

# PROPERTIES OF GASES

## • DIFFUSION

Diffusion is the ability of two or more gases to mix spontaneously until a uniform mixture is formed.

Example: A person wearing a lot of perfume walks into an enclosed room, eventually in time, the entire room will smell like the perfume.

## • EFFUSION

Effusion is the ability of gas particles to pass through a small opening or membrane from a container of higher pressure to a container of lower pressure.

The General Rule is: The lighter the gas, the faster it moves.

**Graham's Law of Effusion:**

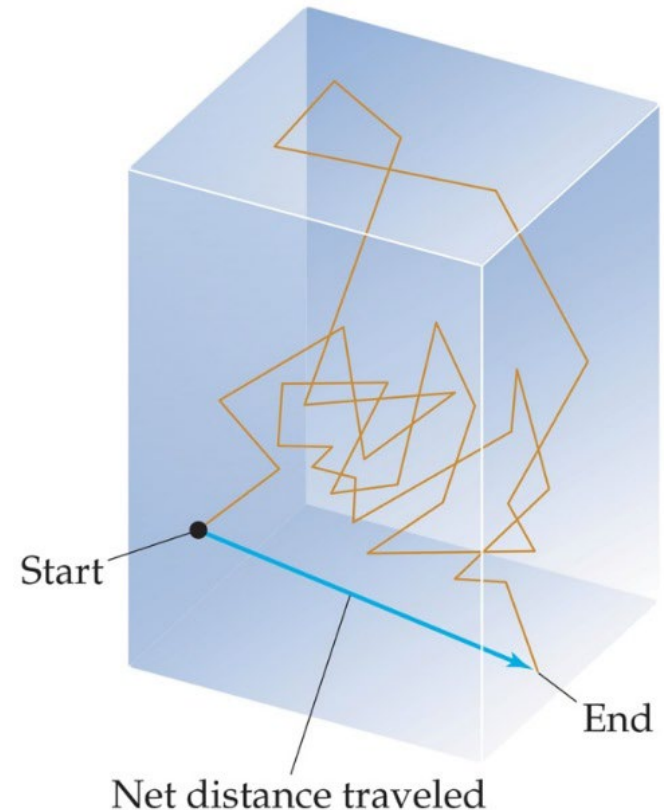
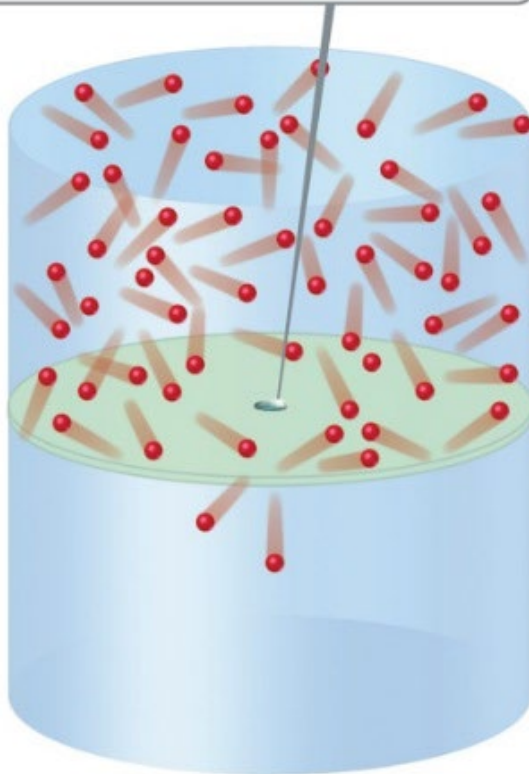
$$\frac{\text{Rate of effusion of gas A}}{\text{Rate of effusion of gas B}} = \sqrt{\text{molar mass B} / \text{molar mass A}}$$

**The rate of effusion of a gas is inversely proportional to the square root of the molar mass of that gas.**

# Effusion and Diffusion

- **Effusion** is the escape of gas molecules through a tiny hole into an evacuated space
- **Diffusion** is the spread of one substance throughout a space or a second substance.

