energies associated with reactants becoming products
- Apply collision theory to explain how reaction rates can be changed
- Analyze the reaction mechanism for a reacting system
- Represent graphically the energy changes associated with catalyzed and uncatalyzed reactions
- Describe the uses of specific catalysts in a variety of situations

By the end of this chapter, you should know the meaning of these **key terms**:

- activated complex
- activation energy
- bimolecular
- catalyst
- catalytic converter
- collision theory
- $\Delta H$  notation
- elementary processes
- endothermic
- enthalpy
- enzymes
- exothermic
- heterogeneous catalysts
- homogeneous catalysts
- initial rate
- integrated rate law
- KE distribution curve
- kinetic energy (KE),
- metalloenzymes
- molecularity
- overall order
- potential energy (PE)
- product
- rate-determining step
- reactant
- reaction intermediate
- reaction mechanism
- reaction rate
- successful collision
- termolecular
- thermochemical equation



*External tanks of liquid oxygen and hydrogen fuel react to create the energy needed to launch a rocket carrying the space shuttle.*

# 1.1 Measuring the Rate of Chemical Reactions

## Warm Up

In previous Science courses, you were introduced to the concept of rate of change in the position of an object as it moves. You learned that this is the object's velocity. If we don't consider the object's direction, we might use the more general terms, "speed" or "rate." Velocity is a vector quantity while speed is a scalar quantity. When dealing with chemical reactions, we need not concern ourselves with vectors.

Assume a vehicle moves the following distances over the stated periods of time as it travels from Anaheim into Los Angeles:

What is the average velocity (rate) of the car (over the entire time period)?

(a) in km/min \_\_\_\_\_

(b) in km/h \_\_\_\_\_

(c) Why do we refer to this as an *average* rate?

\_\_\_\_\_

(d) A unit of \_\_\_\_\_ is always placed in the denominator when calculating rate.

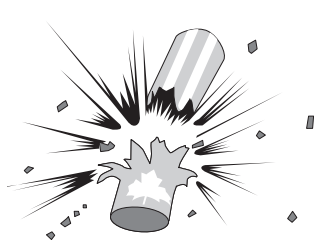
| Distance Travelled (km) | Time (min) |
|-------------------------|------------|
| 0                       | 0          |
| 22                      | 20.0       |
| 62                      | 50.0       |
| 117                     | 90.0       |
| 125                     | 100.0      |

## Measuring Reaction Rate

Chemical reactions involve the conversion of reactants with a particular set of properties into products with a whole new set of properties.

**Chemical kinetics** is the investigation of the rate at which these reactions occur and the factors that affect them.

If you consider familiar reactions like the explosion of a firecracker, the metabolism of the lunch you ate today and the rusting of your bicycle, it is evident that chemical reactions occur at a wide variety of rates (Figure 1.1.1).



Time for reaction: < 1 s



several hours



weeks to many months

**Figure 1.1.1** An explosion, food digestion, and rusting metal all involve chemical reactions but at very different rates.

Reaction rates may be determined by observing either the disappearance of a reactant or the appearance of a product. Deciding exactly what to measure can be a tricky business. There are several things the chemist needs to consider:

- Is there a measurable property associated with the change in quantity of a reactant or product you might use to determine the rate?

- Exactly how might you measure the quantity of reactant or product in the laboratory?
- Finally, what units would be associated with the quantity you measure and consequently, what units will represent the reaction rate?

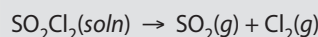
Once these questions have been answered, it is simply a matter of determining the rate using the following equation:

$$\text{average reaction rate} = \frac{\text{change in a measurable quantity of a chemical species}}{\text{change in time}}$$

Experimentally, it turns out that, for most reactions, the rate is greatest at the beginning of the reaction and decreases as the reaction continues. Because the rate changes as a reaction proceeds, reaction rates are generally expressed as averages over a particular time period. As reactants are being consumed during a reaction, the forward rate might be thought of as having a negative value. However, we generally report the rate as an absolute or positive value.

