

## Chapter 5

# The Gaseous State

### Concept Check 5.1

Suppose that you set up two barometers like the one shown in Figure 5.2. In one of the barometers you use mercury, and in the other you use water. Which of the barometers would have a higher column of liquid, the one with Hg or H<sub>2</sub>O? Explain your answer.

#### Solution

The general relationship between pressure ( $P$ ) and the height of a liquid column in a barometer is  $P = gdh$ , where  $g$  is the constant acceleration of gravity and  $d$  is the density. Examination of this relationship indicates that for a given pressure, as the density of the liquid in the barometer decreases, the height of the liquid must increase. In order to make this relationship more apparent, you can rearrange the equation to:

$$gh = \frac{P}{d}$$

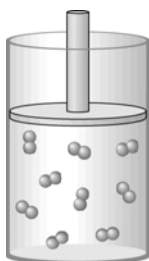
Keeping in mind that you are conducting the experiment at a constant pressure and that gravity is a constant, this mathematical relationship demonstrates that the height of the liquid in the barometer is inversely proportional to the density of the liquid in the barometer.

$$(h \propto \frac{1}{d})$$

This inverse relationship means that as the height of the liquid decreases, the density of the liquid must increase. Since the density of mercury is greater than the density of water, the barometer with the water will have the higher column.

## Concept Check 5.2

To conduct some experiments, a 10.0-L flask equipped with a movable plunger, as illustrated here, is filled with enough  $\text{H}_2$  gas to cause a pressure of 20 atm.



- In the first experiment, we decrease the temperature in the flask by  $10^\circ\text{C}$  and then increase the volume. Predict how the pressure in the flask changes during each of these events and, if possible, how the final pressure compares with your starting pressure.
- Once again we start with the pressure in the flask at 20 atm. The flask is then heated  $10^\circ\text{C}$  followed by a volume decrease. Predict how the pressure in the flask changes during each of these events and, if possible, how the final pressure compares with your starting pressure.

### Solution

- In the first step, when the temperature decreases, the pressure will also decrease. This is because, according to the combined gas law, the pressure is directly proportional to the temperature ( $P \propto T$ ). In the second step, when the volume increases, the pressure will decrease, since according to Boyle's law, pressure and volume are inversely related ( $P \propto 1/V$ ). Both changes result in the pressure decreasing, so the final pressure will be less than the starting pressure.
- In the first step, when the temperature increases, the pressure will also increase. This is because, according to the combined gas law, pressure is directly proportional to the temperature ( $P \propto T$ ). In the second step, when the volume decreases, the pressure will increase, since according to the ideal gas law, pressure and volume are inversely related ( $P \propto 1/V$ ). Both changes result in the pressure increasing, so the final pressure will be greater than the starting pressure.

## Concept Check 5.3

Three 3.0-L flasks, each at a pressure of 878 mmHg, contain He, Ar, and Xe.

- Which of the flasks contains the most atoms of gas?
- Which of the flasks has the greatest density of gas?
- If the He flask was heated and the Ar flask was cooled, which of the three flasks would be at the highest pressure?
- If the temperature of the He was lowered while the Xe was raised, which of the three flasks would have the greatest number of moles of gas?

### Solution

- According to Avogadro's law, equal volumes of any two (or more) gases at the same temperature and pressure contain the same number of molecules (or atoms in this case). Therefore, all three flasks contain the same number of atoms.
- Since density is mass divided by volume, and all three flasks have the same volume (3.0 L), the gas with the largest molar mass, xenon (Xe), will have the greatest density.
- According to the ideal gas law,  $PV = nRT$ , pressure is directly proportional to the temperature. Since the helium flask is being heated, it will have the highest pressure.
- Since the three flasks started with the same number of atoms, and hence the same number of moles, they would all still have the same number of moles no matter how the temperature of the flasks changed.

### Concept Check 5.4

A flask equipped with a valve contains 3.0 mol of  $H_2$  gas. You introduce 3.0 mol of Ar gas into the flask via the valve and then seal the flask.

