Chapter 6

Diffusion

How do chemical and biological reactions take place? Atoms and molecules have no legs. They cannot walk around and come together to form new molecules and the fractal patterns that we have been studying. How do they find other particles with which to react?

One answer to this question is **mixing**. Air circulates in a room due to differences in temperature and the stirring as people come and go. But chemical and biological reactions go on even in stillness and in cell structures where physical mixing is small or absent. In such circumstances, atoms and molecules get their legs from **diffusion**. Diffusion is the spread of atoms and molecules due to their random motion from regions of greater concentration into regions of smaller concentration. Without diffusion, life as we know it would be impossible. This chapter describes the process of diffusion.

Imagine the following scenario (as shown in Figure 6.1): In one corner of a school laboratory, Barry opens a bottle of ammonia. Jennifer, who is sitting in the opposite corner of the classroom, grabs her nose and shouts, "Barry, close that bottle!" Barry does so, but Jennifer continues to smell the ammonia, so she sensibly walks out of the laboratory.

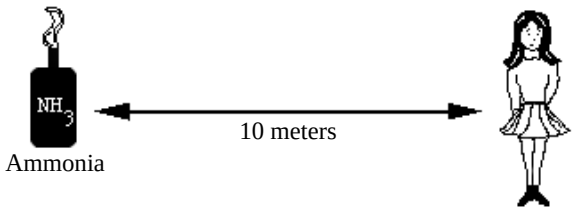

Figure 6.1: When does Jennifer smell the ammonia?

Q6.1: Discuss this Ammonia Story. What questions do you have about it? Discuss answers to your questions and answer the questions below:

A quick guess: How soon will Jennifer smell the ammonia in *still* air?

What is carrying the odor to Jennifer? What moves across the room?

Whatever carries the odor across the room: How does it travel? in a straight line? along a jagged path? Or does it simply ride with the air as the air circulates?

6.1 The Diffusion Chamber

Ammonia gas is invisible as it moves through the air from Barry's opened bottle to Jennifer's nose. There is a simple demonstration that makes visible some consequences of this motion of ammonia. The demonstration uses what is called a **diffusion chamber**. This is a popular chemistry experiment in which two different gases, typically am-

monia (NH_3) and hydrogen chloride (HCl) diffuse from opposite ends of a closed glass tube (Figure 6.2). Eventually the two gases meet and react, forming a disk of white dust made of the solid ammonium chloride (NH_4Cl). We say that the ammonium chloride is *precipitated out* of the gas.

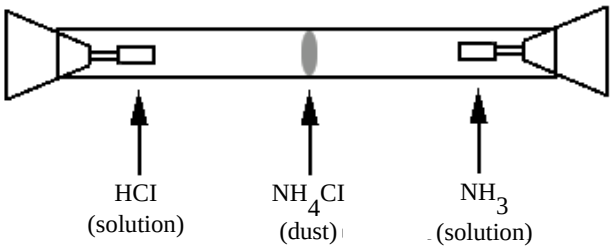

Figure 6.2: Diffusion Chamber Demonstration. The acid hydrogen chloride HCl (in water) is placed at one end, and evaporates as HCl gas. Ammonia, which is a water solution of ammonium hydroxide, is placed at the other end, and gives off ammonia gas, NH_3. The two gases diffuse down the tube. Where these gases first meet, they react chemically to make a disk-shaped cloud of dust composed of (the solid) ammonium chloride NH_4Cl.

Later you will be able to perform this experiment using small tubes supplied in your laboratory kit.

Q6.2: *Guess where* along the tube the disc will form and *how long a time* it will take before the disk appears. Write down your guesses.

HandsOn 25: The Diffusing Checkers Model

The ammonia molecules and the hydrogen chloride molecules move in the same way that air molecules move. All molecules follow jagged

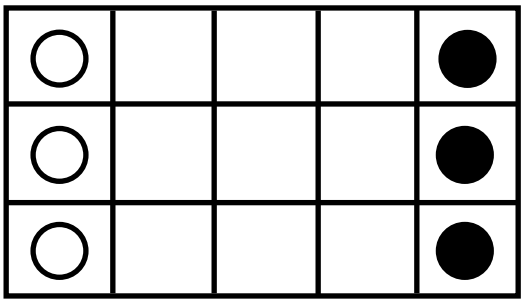

Figure 6.3: Initial position of black checkers (filled circles) and red checkers (open circles) in the "Diffusion Checkers" activity.

paths because they collide with one another. We do not have the computing power or the numerical accuracy to follow each particle in order to predict every collision and its consequences. Instead, we model the diffusion process by assuming that the motion of each particle is a random walk (Chapters 2 and 3). Is this a good model? Lets find out.

Use the corner of a checkerboard or draw a grid to set up the array of checkers shown in Figure 6.3. In this figure, black checkers are shown black and red checkers are shown as unfilled circles. One color of checker, say the red, represents a hydrogen chloride (HCl) molecule. The other color checker, the black, represents an ammonia molecule (NH_3). They diffuse into the center from both sides.