### Quick Check

Thionyl chloride is a reactive compound used in a variety of organic synthesis reactions. Due to its potential to release dangerous gases explosively on contact with water, it is controlled under the Chemical Weapons Convention in the United States. It can be decomposed in solution with an organic solvent according to the reaction:



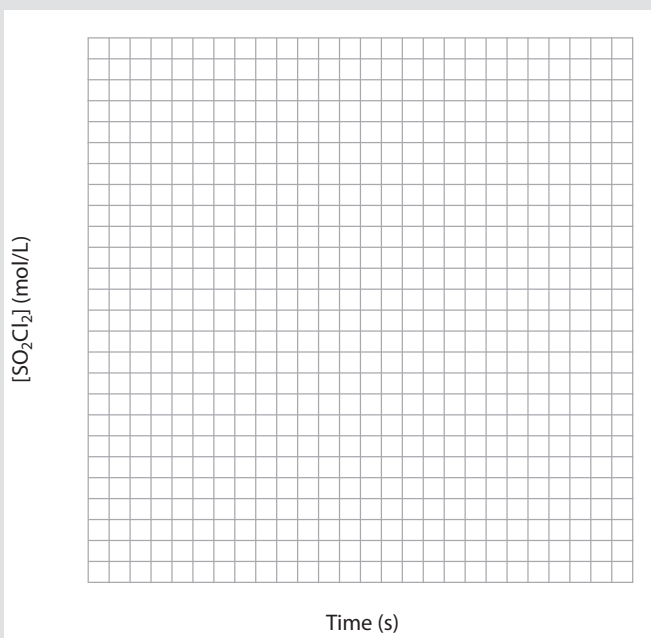
Removal of small samples called aliquots and titration of these samples as the reaction proceeds produces the data given in the table on the next page.

Note: Ideally, a reaction should be *monitored* as it proceeds without interference. In a technique such as this, it is critical to remove as small an aliquot as possible so that the sampling's interference with the subject reaction is minimal. It is also important to complete the titration as quickly as possible because the reaction, of course, continues to occur within the sample. Nonetheless, removal and sampling of small aliquots is one technique for monitoring the rate of a chemical reaction.

Use the grid provided on this page to produce a graph of concentration of thionyl chloride versus time.

| [SO <sub>2</sub> Cl <sub>2</sub> ]<br>(mol/L) | Time<br>(seconds) |
|-----------------------------------------------|-------------------|
| 0.200                                         | 0                 |
| 0.160                                         | 100.              |
| 0.127                                         | 200.              |
| 0.100                                         | 300.              |
| 0.080                                         | 400.              |
| 0.067                                         | 500.              |
| 0.060                                         | 600.              |

(Quick Check continued on next page)

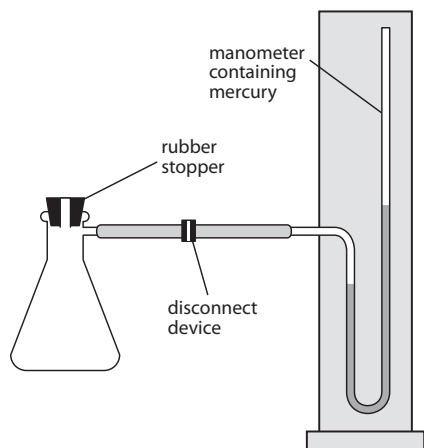


## Quick Check (continued)

1. What would the slope of this graph ( $\Delta[\text{SO}_2\text{Cl}_2]/\Delta\text{time}$ ) represent?  
\_\_\_\_\_
2. How does the slope of the graph change as time passes?  
\_\_\_\_\_
3. What does this indicate about the reaction rate?  
\_\_\_\_\_
4. What is the average rate of decomposition of thionyl chloride?  
\_\_\_\_\_
5. How does the rate at 500 s compare to the rate at 300 s?  
\_\_\_\_\_
6. Suggest a way to determine the rate at the particular times mentioned in question 5. The rates at those particular instants are called **instantaneous rates**.  
\_\_\_\_\_  
\_\_\_\_\_
7. Calculate the instantaneous rates of reaction at 500 s and 300 s (if you're unsure of how to do this, ask a classmate or your teacher).  
\_\_\_\_\_  
\_\_\_\_\_