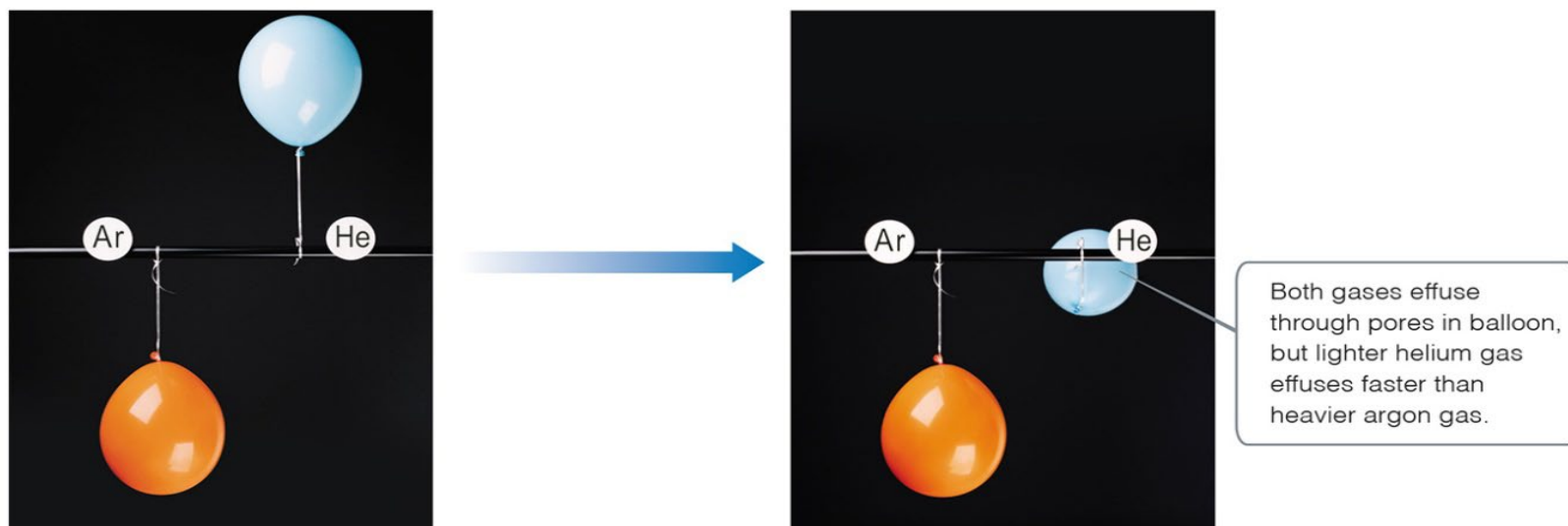
Gas molecules in top half effuse through pinhole only when they happen to hit the pinhole.



# Graham's Law Describes Diffusion and Effusion

- Graham's law relates the molar mass of two gases to their rate of speed of travel.
- The “lighter” gas always has a faster rate of speed.

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$



# LECTURE EXAMPLES

## Problems on Effusion & Molecular speed

1. A sample of unknown gas was found to have to effuse at a rate equal to 1.21 times that of hydrogen sulfide gas. What is the molar mass of the unknown gas. Identify the gas if it is a homonuclear diatomic gas.
2. Place the following gases in order of increasing average molecular speed at 20.0 °C.  
 $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{I}_2$ ,  $\text{HBr}$
3. Calculate the rms speed of  $\text{H}_2\text{S}$  (g) at 20.0 °C.

## Practice Exercise 10.14 Applying Graham's Law

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An unknown gas composed of homonuclear diatomic molecules effuses at a rate that is 0.355 times the rate at which  $\text{O}_2$  gas effuses at the same temperature. Calculate the molar mass of the unknown and identify it.

$$\frac{r_x}{r_{\text{O}_2}} = \sqrt{\frac{\mathcal{M}_{\text{O}_2}}{\mathcal{M}_x}}$$

$$\frac{r_x}{r_{\text{O}_2}} = 0.355 = \sqrt{\frac{32.0 \text{ g/mol}}{\mathcal{M}_x}}$$

Interpretation of  
“0.355 times the rate...”

$$\frac{32.0 \text{ g/mol}}{\mathcal{M}_x} = (0.355)^2 = 0.126$$

$$r_x = 0.355 \times r_{\text{O}_2}$$

$$\mathcal{M}_x = \frac{32.0 \text{ g/mol}}{0.126} = 254 \text{ g/mol}$$

Because we are told that the unknown gas is composed of homonuclear diatomic molecules, it must be an element. The molar mass must represent twice the atomic weight of the atoms in the unknown gas.

We conclude that the unknown gas must have an atomic weight of 127 g/mol and therefore **is  $\text{I}_2$** .