Now put your finger on each checker in turn and flip a coin. If the coin comes up a head, move that checker to the right. If the coin is a tail, move the checker to the left. Exceptions: If a head occurs for any checker in the right-hand column, the checker cannot move right, so that checker takes no step and "loses its turn." Go on to the next checker. Similarly, if a tail occurs for any checker in the left column, it cannot move left, so does not move at all during that turn.

Whenever a black checker and a red checker move into the same square, they have a chemical reaction, bond together, and stop moving. For example, in Figure 6.4 one square in the bottom row contains both a black checker and red checker.

In this case the two join together and stop moving. The joined checkers represents a molecule of the solid ammonium chloride (NH_4Cl) dust that results when a red-checker HCl molecule and a black-checker

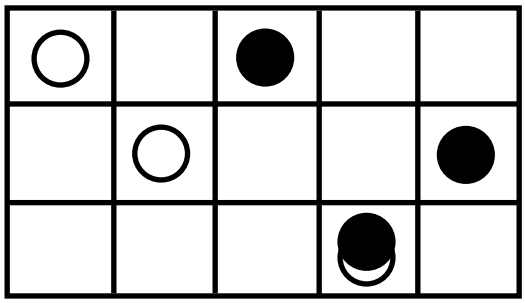

Figure 6.4: A black and a red checker are in the same square. This leads to their "chemical combination" into a stationary "dust particle."

NH_3 molecule combine chemically.

The single checkers that remain on the grid continue to move by the same coin-flipping rules until every checker is bonded with another (by moving into the same square).

Record in which columns the "bonded molecules" are distributed. Then repeat the exercise from the beginning and record the distribution of the bonded molecules in the second set. Are the two sets of results similar or different? If several groups have done the exercise, sum and tabulate the results to see if a pattern emerges in the positions of the bonded molecules.

END ACTIVITY

SimuLab 15: The Diffusion Chamber Simulation

The **Diffusion Chamber** program carries out the diffusing checkers model with computer speed, many more "checkers," and a longer chamber. With this program you can change the model in various ways in order to compare the results with experiment.

Start the **Diffusion Chamber** program. You will see two diffusion chambers, one above the other. Later this arrangement will allow you to compare diffusion under different circumstances. For now just use the upper chamber. In the selections on the right, choose **m(green) = m(blue)** which means that the two diffusing molecules have the same mass, **Infinite Particles** which means particles are renewed from a source at each end of the chamber, and **1-D Random** which means that the model is a one-dimensional random walk. Start the run with

the upper chamber.

Q6.3: At what time (displayed at the lower right of the panel) are there a "significant number" of precipitated dust particles? You define "significant."

Q6.4: Is the precipitated dust grouped around the center of the tube or near some other location?

Now choose a topic from the list below and carry out a brief investigation using the **Diffusion Chamber** program. Different groups in the class may choose different topics.

For comparison, you can use both chambers in the display, if you wish, running them simultaneously. To increase the statistical accuracy of your results, you can increase the number of particles using the **Size** menu items (but then the process will take longer).

1. **Chamber Length:** For diffusion chambers of different lengths, what are the different times for a "significant number" of dust particles to be precipitated? Make a prediction: For a chamber half as long, do you expect this time to be cut in half? Change the length of the chamber by dragging the right hand end or by clicking on the **Set** box at the upper right of the control panel and entering a number. Record your data and make a graph of the "diffusion time" as a function of chamber length. Is the result what you predicted?

2. **Mass Ratio of Molecules:** When two molecules of different mass have the same kinetic energy, the molecule with the larger mass moves more slowly. Here is the reason: At a given common temperature, all molecules in a gas have the same *average* kinetic energy ($mv^2/2$), so one would expect the molecules with larger mass m to move slower, on the average. Perhaps slower-moving more massive molecules will diffuse more slowly than less massive

molecules. Therefore, perhaps the initial precipitation disk will not occur in the middle of the tube. Is this true?

In the diffusion chamber demonstration, HCl has a molecular weight (atomic mass) of $1 + 35.5 = 36.5$, while NH_3 has a molecular weight of $14 + 3 = 17$, about half as much. As a result of this difference, which molecule do you expect to diffuse faster. Do you expect the initial precipitation disk to form nearer the end of the chamber from which HCl is diffusing, or nearer the end from which NH_3 is diffusing? How much nearer? Write down your predictions.

Test your predictions with the **Diffusion Chamber** program. You can try two different mass ratios in the two panels at the same time, determing the location of the initial precipitation "disk" in each case.

Do you obtain more accurate results with molecules of smaller size? **Note:** The "Length" of the chamber is measured in the number of horizontal positions that can be occupied by the diffusing molecules. When you choose a smaller size for the molecules, more of them can line up from right to left in a given chamber. In this case, the *number* displayed for the "Length" is larger for a chamber that shows the same size on the screen.