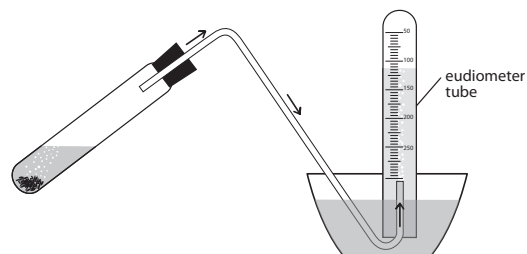
## Reaction Measuring Techniques

The technique used to measure the change in the quantity of reactant or product varies greatly depending on the reaction involved and the available apparatus. In many cases, the reactant or product involved in a reaction may be measured directly. As in the Quick Check above, the concentration of a reactant in solution may be determined from time to time as the reaction proceeds by the titration of an aliquot of the reacting species. If a gas is being formed or consumed in a closed system, a manometer may be used to measure the change in pressure (Figure 1.1.2(a)). Gas production might also be measured using a pneumatic trough and a gas volume measuring tube called a eudiometer (Figure 1.1.2(b)). Of course, if a gas is leaving an open system, there will be a change in mass that could easily be measured using a balance.



(a) A manometer measures the partial pressure of a gas formed in a reaction

**Figure 1.1.2** A manometer (a) and a eudiometer (b) are two different devices that can be used to measure the production of a gas from a reaction in a closed system.



(b) A eudiometer measures the volume of gas produced during a reaction.

If the amount of a reactant or a product can't be monitored directly, a chemist can monitor some property of the reacting mixture that correlates in a known manner with the quantity of a reactant or a product. If a reaction is occurring in aqueous solution, the solution's color and pH (acidity) are properties that might indicate the quantity of reactant or product present.

A pH electrode is one type of ion selective electrode (ISE) that can be used to measure acidity. The concentrations of many types of ions can be measured with different ISEs. The ion's concentration correlates with the charge that builds up as the ion diffuses across the ISE's membrane. It is simplest if only one chemical involved in the reaction affects the monitored property. If the property is influenced by more than one chemical, then their relative influences must be known. Reactions involving color changes may be colorimetrically analyzed using a spectrophotometer.

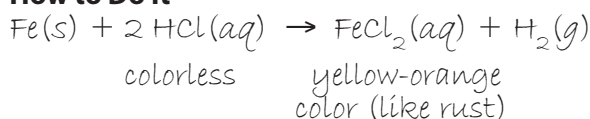
### Sample Problem — Determining the Rate of a Reaction in the Laboratory

State five different methods for measuring the rate of the reaction of an iron nail in concentrated hydrochloric acid.

#### What to Think About

1. Begin by writing a balanced chemical equation. It is very important to consider the states (and any colors) of all species.
2. Decide if there is a property associated with the quantity of reactant consumed or product produced that you might measure to monitor the reaction rate.
3. Decide exactly how you might measure this property and what unit would be associated with it.

#### How to Do It



The first species,  $\text{Fe}(s)$  is a solid that will be consumed during the reaction.

A balance could be used to determine the mass of the iron before and after the reaction was completed. The time would also need to be recorded.