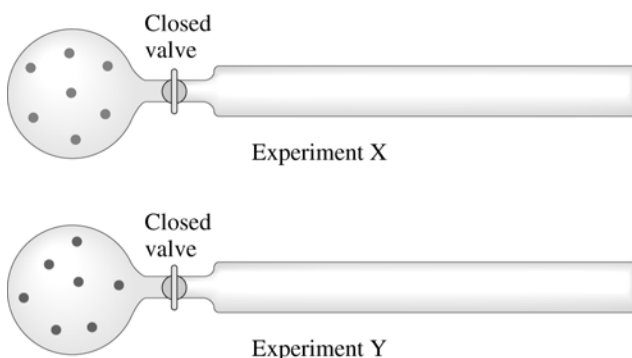
- What happens to the pressure of just the  $H_2$  gas in the flask after the introduction of the Ar? If it changes, by what factor does it do so?
- How do the pressures of the Ar and the  $H_2$  in the flask compare?
- How does the total pressure in the flask relate to the pressures of the two gases?

### Solution

- In a mixture of gases, each gas exerts the pressure it would exert if it were the only gas in the flask. The pressure of  $H_2$  is the same whether it is in the flask by itself or with the Ar. Therefore, the pressure of  $H_2$  does not change.
- According to the ideal gas law,  $PV = nRT$ , pressure ( $P$ ) is directly proportional to the number of moles ( $n$ ). Since the number of moles of  $H_2$  and the number of moles of Ar are equal, their pressures are also equal.
- The total pressure is equal to the sum of the pressures of the  $H_2$  gas and the Ar gas in the container. The total pressure will also be equal to twice the pressure of the  $H_2$  gas when it was in the flask by itself. It is also equal to twice the pressure that the Ar gas would exert if it were in the flask by itself.

### Concept Check 5.5

Consider the following experimental apparatus.



In this setup, each round flask contains a gas and the long tube contains no gas (that is, it is a vacuum).

- We use 1.0 mol of He for experiment X and 1.0 mol of Ar for experiment Y. If both valves are opened at the same time, which gas would you expect to reach the end of the long tube first?
- If you wanted the Ar to reach the end of the long tube at the same time as the He, what experimental condition (that is, you cannot change the equipment) could you change to make this happen?

### Solution

- The rate of effusion is inversely proportional to the square root of the molecular weight of the gas at constant temperature and pressure. Thus, He (molecular weight 4.00 amu) will diffuse faster than Ar (molecular weight 39.95 amu) and reach the end of the tube first.
- The speed of an atom is directly proportional to the absolute temperature. If you raise the temperature of the Ar, you can make it reach the end of the tube at the same time as the He.

### Concept Check 5.6

A 1.00-L container is filled with an ideal gas, and the recorded pressure is 350 atm. We then put the same amount of a real gas into the container and measure the pressure.

- If the real gas molecules occupy a relatively small volume and have large intermolecular attractions, how would you expect the pressures of the two gases to compare?
- If the real gas molecules occupy a relatively large volume and there are negligible intermolecular attractions, how would you expect the pressures of the two gases to compare?

- c. If the real gas molecules occupy a relatively large volume and have large intermolecular attractions, how would you expect the pressures of the two gases to compare?

### Solution

- a. If the real gas molecules occupy a relatively small volume, then the volume of the gas is essentially equal to the volume of the container, the same as for an ideal gas. However, if there were large intermolecular attractions, the pressure would be less than for an ideal gas. Therefore, the pressure would be greater for the ideal gas.
- b. If the real gas molecules occupy a relatively large volume, then the volume available for the gas is less than for an ideal gas, and the pressure would be greater. If there are negligible intermolecular attractions, then the pressure is essentially the same as for an ideal gas. Overall, the pressure would be less for the ideal gas.
- c. Since the effects of molecular volume and intermolecular attractions on the pressure of a real gas are opposite, you cannot determine how the pressures of the two gases compare.

### Conceptual Problem 5.23

Using the concepts developed in this chapter, explain the following observations.

- a. Automobile tires are flatter on cold days.
- b. You are not supposed to dispose of aerosol cans in a fire.
- c. The lid of a water bottle pops off when the bottle sits in the sun.
- d. A balloon pops when you squeeze it.