## Practice Exercise 1

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In a system for separating gases, a tank containing a mixture of hydrogen and carbon dioxide is connected to a much larger tank where the pressure is kept very low. The two tanks are separated by a porous membrane through which the molecules must effuse. If the initial partial pressure of each gas is 5.00 atm, what will be the mole fraction of hydrogen in the tank after the partial pressure of carbon dioxide has declined to 4.50 atm?

(a) 52.1%       $\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$        $\frac{r_{\text{H}_2}}{r_{\text{CO}_2}} = \left( \frac{44\text{g/mol}}{2\text{g/mol}} \right)^{1/2} = 4.69$   
(b) 37.2%  
(c) 32.1%

(d) 4.68%      So hydrogen effuses 4.69 times faster than carbon dioxide.  
(e) 27.4%

Rate of effusion of  $\text{CO}_2$  is  $\Delta P / \Delta t = (4.50 - 5.00) / (t - 0) = 0.5/t$

$r_{\text{H}_2} = 4.69 \times r_{\text{CO}_2} = 4.69(.5/t) = 2.35/t$  so  $5 - 2.35 = 2.65$  atm (left in tank)

$P_T = P_{\text{H}_2} + P_{\text{CO}_2} = 4.50 + 2.65 = 7.15$  atm

$\chi = 2.65 / 7.15 = 0.371$

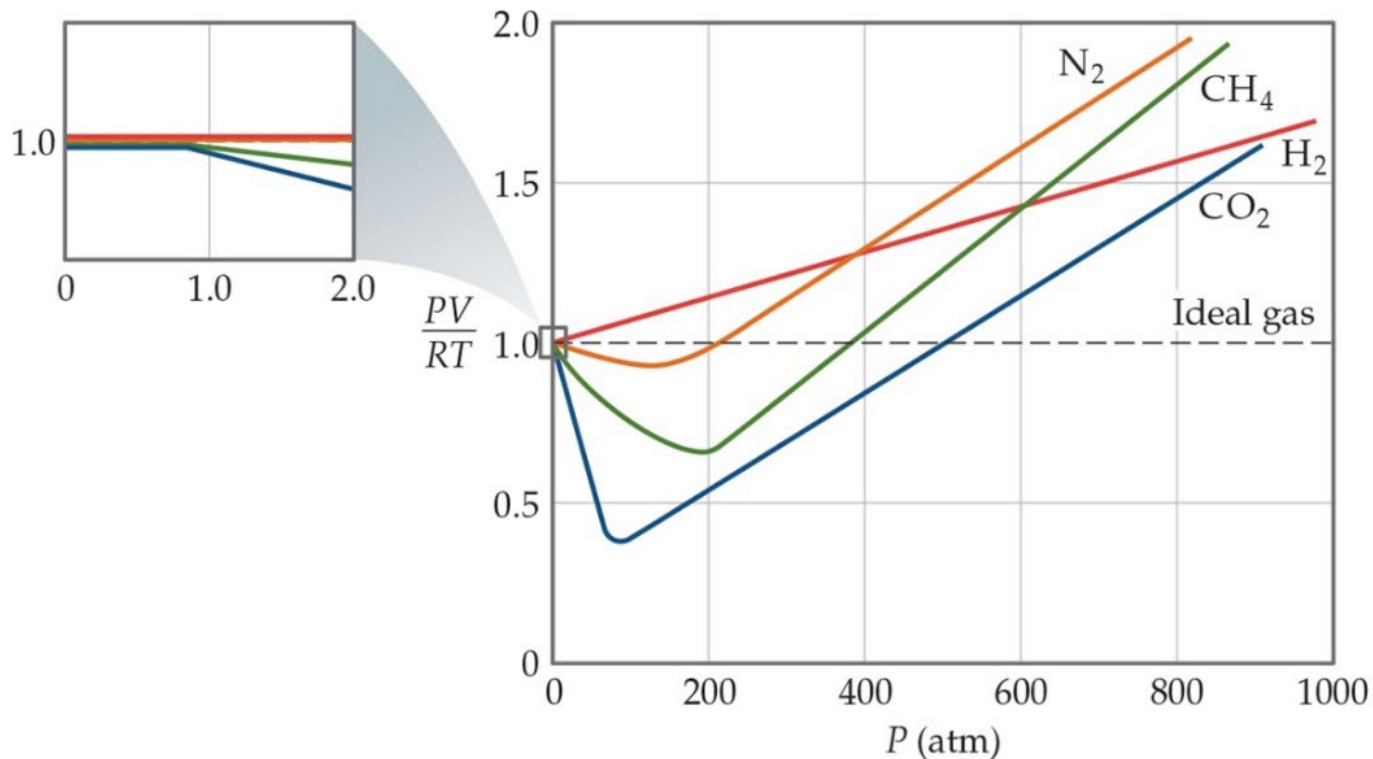
# LECTURE QUIZ # 20A

## Problems on Effusion & Molecular speed

1. A sample of methane was found to have to effuse at a rate equal to 1.32 times that of an unknown homonuclear diatomic gas. What is the molar mass of the unknown gas. Identify the gas.
2. Place the following gases in order of increasing average molecular speed at 25.0 °C.  
 $\text{CO}$ ,  $\text{SF}_6$ ,  $\text{H}_2\text{S}$ ,  $\text{Cl}_2$ ,  $\text{HI}$
3. Calculate the rms speed of  $\text{CO}$  and  $\text{SF}_6$  at 25.0 °C.

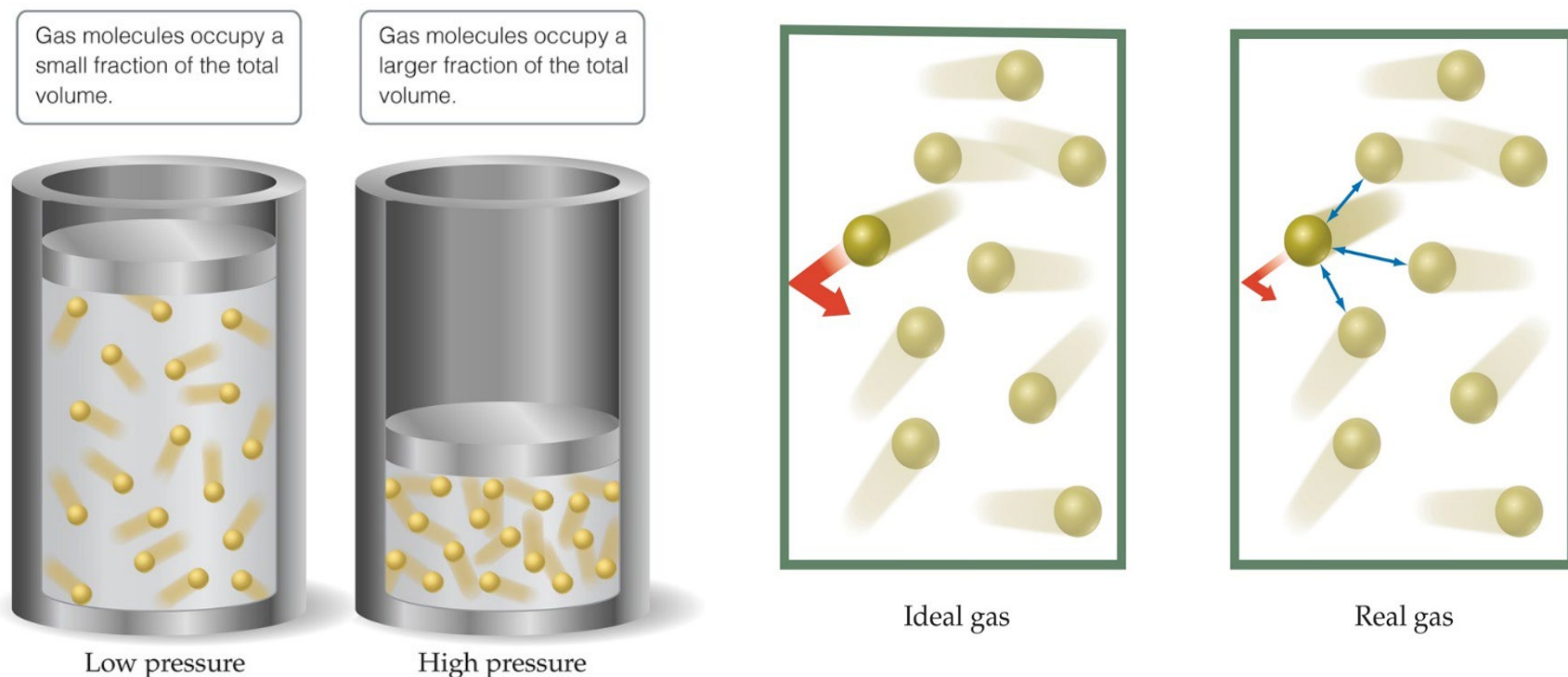
# Real Gases

- In the real world, the behavior of gases conforms to the ideal-gas equation only at relatively high temperature and low pressure.
- Even the same gas will show wildly different behavior under high pressure at different temperatures.