3. **Motion of Particles:** Our simplest model forces the molecules to execute a random walk on one dimension—each one moving back and forth along a line. What is different if the molecules can move in two dimensions, executing the so-called "2-D random walk"? Will it take longer for the initial precipitation disk to form? Will this disk appear in a different place? Write down your preductions, then test them by changing the **Motion of Particles** setting to **2-D Random**. Write down your results and compare them with your predictions.

   A third way that particles might move is *ballistic*. This means constant velocity in a straight line along the length of the tube. What do you expect to happen in this case? Will formation of the precipitation disk occur more quickly or more slowly than for

a random walk? Will ballistic motion change the location of the initial precipitation disk? Write down your predictions.

Try the **Ballistic** setting for **Motion of Particles** and compare the results with your predictions. Predict what will happen if you carry out the ballistic experiment with the **Infinite Particles** setting, then the **No new particles** setting. Compare the results with your predictions.

END ACTIVITY

Before going on to a laboratory experiment with diffusion chambers made of small tubes, we try to estimate numerical values for some of the results to expect in such experiments. To simplify the analysis, we return to the one-dimensional random walk model for diffusion.

From the **ManyWalkers** program (SimuLab 8 on page 53) we know that in a one-dimensional random walk the average of the square of distance traveled is proportional to the number of steps. Let $\langle x^2 \rangle_{\text{avg}}$ stand for this average square, let N be the number of steps, and let L_{step} be the average length of each step, the average distance between collisions. Then the result can be written as:

$$\langle x^2 \rangle_{\text{avg}} = N L_{\text{step}}^2. \tag{6.1}$$

Why L_{step}^2? This must be entered in the equation as a square to make the units correct, since N here has no units.

Notice that for uniform "ballistic" motion in a straight line, the formula would be $N = x/L$ (without the squares).

Q6.5: How many steps N will the ammonia molecule take to be detected a distance x away? To begin to answer this question we need to know the speed of the molecules at room temperature and the average distance that a molecule moves between collisions. Here are approximate values for these two quantities. Later you will derive your own values for these quantities.

1. Speed of gas molecules. A gas molecule at room temperature moves with an average speed approximately equal to that of a rifle bullet, about 600 meters/second. Why doesn't this hurt? This speed is approximately 2200 kilometers/hour (or 1300 miles/hour). Why don't you feel a 2200 kilometer/hour wind all the time?

2. Distance between collisions. A gas molecule in the air travels a distance between collisions (the length of one step) approximately equal to $L_{\text{step}} = 1000 \times 3 \times 10^{-10}$ meters $= 3 \times 10^{-7}$ meters. How does this distance compare with the diameter of one hair on your head? This distance is equal to how many times the diameter of an atom?

From these quantities and earlier equations, answer the following questions:

Q6.6: Suppose that the molecule travels in a straight line, taking steps only in the forward direction. How many steps N would it take for the molecule to travel $x = 10$ centimeters?

Q6.7: In contrast, suppose that the molecule travels in a one-dimensional random walk. How many steps (collisions) N will it take to travel $x = 10$ centimeters?

Q6.8: Let the time t_{step} represent the average time that elapses between collisions. Find an expression for t_{step} as a function of the particle's average velocity and the average distance traveled in each step.

Q6.9: Therefore how many seconds t are required for the molecule to move 10 centimeters, on the average, in a one-dimensional random walk? Express your answer in an everyday unit, such as hours or days or years.

Q6.10: What if the total distance traveled is one centimeter instead of 10 centimeters. How long is required, on the average, for the molecule to cover a distance of one centimeter.

END ACTIVITY

HandsOn 26: Deriving the Motion of Molecules

In the following exercise you derive the speed of gas molecules and the distance between collisions, two values that were previously given to you. To do this, you may need to review a little Newtonian mechanics and thermodynamics.

1. **Speed of gas molecules.** The average kinetic energy of a molecule in a gas at absolute temperature T is approximately $(3/2)kT$, where k is Boltzmann's constant (1.381×10^{-23} joules/degree Kelvin), i.e.,

$$\frac{3}{2}kT = \frac{1}{2}mv_{\text{avg}}^2. \tag{6.2}$$

From this, find an expression for the average speed v_{avg} of a gas molecule at room temperature (approximately 300 Kelvin).

Q6.11: Using this expresion, first write an expression for v_{avg}. Using this new expression and the mass of an ammonia molecule, $17 \times 1.66 \times 10^{-27}$kg, find the value of v_{avg}.