### Solution

- a. The volume of the tire and the amount of air in the tire remain constant. From the ideal gas law,  $PV = nRT$ , under these conditions the pressure will vary directly with the temperature ( $P \propto T$ ). Thus, on a cold day, you would expect the pressure in the tires to decrease, and they would appear flatter.
- b. Aerosol cans are filled with a fixed amount of gas in a constant volume. From the ideal gas law, under these conditions the pressure will vary directly with the temperature ( $P \propto T$ ). If you put an aerosol can in a fire, you will increase the temperature, and thus the pressure. If the pressure gets high enough, the can will explode.
- c. As the water bottle sits in the sun, the liquid water warms up. As the temperature of the water increases, so does its vapor pressure (Table 5.6). If the pressure gets high enough, it will pop the lid off the bottle.
- d. The amount of air in the balloon and the temperature remain constant. From the ideal gas law under these conditions, the pressure is inversely proportional to the volume ( $P \propto 1/V$ ). Thus, as you squeeze the balloon, you decrease the volume, resulting in an increase in pressure. If you squeeze hard enough and make the volume small enough, the balloon will pop.

### Conceptual Problem 5.24

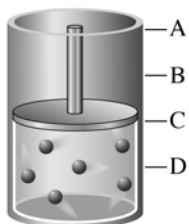
You have three identical flasks, each containing an equal amount of  $\text{N}_2$ ,  $\text{O}_2$ , or He. The volume of the  $\text{N}_2$  flask is doubled, of the  $\text{O}_2$  flask is halved, and of the He flask is reduced to one-third of the original. Rank the flasks from highest to lowest pressure both before and after the volume is changed, and indicate by what factor the pressure has changed.

#### Solution

Since each of the flasks is identical and each contains an equal amount of gas, the initial pressure in the  $\text{N}_2$  flask, the  $\text{O}_2$  flask, and the He flask will be the same. After the changes, the pressure in the He flask would be highest, with a pressure equal to three times the original. Next would be the  $\text{O}_2$  flask, with a pressure equal to two times the original. Last would be the  $\text{N}_2$  flask, with a pressure equal to one-half the original.

### Conceptual Problem 5.25

Consider the following glass container equipped with a movable piston.



- By what factor (increase by 1, decrease by 1.5, etc.) would you change the pressure if you wanted the volume to change from volume C to volume D?
- If the piston were moved from volume C to volume A, by what factor would the pressure change?
- By what factor would you change the temperature in order to change from volume C to volume B?
- If you increased the number of moles of gas in the container by a factor of 2, by what factors would the pressure and the volume change?

#### Solution

- The pressure and volume of a gas are inversely proportional; therefore, an increase by a factor of 2 in pressure would decrease the volume by  $\frac{1}{2}$  (C to D).

- b. The pressure and volume of a gas are inversely proportional; therefore, a decrease by a factor of 2 in pressure would double the volume (C to A).
- c. The volume and temperature of a gas are directly proportional; therefore, an increase in kelvin temperature by a factor of 1.5 would result in an increase in volume by a factor of 1.5 (C to B).
- d. Since the piston can move, the pressure would not change (it would be equal to the starting pressure). The volume of gas is directly proportional to the number of moles; therefore an increase in the number of moles by a factor of 2 would cause the volume to increase by 2 (C to A).

### Conceptual Problem 5.26

A 3.00-L flask containing 2.0 mol of  $O_2$  and 1.0 mol of  $N_2$  is in a room with a temperature of  $22.0^\circ C$ .

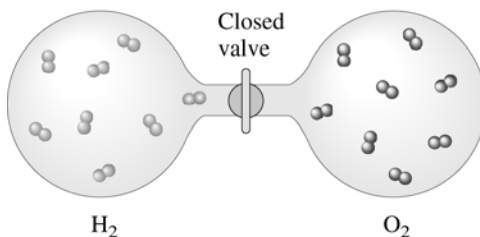
- a. How much (what fraction) of the total pressure in the flask is due to the  $N_2$ ?
- b. The flask is cooled and the pressure drops. What happens, if anything, to the mole fraction of the  $O_2$  at the lower temperature?
- c. 1.0 L of liquid water is introduced into the flask containing both gases. The pressure is measured about 45 minutes later. Would you expect the measured pressure to be higher or lower?
- d. Given the information in this problem and the conditions in part c., would it be possible to calculate the pressure in the flask after the introduction of the water? If it is not possible with the given information, what further information would you need to accomplish this task?