# Deviations from Ideal Behavior



The assumptions made in the kinetic-molecular model (negligible volume of gas molecules themselves, no attractive forces between gas molecules, etc.) break down at high pressure and/or low temperature.

## Corrections for Nonideal Behavior

- The ideal-gas equation can be adjusted to take these deviations from ideal behavior into account.
- One equation corrected for real gases is known as the **van der Waals equation**.
- The pressure adjustment is due to the fact that molecules attract and repel each other.
- The volume adjustment is due to the fact that molecules occupy some space on their own.

# The van der Waals Equation

**Table 10.3** Van der Waals Constants for Gas Molecules

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

Substance	$a(\text{L}^2 \cdot \text{atm/mol}^2)$	$b(\text{L/mol})$
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0510
H <sub>2</sub>	0.244	0.0266
N <sub>2</sub>	1.39	0.0391
O <sub>2</sub>	1.36	0.0318
F <sub>2</sub>	1.06	0.0290
Cl <sub>2</sub>	6.49	0.0562
H <sub>2</sub> O	5.46	0.0305
NH <sub>3</sub>	4.17	0.0371
CH <sub>4</sub>	2.25	0.0428
CO <sub>2</sub>	3.59	0.0427
CCl <sub>4</sub>	20.4	0.1383

## Real Gases: Deviations from Ideality

To review, molecules of an ideal gas have no significant volume and do not attract each other. Real gases approximate this behavior at low pressures and elevated temperatures; real gases deviate from ideality at *high pressures* and *low temperatures*.

The molecules in a real gas at relatively low pressure have practically no attraction for one another, because they are far apart. Thus they behave almost like molecules of ideal gases. However, if they crowd the molecules close together by increasing the pressure, then the effect on the force of attraction between the molecules increases (see *“P” correction for molecular attraction on the next slide*).

## Real Gases: Deviations from Ideality

In the case of low temperatures, intermolecular attraction between molecules is more pronounced because the molecules move more slowly, their kinetic energy is smaller relative to the attractive forces, and they fly apart less easily after collisions with one another. This results in a decrease in *volume* (see “*V*” *correction for volume of molecules below*).

An equation by Johannes van der Waals was constructed in 1879 to correct for the volume of real gas molecules and the attractive forces that exist between them:

$$\left( P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

( “P” correction) ( “V” correction)

### Real Gases: Deviations from Ideality

The variables,  $a$  and  $b$  are constants that depend on the gas (this information will be provided on a case-by-case basis) known as the van der Waals parameters, and the other terms have their usual meaning in a gas equation. The parameter  $a$  represents the role of attractive forces, and  $b$  represents the role of repulsive forces. Once these parameters have been determined, they can be used in the van der Waals equation to predict the pressure of a certain gas under the conditions of interest.

The van der Waals parameters will be given on a case-by-case basis, depending on the identity of your particular gas. Note that the values of BOTH  $a$  and  $b$  generally INCREASE with an increase in mass of the molecule and with an increase in the complexity of its structure. Larger, more massive molecules not only have larger volumes, they also tend to have greater intermolecular attractive forces.

## Sample Exercise 10.15 Using the van der Waals Equation

If 10.00 mol of an ideal gas were confined to 22.41 L at 0.0 °C, it would exert a pressure of 10.00 atm. Use the van der Waals equation and Table 10.3 to estimate the pressure exerted by 1.000 mol of  $\text{Cl}_2(\text{g})$  in 22.41 L at 0.0 °C.

TABLE 10.3 Van der Waals Constants for Gas Molecules

Substance	$a$ ( $\text{L}^2\text{-atm/mol}^2$ )	$b$ ( $\text{L/mol}$ )
He	0.0341	0.02370
Ne	0.211	0.0171
Ar	1.34	0.0322
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CO <sub>2</sub>	3.59	0.0427
CCl <sub>4</sub>	20.4	0.1383

### Solution

**Analyze** We need to determine a pressure. Because we will use the van der Waals equation, we must identify the appropriate values for the constants in the equation.