2. **Distance between collisions.** A gas molecule will experience a collision if the distance from its center to another molecule is equal to the sum of their two radii, or approximately equal to the *diameter* d of a single molecule. We can think of a moving molecule as sweeping out a volume in one second which is equal to its velocity v (meters/second) times the area $A = \pi d^2$, where d is this diameter (see Figure 6.5);

$$\frac{\text{volume}}{\text{second}} = v\pi d^2. \tag{6.3}$$

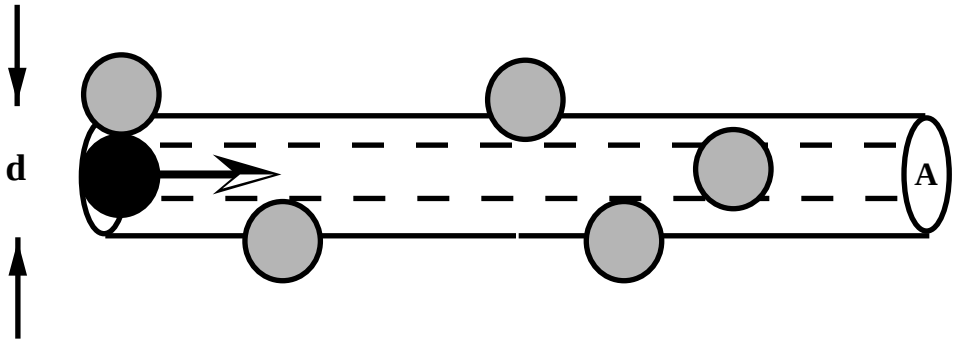

Figure 6.5: A moving molecule collides with any other molecule whose center lies within a cylinder of radius equal to the twice the radius of the molecules.

The moving molecule will collide with any other molecule whose center lies in this volume. (Of course whenever the molecule hits another molecule, it changes direction. So the cylinder shown in the figure will be broken up into many short segments. But the volume swept out will still be given approximately by the expression above.)

How many gas molecules are to be found with their centers inside this volume V, on the average? Let the density of gas molecules

be n (molecules/meter^3). Then the average number of molecules whose centers are to be found in this volume is nV. But the volume V is swept out by the incident particle in one second. Therefore the average number of collisions per second is given by the expression

$$(\text{collisions/second}) = \frac{nV}{\text{second}} = nv_{\text{avg}}\pi d^2. \tag{6.4}$$

Q6.12: From this result and the average speed of the molecule, find an approximate value for the distance L_{step} the ammonia molecule travels between collisions. To get n, assuming atmospheric pressure and a temperature of 300 Kelvin, use the gas law equation $n = P/kT$, which gives approximatly 2.4×10^{25} molecules/m^3. Finally, for ammonia, the so-called collision diameter d is equal to 3.05×10^{-10}m.

Q6.13: The values for v_{avg} and L_{step} you derived here may be different from the values you used to estimate the time t for the ammonia smell to cross the $x = 10$-centimeter distance. Recalculate the time t using your new values.

Where along the tube will the dust disk appear? It does not appear in the center. Why? Because the ammonia molecules move faster, on the average, than the hydrogen chloride molecules. To see why this is, we need again a little bit of thermodynamics as well as mechanics. The diffusion tube and its contents are at room temperature. This means that the kinetic energies of the ammonia molecules and the hydrogen chloride molecules are, on average, the same. The kinetic energy K of a molecule is given by the expression

$$K = \frac{1}{2}mv^2, \tag{6.5}$$

where m is the mass of the molecule and v is its velocity. Since the two gases are at the same temperature, the average kinetic energies of their molecules are equal

$$\frac{1}{2}m_{\mathrm{HCl}}v_{\mathrm{HCl}}^2 = \frac{1}{2}m_{\mathrm{NH_3}}v_{\mathrm{NH_3}}^2. \tag{6.6}$$

From this we conclude that the ratio of velocities is

$$\frac{v_{\mathrm{NH_3}}}{v_{\mathrm{HCl}}} = \left(\frac{m_{\mathrm{HCl}}}{m_{\mathrm{NH_3}}}\right)^{1/2}. \tag{6.7}$$

Suppose (wrongly!) that the ammonia and hydrogen chloride molecules are fired like rifle bullets from opposite ends of the tube. This corresponds to the "ballistic" setting in the **Diffusion Chamber** program. Then the distance traveled by each in the time t for them to meet would be given by the expressions

$$x_{\mathrm{NH_3}} = v_{\mathrm{NH_3}}t \tag{6.8}$$

and

$$x_{\mathrm{HCl}} = v_{\mathrm{HCl}}t. \tag{6.9}$$

The ratio of these positions is therefore

$$\frac{x_{\mathrm{NH_3}}}{x_{\mathrm{HCl}}} = \frac{v_{\mathrm{NH_3}}}{v_{\mathrm{HCl}}} = \left(\frac{m_{\mathrm{HCl}}}{m_{\mathrm{NH_3}}}\right)^{1/2}. \tag{6.10}$$

Now, the ammonia and hydrogen chloride molecules are definitely *not* fired like rifle bullets from opposite ends of the tube. Instead, these molecules follow a random walk, colliding with air molecules as they *diffuse* along the tube. Evidence for this conclusion comes from the time required for the powder disk of ammonium chloride to form. The disk would form in a small fraction of a second if the molecules traveled directly. Instead, the time required is many seconds.