### Solution

- a. Since 1.0 out of the 3.0 moles of gas in the container is  $N_2$ , the fraction of the pressure due to  $N_2$  is  $1/3$ .
- b. Mole fractions are not a function of temperature, so nothing would happen.
- c. You would expect the pressure to be higher for two reasons. First, the water would occupy some volume, reducing the volume available for the gas to occupy. Thus, according to Boyle's law, as volume decreases, pressure increases. Second, after a time, the water would evaporate, and the vapor pressure due to the water would contribute to the total pressure, thereby increasing it.
- d. Yes, there is enough information in the problem to calculate the pressure in the flask, but you would also need to know the vapor pressure of water at  $22.0^\circ C$  (Table 5.6).

### Conceptual Problem 5.27

Consider the following setup, which shows identical containers connected by a tube with a valve that is presently closed. The container on the left has 1.0 mol of  $\text{H}_2$  gas; the container on the right has 1.0 mol of  $\text{O}_2$ .



*Note:* Acceptable answers to some of these questions might be “both” or “neither one.”

- Which container has the greatest density of gas?
- Which container has molecules that are moving at a faster average molecular speed?
- Which container has more molecules?
- If the valve is opened, will the pressure in each of the containers change? If it does, how will it change (increase, decrease, or no change)?
- 2.0 mol of Ar is added to the system with the valve open. What fraction of the total pressure will be due to the  $\text{H}_2$ ?

### Solution

- The container with the  $\text{O}_2$  has the greater density, since the molar mass of  $\text{O}_2$  (32.00 g/mol) is greater than for  $\text{H}_2$  (2.016 g/mol).
- Since the  $\text{H}_2$  molecules are lighter, they will be moving faster.
- Both containers have the same number of molecules (Avogadro's law).
- The pressure in each of the containers will not change when the valve is opened. Each container starts with the same pressure. Since the total volume remains constant, the pressure will not change.
- The fraction of the total pressure due to the  $\text{H}_2$  would now be 1/4.

### Conceptual Problem 5.28

Two identical He-filled balloons, each with a volume of 20 L, are allowed to rise into the atmosphere. One rises to an altitude of 3000 m while the other rises to 6000 m.

- Assuming that the balloons are at the same temperature, which balloon has the greater volume?
- What information would you need to calculate the volume of each balloon at its respective height?

### Solution

- a. Pressure decreases as you increase in altitude. Thus, the pressure at 6000 m is less than the pressure at 3000 m. For two identical balloons, the balloon at 6000 m will have the greater volume (Boyle's law).
- b. In order to calculate the volume of each balloon, you would need the temperature and pressure on the ground and the temperature and pressure at their respective heights.

### Conceptual Problem 5.29

You have a balloon that contains  $O_2$ . What could you do to the balloon in order to double the volume? Be specific in your answers; for example, you could increase the number of moles of  $O_2$  by a factor of two.

#### Solution

In order to double the volume you could reduce the pressure by  $1/2$ . You could also increase the temperature, but you cannot determine the final temperature without knowing the initial temperature.

### Conceptual Problem 5.30

Three 25.0-L flasks are placed next to each other on a shelf in a chemistry stockroom. The first flask contains He at a pressure of 1.0 atm, the second contains Xe at 1.50 atm, the third contains  $F_2$  and has a label that says 2.0 mol  $F_2$ . Consider the following questions about these flasks.

- a. Which flask has the greatest number of moles of gas?
- b. If you wanted each of the flasks to be at the same pressure as the He flask, what general things could you do to the other two containers to make this happen?

#### Solution

- a. If you assume that the flasks are at ordinary room temperature, say  $25^\circ C$ , then there would be approximately one mole of He (at 1.0 atm) and 1.5 mol of Xe (at 1.5 atm). Thus, the  $F_2$  flask (with 2.0 mol) would contain the greatest number of moles of gas.
- b. You could either decrease the volume, increase the temperature, or both.