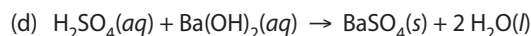
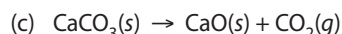
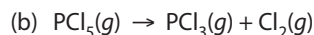
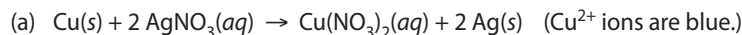
The resulting rate of reaction would be recorded in units of g Fe used/unit of time.

4. A repeat of the same steps would reveal more than five different ways to determine the rate of this particular reaction. Other answers might include:

| $\frac{\Delta[\text{HCl}]}{\text{time}}$ | $\frac{\Delta\text{pH}}{\text{time}}$ | $\frac{\Delta\text{Vol H}_2}{\text{time}}$ | $\frac{\Delta P_{(\text{H}_2)}}{\text{time}}$ | $\frac{\Delta\text{mass H}_2}{\text{time}}$ |
|------------------------------------------|---------------------------------------|--------------------------------------------|-----------------------------------------------|---------------------------------------------|
| titrate                                  | pH meter                              | eudiometer                                 | manometer                                     | balance (open system)                       |
| M/s                                      | pH units/s                            | mL/s                                       | kPa/s                                         | g/s                                         |

## Practice Problems — Determining the Rate of a Reaction in the Laboratory

1. Indicate two methods for determining the rate of each of the following reactions:



2. Why would volume of water **not** be an acceptable answer for question 1(d) above?

3. Why would concentration of copper metal,  $[\text{Cu}(s)]$ , **not** be an acceptable answer for question 1(a) above?



## Calculating Reaction Rate

Once the chemist has decided what quantity of a particular chemical species to measure, he or she may begin to gather data. These data may be used to calculate the rate of the chemical reaction. Data may be presented graphically to monitor the rate throughout the entire reaction, or initial and final data may be used to determine the reaction's average rate as indicated earlier.

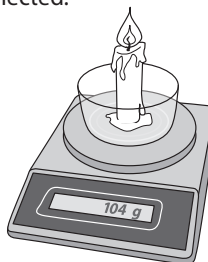
$$\text{average reaction rate} = \frac{\Delta \text{measurable quantity of a chemical species}}{\Delta \text{time}}$$

As chemistry often involves the application of a balanced chemical equation, it is possible to convert from the rate of one reacting species to another by the simple application of a **mole ratio**.

## Sample Problem — Calculating Average Rate from Laboratory Data

A paraffin candle ( $\text{C}_{28}\text{H}_{58}$ ) is placed in a petri dish on an electronic balance and combusted for a period of 15.0 min. The accompanying data is collected.

- Calculate the average rate of combustion of the paraffin over the entire 15 min period.
- Calculate the average rate of formation of water vapor for the same period.
- Note the mass loss in each 3.0 min time increment. Comment on the rate of combustion of the candle during the entire trial. Suggest a reason why the rate of this reaction isn't greatest at the beginning, with a steady decrease as time passes.
- Why don't the mass values drop in a completely constant fashion?



| Time (min) | Mass (g) |
|------------|----------|
| 0          | 180.00   |
| 3.0        | 178.00   |
| 6.0        | 175.98   |
| 9.0        | 173.99   |
| 12.0       | 172.00   |
| 15.0       | 170.01   |

*Continued opposite*

## Sample Problem (Continued)

### What to Think About

1. Write a balanced chemical equation.  
Hydrocarbon combustion always involves reaction with oxygen to form water vapor and carbon dioxide.
2. Think about the system carefully. Consider the balanced equation. What is causing the loss of mass?

### Question (a)

3. Apply the equation with appropriate significant figures to calculate the rate.  
Note that the rate is a negative value as paraffin is lost. To simplify things, reactant and product rates are often expressed as absolute values. Consequently they appear positive.