In many textbooks, Eq. (6.10) is used to describe diffusion, even though molecules do not move ballistically—in straight lines—during the diffusion process. These "derivations" are wrong. However, it sometimes happens in science that a wrong derivation can lead to a correct

result. In the present case, Eq. (6.10) turns out to be correct. This equation is derived form the random walk in Section 28 beginning on page 163. We will use this result in what follows.

The atomic mass of HCl is $1 + 35.5 = 36.5$ and that of NH_3 is $14 + 3 = 17$, approximately half as much. Substituting these values into Eq. (6.10), we have

$$\frac{x_{NH_3}}{x_{HCl}} = \left(\frac{m_{HCl}}{m_{NH_3}}\right)^{1/2} = \left(\frac{36.5}{17}\right)^{1/2} = 1.46. \tag{6.11}$$

According to this theory, then, the ratio of the distances between the powder disk and the ends of the diffusion chapter are approximately 1.5 to one.[1]

Q6.14: Which end will the disk be nearer?

END ACTIVITY

HandsOn 27: Diffusion Chamber

Now carry out the diffusion experiment described below and compare the outcomes with the theory so far developed.

[1]More careful theory—and experiment—give a smaller value than 1.46. There are several reasons for this. One is that HCl (molecular weight 36.5) has more mass than air molecules O_2 (molecular weight 32) and N_2 (molecular weight 28). Therefore HCl is not deflected randomly in each collision; it tends to shoulder aside the lighter air molecules and keep going in the same direction as before the collision. Typically more than one collision is required to randomize its direction of motion. In effect, the step length L is made greater (because it goes farther before changing direction significantly). By equation $x_{avg}^2/L^2 = N_{steps}$, the number of steps is decreased, so the HCl diffuses faster than expected, relative to the lighter molecule NH_3.

CAUTION: The chemicals used in this experiment are hazardous. Use plastic gloves and goggles and all standard precautions. In bending the tubes with a flame, use heat-resistant gloves. Carry out the experiment in a hood if facilities are available and few enough groups are doing the experiment. (With a large class and no use of hoods, the fumes from this experiment have been known to set off fire alarms.)

This experiment works best when carried out by three people. One person acts as timekeeper/data collector, while the other two handle the apparatus and read the measurements from the glass tube during the experiment. Materials for each group of three students:

- Glass tubing, 2 to 3 mm internal diameter, one length of 20 centimeters and one length of 30 centimeters (supplied in the laboratory kit).
- Four 3.7 milliliter vials with caps.
- Six squares of parafilm, 3 centimeter by 3 centimeter.
- Hydrochloric acid (HCl) with specific gravity 1.19. It should be fresh, not left over from last year.
- Ammonium Hydroxide (NH_3OH) with specific gravity 0.90. This also should be fresh.
- Two graduated cylinders, 10 ml or more
- One stopwatch

1. Add a scale and parafilm "skirts" to the tube. With a marker and a ruler, label the tubing with dashes every half centimeter, starting at one end of the tube, continuing around the bend, along the main length of tube, and around the second bend to the other end of the tube. This is done in order to keep track of position. Cut a tiny slit in the centers of two sheets of parafilm. Place the

end of the tubing through the slit sliding it about 1.5 centimeters up the side to create a "skirt" of parafilm. Be sure that the film does not stretch to cover the end of the tube. Pinch the parafilm around the tube with a slight twisting motion, so that nothing can pass between the parafilm and the tube, while leaving the "skirt" spread out. Repeat this procedure for the opposite side.

2. Prepare the solutions by first labeling the graduated cylinders and the vials as containing HCl or NH_3OH solutions (one for each container). Pour 3.5 mL of HCl from the stock solution into a10 mL labeled graduated cylinder and immediately cover this with parafilm. Repeat this procedure with the NH_3OH and set aside. Pour the HCl solution from the graduated cylinder into the vial labled HCl and immediately cap to minimize the loss of vapor. Repeat this with NH_3OH. Each of the vials should be almost full of solution. Set everything else aside, except for the two labeled vials and the 20 mm bent glass tube.

3. Carry out the experiment. Start by completely loosening the caps on the vials but do not remove them. The goal in what follows is to insert the ends of the tubes in the vials as smoothly as possible, without jolts. One person holds each end of the tube and simultaneously they remove the caps from the vials and smoothly place the two ends of the tubing into the vials so that the tubes dip below the level of the liquid at each end. Then fold the parafilm around the mouth of each vial to create an air-tight seal. As the tubes enter the vials, the timekeeper begins timing the experiment, thereafter calling out ten second intervals.

4. Look for a precipitation disk composed of solid ammonium chloride NH_4Cl, in the form of dust, due to the reaction of the NH_3OH and HCl vapors. You may have to wait up to a minute before the appearance of this disk. The initial position of the disk and the time of its appearance are your major experimental results. You may be interested in continuing to time for 6–10 minutes as you record the position of the precipitation disk while it moves along the tube. In which direction does this move: toward the HCl end or toward the NH_3 end? Later you can try to explain this effect.