**Plan** Rearrange for P

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

## Sample Exercise 10.15 Using the van der Waals Equation

**Solve** Substituting  $n = 10.00$  mol,  $R = 0.08206$  L-atm/mol-K,  $T = 273.2$  K,  $V = 22.41$  L,  $a = 6.49$  L<sup>2</sup>-atm/mol<sup>2</sup>, and  $b = 0.0562$  L/mol:

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$P = \frac{(10.00 \text{ mol})(0.08206 \text{ L-atm/mol-K})(273.2 \text{ K})}{22.41 \text{ L} - (10.00 \text{ mol})(0.0562 \text{ L/mol})} - \frac{(10.00 \text{ mol})^2(6.49 \text{ L}^2\text{-atm/mol}^2)}{(22.41 \text{ L})^2}$$
$$= 10.26 \text{ atm} - 1.29 \text{ atm} = 8.97 \text{ atm}$$

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**Comment** Notice that the term 10.26 atm is the pressure corrected for molecular volume. This value is higher than the ideal value, 10.00 atm, because the volume in which the molecules are free to move is smaller than the container volume, 22.41 L. Thus, the molecules collide more frequently with the container walls and the pressure is higher than that of a real gas. The term 1.29 atm makes a correction in the opposite direction for intermolecular forces. The correction for intermolecular forces is the larger of the two, and thus the pressure 8.97 atm is smaller than would be observed for an ideal gas.



## Sample Integrative Exercise Putting Concepts Together

Cyanogen, a highly toxic gas, is 46.2% C and 53.8% N by mass. At 25 °C and 751 torr, 1.05 g of cyanogen occupies 0.500 L. **(a)** What is the molecular formula of cyanogen? Predict **(b)** its molecular structure and **(c)** its polarity.

### Solution

**Analyze** We need to determine the molecular formula of a gas from elemental analysis data and data on its properties. Then we need to predict the structure of the molecule and from that, its polarity.

**(a) Plan** We can use the percentage composition of the compound to calculate its empirical formula. (Section 3.5)  
Then we can determine the molecular formula by comparing the mass of the empirical formula with the molar mass. (Section 3.5)

**Solve** To determine the empirical formula, we assume we have a 100-g sample and calculate the number of moles of each element in the sample:

$$\text{Moles C} = (46.2 \text{ g C}) \left( \frac{1 \text{ mol C}}{12.01 \text{ g C}} \right) = 3.85 \text{ mol C}$$

$$\text{Moles N} = (53.8 \text{ g N}) \left( \frac{1 \text{ mol N}}{14.01 \text{ g N}} \right) = 3.84 \text{ mol N}$$

## Sample Integrative Exercise Putting Concepts Together

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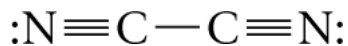
Because the ratio of the moles of the two elements is essentially 1:1, the empirical formula is CN. To determine the molar mass, we use Equation 10.11.

$$\begin{aligned}\mathcal{M} &= \frac{dRT}{P} = \frac{(1.05 \text{ g}/0.500 \text{ L})(0.08206 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K})(298 \text{ K})}{(751/760) \text{ atm}} \\ &= 52.0 \text{ g/mol}\end{aligned}$$

The molar mass associated with the empirical formula CN is  $12.0 + 14.0 = 26.0 \text{ g/mol}$ . Dividing the molar mass by that of its empirical formula gives  $(52.0 \text{ g/mol})/(26.0 \text{ g/mol}) = 2.00$ . Thus, the molecule has twice as many atoms of each element as the empirical formula, giving the molecular formula  $\text{C}_2\text{N}_2$ .

**(b) Plan** To determine the molecular structure, we must determine the Lewis structure. (Section 8.5) We can then use the VSEPR model to predict the structure. (Section 9.2)

**Solve** The molecule has  $2(4) + 2(5) = 18$  valence-shell electrons. By trial and error, we seek a Lewis structure with 18 valence electrons in which each atom has an octet and the formal charges are as low as possible. The structure



meets these criteria. (This structure has zero formal charge on each atom.)

## Sample Integrative Exercise Putting Concepts Together

Continued

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The Lewis structure shows that each atom has two electron domains. (Each nitrogen has a nonbonding pair of electrons and a triple bond, whereas each carbon has a triple bond and a single bond.) Thus, the electron-domain geometry around each atom is linear, causing the overall molecule to be linear.

**(c) Plan** To determine the polarity of the molecule, we must examine the polarity of the individual bonds and the overall geometry of the molecule.

**Solve** Because the molecule is linear, we expect the two dipoles created by the polarity in the carbon–nitrogen bond to cancel each other, leaving the molecule with no dipole moment.