### Question (b)

4. Now apply appropriate molar masses along with the mole ratio to convert the rate of consumption of paraffin to the rate of formation of water vapor as follows:

mass paraffin (per minute)  
→ moles paraffin  
→ moles water vapor  
→ mass water vapor (per min)

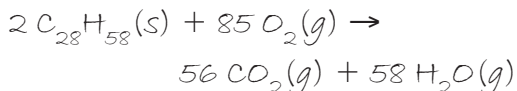
### Question (c)

5. Notice the mass loss in each 3.0 min time increment recorded in the table.

### Question (d)

6. Explain why the mass values do not drop in a completely constant fashion.

### How to Do It



In this case, all mass loss is due to the combusted paraffin. This paraffin is converted into two different gases: carbon dioxide and water vapor.

$$\frac{170.01 \text{ g} - 180.00 \text{ g}}{15.0 \text{ min} - 0 \text{ min}} = -0.666 \text{ g/min}$$

$$\begin{aligned} & \frac{0.666 \text{ g C}_{28}\text{H}_{58}}{\text{min}} \times \frac{1 \text{ mol C}_{28}\text{H}_{58}}{394.0 \text{ g C}_{28}\text{H}_{58}} \\ & \times \frac{58 \text{ mol H}_2\text{O}}{2 \text{ mol C}_{28}\text{H}_{58}} \times \frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \\ & = 0.882 \text{ g H}_2\text{O/min} \end{aligned}$$

The rate of consumption of paraffin seems to be nearly constant. This may be due to the  $[\text{O}_2]$  being very plentiful and so essentially constant. As well, the quantity of molten paraffin at the reacting surface stays constant through the entire reaction. As this reaction proceeds, there is no decrease in  $[\text{reactants}]$  to lead to a decrease in reaction rate.

There is some variation in rate. This is due to the expected uncertainty associated with all measuring devices (in this case, the balance).

## Practice Problems — Calculating Average Rate

1. A piece of zinc metal is placed into a beaker containing an aqueous solution of hydrochloric acid. The volume of hydrogen gas formed is measured by water displacement in a eudiometer every 30.0 s. The volume is converted to STP conditions and recorded.

(a) Determine the average rate of consumption of zinc metal over the entire 150.0 s in units of g/min.

|                                  |   |      |      |      |       |       |
|----------------------------------|---|------|------|------|-------|-------|
| Volume H <sub>2</sub> (STP) (mL) | 0 | 15.0 | 21.0 | 24.0 | 25.0  | 25.0  |
| Time (seconds)                   | 0 | 30.0 | 60.0 | 90.0 | 120.0 | 150.0 |

(b) When is the reaction rate the greatest?

(c) What is the rate from 120.0 to 150.0 s?

(d) Assuming there is still a small bit of zinc left in the beaker, how would you explain the rate at this point?

2. A 3.45 g piece of marble (CaCO<sub>3</sub>) is weighed and dropped into a beaker containing 1.00 L of hydrochloric acid. The marble is completely gone 4.50 min later. Calculate the average rate of reaction of HCl in mol/L/s. Note that the volume of the system remains at 1.00 L through the entire reaction.

## Using Rate as a Conversion Factor

A **derived unit** is a unit that consists of two or more other units. A quantity expressed with a derived unit may be used to convert a unit that measures one thing into a unit that measures something else completely. One of the most common examples is the use of a rate to convert between distance and time.

The keys to this type of problem are:

- determining which form of the conversion factor to use, and
- deciding where to start.

## Sample Problem — Using Rate as a Conversion Factor

A popular organic chemistry demonstration is the dehydration of sucrose, C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>, using sulfuric acid to catalyze the dehydration. The acid is required for the reaction, but it is still present once the reaction is complete, primarily in its intact form and partially as dissolved sulfur oxides in the water formed. Because of this, it does not appear at all in the reaction. The product is a large carbon cylinder standing in a small puddle of water as follows: C<sub>12</sub>H<sub>22</sub>O<sub>11</sub>(s) → 11 H<sub>2</sub>O(g) + 12 C(s). Due to the exothermicity of the reaction, much of the water is released as steam, some of which contains dissolved oxides of sulfur. Ask your teacher to perform the demonstration for you, ideally in a fume hood.