5. Before moving the tube and vials, examine each end of the immersed tube and record the position of the liquid level inside the tube. This is the zero point from which you will measure the distance to the initial position of the disk.

6. Compare the location of the initial position of the disk (the ratio of distances from each end) with that predicted by the theory so far developed in this chapter. Compare the time of appearance of the disk with that predicted by the theory.

7. Now prepare to carry out the experiment once more, this time with a tube of length 30 centimeters. *Predict* what results you expect for the location of the first appearance of the disk and the time for this first appearance. Carry out the experiment and compare your results to your predictions.

END ACTIVITY

HandsOn 28: Location of the Precipitation Point (Advanced)

The following derivation uses a full complement of mathematics. Its purpose is to clarify the usual derivations of the location of the precipitation point in a diffusion tube (found in many chemistry books, for example) are inexact in their procedure, though correct in the final outcome.

Normal distribution. The *normal* or *Gaussian* distribution describes the results of a random walk. This is the distribution observed in Chapter 2. The Gaussian distribution[2] describes the probability $P(x)$ that a walker who starts at $x = 0$ will be at position x after taking N steps randomly back and forth along a line, each step of average length

[2] $e = 2.71828$ is the base of natural logarithms. Also, the factor 2 in the denominator of the exponent in Eq. (6.12) describes the random walk in one dimension. For a two-dimensional random walk, x becomes r, the distance from the origin, and the factor in the denominator of the exponent takes the value 4. The value 6 applies to a random walk in three dimensions. In this section, we limit ourselves to the one-dimensional random walk.

$L_{\rm step}$

$$P(x) = \frac{1}{\sqrt{2\pi L_{\rm step}^2 N}} e^{-x^2/(2L_{\rm step}^2 N)}, \tag{6.12}$$

In our model of the diffusion chamber, molecules diffuse from the two ends. We can choose $x = 0$ for the origin of one molecule, and $x = \ell$ for the origin of the other molecule, where ℓ is the length of the diffusion chamber. Then the probability $P_1(x)$ of finding a molecule of the first type at position x is

$$P_1(x) = \frac{1}{\sqrt{2\pi L_{\rm step}^2 N_1}} e^{-x^2/(2L_{\rm step}^2 N_1)}, \tag{6.13}$$

and, similarly, probability $P_2(x)$ of finding a molecule of the second type at position x is

$$P_2(x) = \frac{1}{\sqrt{2\pi L_{\rm step}^2 N_2}} e^{-(\ell-x)^2/(2L_{\rm step}^2 N_2)}. \tag{6.14}$$

Here N_1 and N_2 are the number of steps taken by the different kinds of molecules in the same time, and we assume that the average length $L_{\rm step}$ of one step is the same for both kinds of molecules.

There is precipitation of solid (dust) when two molecules of different kinds meet one another and react. The first precipitation occurs when the *first* molecules to meet each other, namely in the extreme tails of the two distributions. Hence, the probability of "meeting the tails" of the two distributions would be the product $P_1(x) \times P_2(x)$, which would be also the probability $P_{\rm pre}(x)$ of observing precipitation at position x

$$P_{\rm pre}(x) = P_1(x) \times P_2(x) = \frac{1}{c} e^{-x^2/(2L_{\rm step}^2 N_1)} e^{-(\ell-x)^2/(2L_{\rm step}^2 N_2)}, \tag{6.15}$$

where the product of the two square roots from (6.13) and (6.14) is denoted by c (a constant that does not depend on x). Next, applying the standard property of the exponential fraction

$$e^A e^B = e^{A+B},$$

we can write Eq. (6.15) in the form

$$P_{\rm pre}(x) = \frac{1}{c} e^{-[x^2/(2L_{\rm step}^2 N_1) + (\ell-x)^2/(2L_{\rm step}^2 N_2)]}, \tag{6.16}$$

We want to find the position x at which the precipitation is the most likely, that is, the peak of the probability given by Eq. (6.16). It occurs for that x for which the expression

$$-[x^2/(2L_{\text{step}}^2 N_1) + (\ell - x)^2/(2L_{\text{step}}^2 N_2)]$$

is least negative. If you are familiar with calculus, find this by taking the derivative of this precipitation probability $P_{\text{pre}}(x)$ with respect to x and setting the result equal to zero. The primary outcome is the derivative of the exponent. When the derivative of the exponent is set equal to zero, it yields:

$$\frac{x}{N_1} = \frac{\ell - x}{N_2}. \tag{6.17}$$

This says that the ratio of distances of the peak from the two ends has the value:

$$\frac{x}{\ell - x} = \frac{N_1}{N_2}. \tag{6.18}$$

Now we make the argument that for a given average step length, the number of steps taken is proportional to the average velocity, which is inversely proportional to the square root of the mass [see Eq. (6.2)]. Thus the result is:

$$\frac{x}{\ell - x} = \left(\frac{m_2}{m_1}\right)^{1/2}. \tag{6.19}$$

Hence the initial precipitation occurs at a location whose ratio of distances from the two ends is inversely proportional to the square root of the ratio of the masses.