Given a rate of decomposition of sucrose of 0.825 mol/min, how many grams of C(s) could be formed in 30.0 s?

*Continued opposite*

## Sample Problem (Continued)

### What to Think About

1. You need to know *where you are going* in order to determine *how to get there*.

In this problem, you want to determine the mass of carbon in *grams*. Essentially, the question is: Do you use the rate as is or do you take the reciprocal? As time needs to be cancelled, use the rate as is. Once you have determined the need to convert time into mass, consider which form of the conversion factor to use.

2. Now design a “plan” for the “conversion route,” using the rate, the mole ratio, and the molar mass.

### How to Do It

As your answer contains one unit, begin with a number having one unit, in this case the time.

time  $\rightarrow$  moles sucrose  $\rightarrow$  moles carbon  
 $\rightarrow$  mass of carbon

$$\begin{aligned} 30.0 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} \times \frac{0.825 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}}{1 \text{ min}} \\ \times \frac{12 \text{ mol C}}{1 \text{ mol C}_{12}\text{H}_{22}\text{O}_{11}} \times \frac{12.0 \text{ g C}}{1 \text{ mol C}} \\ = 59.4 \text{ g C} \end{aligned}$$

## Practice Problems — Using Rate as a Conversion Factor

1. Ozone is an important component of the atmosphere that protects us from the ultraviolet rays of the Sun. Certain pollutants encourage the following decomposition of ozone:  $2 \text{ O}_3(g) \rightarrow 3 \text{ O}_2(g)$ , at a rate of  $6.5 \times 10^{-4} \text{ M O}_3/\text{s}$ . How many molecules of  $\text{O}_2$  gas are formed in each liter of atmosphere every day by this process? (As this problem provides a rate in units of mol/L/s and requires molecules/L as an answer, we can simply leave the unit “L” in the denominator the entire time.)
  2. Propane gas combusts in camp stoves to produce energy to heat your dinner. How long would it take to produce 6.75 L of  $\text{CO}_2$  gas measured at STP? Assume the gas is combusted at a rate of  $1.10 \text{ g C}_3\text{H}_8/\text{min}$ . Begin by writing a balanced equation for the combustion of  $\text{C}_3\text{H}_8$ .
- 
3. A 2.65 g sample of calcium metal is placed into water. The metal is completely consumed in 25.0 s. Assuming the density of water is  $1.00 \text{ g/mL}$  at the reaction temperature, how long would it take to consume 5.00 mL of water as it converts into calcium hydroxide and hydrogen gas?

## 1.1 Activity: Summarizing a Concept in Kinetics

### Question

How can you summarize the methods that are useful for measuring the rate of a chemical reaction?

### Background

As you're moving through any course in senior high school or university, it is very useful to summarize the concepts you learn into "chunks" of material. These summary notes may take the form of bulleted points or tables or charts.

### Procedure

1. Use the outline provided below to organize what you've learned about methods that are useful for measuring the rates of various chemical reactions.
2. For each method, provide a balanced chemical equation for a reaction that could be measured using that method. Do not repeat equations that were already used in this section of the book. Your textbook and the Internet may be helpful for finding examples if you're having trouble recalling the major reaction types.
3. The first row has been completed as an example of what is expected. Note that the same property may be used multiple times (for example, with different states of species).

| Property      | State of Species | Apparatus Used | Units | Sample Reaction                                                                     |
|---------------|------------------|----------------|-------|-------------------------------------------------------------------------------------|
| Mass          | solid            | balance        | g/min | $2\text{K}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{KOH}(aq) + \text{H}_2(g)$ |
| Mass          | gas              |                |       |                                                                                     |
| Volume        |                  |                |       |                                                                                     |
| Concentration |                  |                |       |                                                                                     |
| pH            |                  |                |       |                                                                                     |
| Color         |                  |                |       |                                                                                     |
| Pressure      |                  |                |       |                                                                                     |
| Conductivity  |                  |                |       |                                                                                     |
|               |                  |                |       |                                                                                     |