Here we note that the use of distributions (6.13) and (6.14) is correct only for the *first* precipitation. When the precipitation has depleted the molecules in the tails of the distributions, then the distributions are no longer Gaussian. In fact, it turns out that when a steady state has been reached (when precipitation removes molecules at the same rate as new molecules leave the two ends of the diffusion tube), the distributions become straight lines descending from each end to zero at the point x given by Eq. (6.19).

END ACTIVITY

6.2 Periodic Precipitation: Liesegang Rings

In the diffusion chamber experiment, diffusion is coupled with a chemical reaction. Ammonia and hydrogen chloride gases react to form the solid (dust) ammonium chloride in the form of a disk. This as an example of a pattern formation process called **reaction-diffusion**, a combination of diffusion and chemical reaction.

In the diffusion tube experiment the resulting pattern was simple: a disk of ammonium chloride dust. However, reaction-diffusion processes have been linked to more complicated patterns observed in stones called agates, the stripes of the zebra, and the development of embryos.

Here you will study a more complex reaction-diffusion pattern that results when ions diffuse through a gel rather than gases diffusing through air. A gel (for example, Jello) can be thought of as water loosely confined and kept from flowing by a network of transparent "bags" consisting of criss-crossed long-chain molecules.

In the experiment described here, potassium chromate is dispersed uniformly through a gel in a small cylindrical container and copper sulfate crystals are placed on top of the gel. Copper ions go into solution and diffuse through the gel. When they meet chromate ions, they join to form insoluble copper chromate, which has a green color and thus becomes visible. Surprisingly, the result is not one disk, but a series of parallel disks. These are called **Liesegang rings**, after the German chemist Z. Q. Liesegang, who first reported them.[3]

There are clear similarities between the Liesegang experiment and the diffusion tube experiment. In both experiments:

- the reaction is dependent on the diffusion of the reactants,
- the reaction is between two different molecules and results in the precipitation of a salt, and
- in both reactions the chemical reactants diffuse along a cylinder.

[3]His original experiments took place in a flat dish with the copper sulfate placed at the center, so the pattern was, in fact, rings.

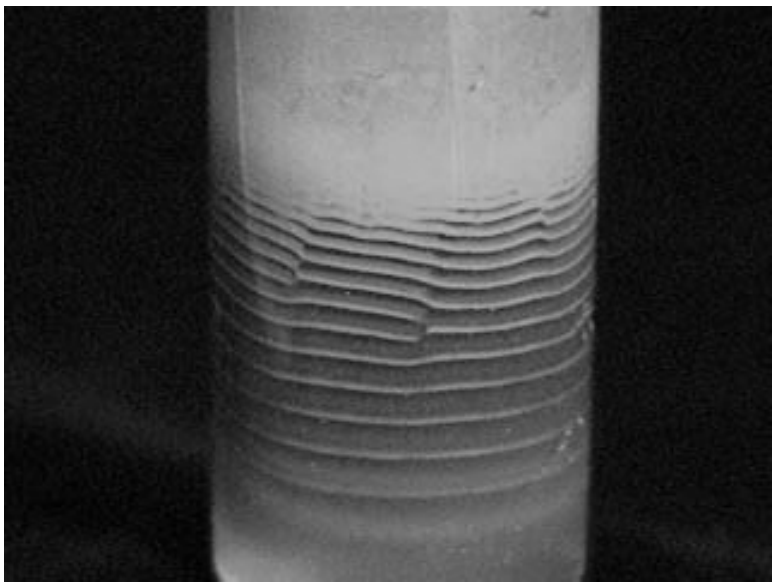

Figure 6.6: Multiple parallel Liesegang rings in silica gel.

There are, however, some differences between the two diffusion experiments:

- one of the reactants, the potassium chromate, is initially uniformly distributed along the cylinder in the Liesegang experiment,
- the diffusion takes place in a gel as opposed to air, and of course
- multiple disks appear instead of a single disk.

Q6.15: Can you think of other differences and similarities between the diffusion chamber and Liesegang experiments?

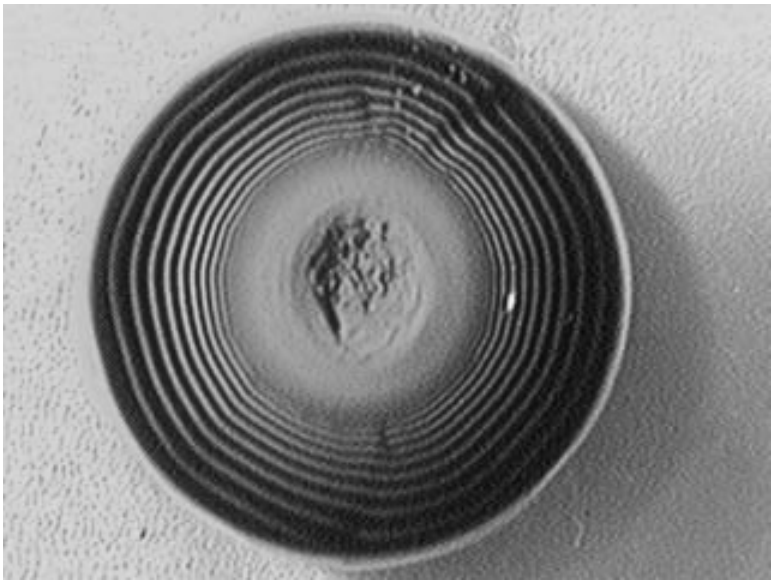

Figure 6.7: Circular Liesegang rings in a petri dish of agar gel.

Q6.16: Can you account for the appearance of multiple parallel disks in Figures 6.6 and 6.7? Think of what happens as the copper sulfate diffuses into the gel? Will a precipitate of copper chromate appear? If so, what will that do to the local concentration of chromate ion? What will be the consequence for diffusion of chromate ion to or from nearby regions? What happens to the local concentration of the copper ions diffusing through the gel? What happens next?

Q6.17: Can you make a guess as to how long you may have to wait to observe a pattern? Hint: A generalization of the result obtained in Appendix 6-A to cases when randomness of steps is caused by collisions with other particles turns out to be

$$\langle x^2 \rangle_{\text{avg}} = 2Dt,$$

where the proportionality constant D is called the diffusion constant, and its value varies from material to material. The value of the diffusion constant for copper sulfate in the gel is roughly what it is in water, on the order of 10^{-6} cm^2/sec. The preceding equation is usually called the *diffusion equation.*

HandsOn 29: Liesegang Experiment

For this experiment[4], you will need the following materials:

- Glacial acetic acid (17.4 M)
- Potassium Chromate (K_2CrO_4)
- Sodium Silicate solution (commercial water glass) with specific gravity 1.38–1.42 g/ml
- Copper Sulfate crystals
- distilled water
- one 2 dram vial (7.4 ml), actually holds up to 10 ml
- two 50 ml beakers
- 5 ml pipette calibrated in 0.1 ml units

[4]This version of the Liesegang experiment was adapted from: J. E. Forman, *Journal of Chemical Education* **67**, 720 (1990).

- 0.1 ml pipette calibrated in 0.01 ml units

In the following, it is assumed that the experiment will be done with approximately 8 ml of gel. For other sizes, scale the ingredients proportionately. Leave space at the top of the vial for the copper sulfate.

1. Make 4 ml of sodium silicate solution by adding 0.6 ml of sodium silicate (specific gravity 1.38–1.42) to 3.4 ml of distilled water. This produces a solution with specific gravity 1.06.

2. Make 4 ml of acetic acid solution by adding 0.09 ml of glacial acetic acid to 3.9 ml of distilled water. To this add 0.19 g of potassium chromate. Make this solution in the vial.

3. Pour the sodium silicate solution made in Step 1 into the vial containing the acetic acid solution of Step 2. Put on the cap (quickly) and mix all the reagents by inverting the vial about 10 times. Don't agitate the vial – this will introduce air bubbles into the gel and may distort the pattern.

4. Leave the gel in a safe place where it will not be moved or shaken. The solution will gel in 5 to 20 minutes. Let it harden for several hours if possible.

5. After hardening, add between 0.5 g and 1.0 g of copper sulfate crystals to the top of the gel. Try to cover the surface uniformly.

6. You will start seeing patterns after roughly 24 hours. The pattern will continue forming for one and a half weeks to two weeks.

7. Observe the pattern formed. Record the time it takes for portions of the pattern to develop. Measure the distances between portions of the pattern.

Q6.18: Compare your predicted pattern with what you observed. Is the symmetry what you expected? Refine your speculation about the source of the multiple rings.

Q6.19: Did the pattern take as long to develop as you expected? Does the diffusion equation above provide an approximate relation between the time t for a single ring to form?

END ACTIVITY

Research Projects

Research projects can be published on our Web site.

Try the suggestions below, design your own, or write an essay using any of the questions throughout this chapter as inspiration.

- **Diffusion Chamber Simulation.** In HandsOn 15, we suggested several topics for further explanation. Choose one and write an in-depth project report. If you can, explain your results by making use of the derivations offered throughout the chapter. Be sure to compare your results from the simulation with your experimental results.

- **Liesegang Patterns.** Try the experiment with the agar gel you prepared for the Bacterial Growth experiments. You could also try the experiment in a petri dish instead of a vial. Write a report which compares your results to those obtained from the traditional experiment described in HandsOn 29.

- **Drawing Comparisons and Distinctions.** (a) Write a report which summarizes similarities and/or differences between the diffusion chamber and Liesegang experiments. (b) Summarize similarities and differences between the experiments in this chapter with others in the previous chapters, for example bacterial growth or termite foraging.