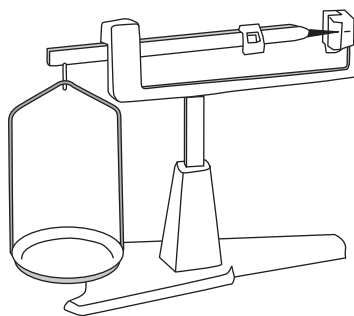
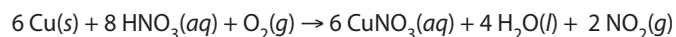
### Results and Discussion

1. You will find it extremely helpful to produce similar formats to help you summarize material for study in the remaining sections of this course. Dedicate a section of your notebook for these summary notes and refer to them from time to time to help you prepare for your unit and final examinations.

## 1.1 Review Questions

1. Give three reasons why the distance-time data in the Warm Up at the beginning of this section is so different from the property-time data collected for a typical chemical reaction.

2. Consider the following reaction, which could be done in either flask, using any of the equipment shown:



- (a) If 5.00 g of copper solid is completely reacted in 250.0 mL of excess nitric acid in 7.00 min at STP, calculate the rate of the reaction in:

(i) g Cu/min

(ii) g NO<sub>2</sub>/min

(iii) mol HNO<sub>3</sub>/min

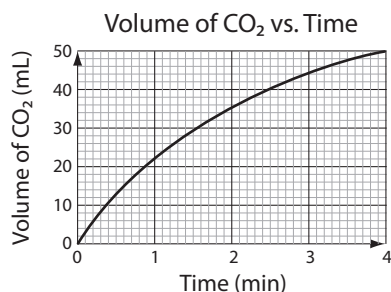
- (b) Assume the reaction continues at this average rate for 10.0 min total time. Determine the final:

(i) mL NO<sub>2</sub> formed at STP

(ii) molarity of CuNO<sub>3</sub>

- (c) Describe SIX ways you might measure the reaction rate. Include the equipment required, measurements made and units for the rate. You may use a labeled diagram.

3. Consider the graph for the following reaction:  
 $\text{CaCO}_3(s) + 2 \text{HCl}(aq) \rightarrow \text{CaCl}_2(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$



Recall the discussion of the *instantaneous rate* earlier in this section.

- (a) Determine the instantaneous rate at the following times:

(i) an instant after 0 min (This is the *initial rate*.)

(ii) 1 min

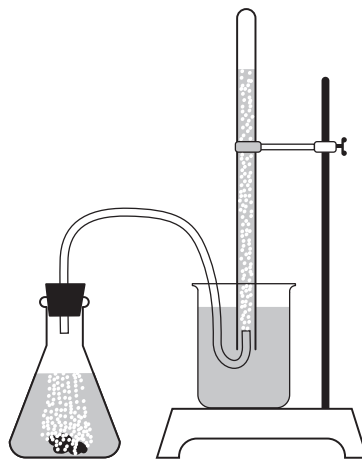
(iv) 4 min

- (b) How do these rates compare? What do you suppose causes this pattern?

4. Here is a table indicating the volume of gas collected as a disk of strontium metal reacts in a solution of hydrochloric acid for 1 min.



| Time (seconds) | Volume of Hydrogen at STP (mL) |
|----------------|--------------------------------|
| 0              | 0                              |
| 10.0           | 22.0                           |
| 20.0           | 40.0                           |
| 30.0           | 55.0                           |
| 40.0           | 65.0                           |
| 50.0           | 72.0                           |
| 60.0           | 72.0                           |



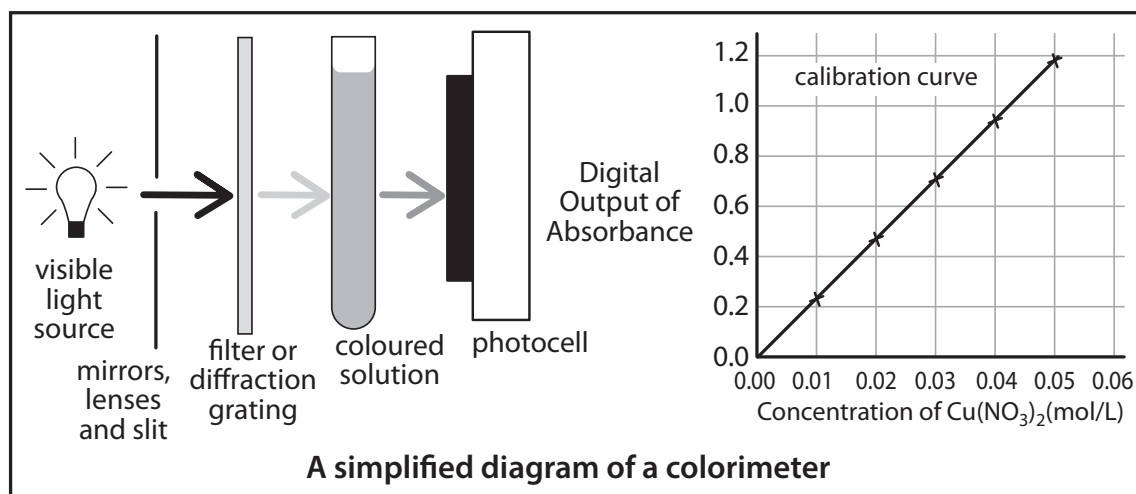
- (a) Calculate the average rate of reaction in moles of  $\text{HCl}$  consumed/second over the first 50.0 s.

(b) Calculate the mass of strontium consumed in this 50.0 s period.

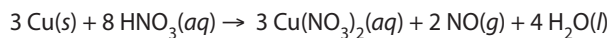
(c) Why did the volume of gas collected decrease in each increment until 50.0 s?

(d) Why did the volume of gas remain unchanged from 50.0 s to 60.0 s?

5. The spectrophotometer works by shining a single wavelength of light through a sample of a colored solution. A photocell detects the amount of light that passes through the solution as % **transmittance** and the amount of light that does not pass through as the **absorbance**. The more concentrated the solution, the darker the color. Dark color leads to a lower percentage of light transmitted and thus a higher absorbance. There is a direct relationship between absorbance and the concentration of a colored solution. The "calibration curve" (actually a straight line) below was created using solutions of *known*  $\text{Cu}(\text{NO}_3)_2$  concentration.



A copper sample was reacted with 250 mL of nitric acid by the following reaction:



As the reaction proceeded, small aliquots were removed and placed in a cuvette (the special test tube used to hold a sample in the spectrophotometer). The cuvettes were then placed in the instrument and the absorbances were recorded as follows:

| Time (seconds) | Absorbances (no unit) | Concentration of Copper(II) Ion (mol/L) |
|----------------|-----------------------|-----------------------------------------|
| 0              | 0                     | 0 mol/L                                 |
| 20.            | 0.40                  |                                         |
| 40.            | 0.70                  |                                         |
| 60.            | 0.90                  |                                         |
| 80.            | 1.00                  |                                         |

Find the absorbances on the standard graph and record the corresponding concentrations of the copper(II) ions (equal to the concentration of  $\text{Cu}(\text{NO}_3)_2$ ) in the table.

(a) Calculate the average rate of the reaction from time 0 s to 80. s in units of M of  $\text{HNO}_3(\text{aq})/\text{s}$ .

(b) What mass of  $\text{Cu}(\text{s})$  will be consumed during the 80. s trial?

(c) What will you observe in the main reaction flask as the reaction proceeds?