

## Gas Laws

Gas laws are used to demonstrate gas behavior. The ideal-gas law is a broad description of gas behavior from which more specific laws, the individual gas laws, are combined. This handout will examine individual gas laws, the ideal-gas law, and describe how they can be applied to find the density and partial pressure of a gas. In addition, the topic of non-ideal gas behavior will be explored using the van der Waals equation.

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### The Individual Gas Laws

Pressure (P), volume (V), number of moles (n), and temperature (T) are the four variables required to define the physical condition of a gas. The individual gas laws describe the relationship between two of the four gas law variables, given that the remaining two variables are held constant. The table below illustrates which individual gas law should be used, depending on the circumstance.

Avogadro's Law	Boyle's Law	Charles's Law	Gay-Lussac's Law
$\frac{V_1}{n_1} = \frac{V_2}{n_2}$	$P_1V_1 = P_2V_2$	$\frac{V_1}{T_1} = \frac{V_2}{T_2}$	$\frac{P_1}{T_1} = \frac{P_2}{T_2}$
<b>Constant:</b> pressure, temperature	<b>Constant:</b> moles, temperature	<b>Constant:</b> pressure, moles	<b>Constant:</b> volume, moles

**Examples:**

Determine which individual gas law best describes the following situations:

a. As we inhale, the rib cage expands, and the diaphragm moves downward, increasing the volume of the lungs and decreasing the gas pressure inside the lungs. Exhalation is the reverse process—the volume of the lungs decreases and the gas pressure increases, forcing air out of the lungs.

*Answer:* Boyle's Law, which describes how the two variables V and P change in relation to each other. As volume increases, pressure decreases, and vice versa. Volume and pressure are inversely proportional.

b. A common problem car owners may encounter is slightly deflated tires when the temperature begins to drop during the winter months.

*Answer:* Charles's Law, which describes how V and T change in relation to each other. As the temperature decreases, the volume of the tires also decreases. Volume and temperature are directly proportional.

c. You are blowing up a balloon and notice that as you add more air, the balloon gets bigger.

*Answer:* Avogadro's Law, which describes how the two variables  $V$  and  $n$  change in relation to each other. As the number of moles of gas inside the balloon increase, the volume also increases. Volume and number of moles are directly proportional.

d. A common warning on aerosol cans is to avoid extreme temperatures, lest the container explode due to the resulting increase in pressure.

*Answer:* Gay-Lussac's Law, which describes how the two variables  $T$  and  $P$  change in relation to each other. Aerosol containers should be kept away from extreme heat because as temperature increases, pressure increases. Temperature and pressure are directly proportional.

### **The Ideal-Gas Law**

The ideal-gas law offers a broad description of gas behavior. It is obtained by combining the individual gas laws previously described. The ideal-gas law assumes there are no intermolecular forces, and the combined volume of the molecules is negligible.

The ideal-gas law also introduces the gas constant, represented by the variable " $R$ ." There are many possible values and units of  $R$ , and the value it has should be selected based on the units given in the problem (note:  $T$  must *always* be expressed in kelvins for ideal-gas law problems).

Common units and values of  $R$  include:

- 0.08206 L-atm/mol-K
- 8.314 J/mol-K
- 62.36 L-torr/mol-K

The relationship between the gas constant R and the familiar variables P, V, n, and T can be expressed using the following equation:

$$P \cdot V = n \cdot R \cdot T$$

The ideal-gas law can also be used to describe the state of a gas at two different time frames, which is demonstrated by the next equation. The variables on the left side of the equation represent one time frame, while those on the right represent the other time frame.

$$\frac{P_1 V_1}{n_1 R T_1} = \frac{P_2 V_2}{n_2 R T_2}$$

### **STP Conditions**

STP is a concept used in many gas law word problems. STP is an abbreviation for standard temperature and pressure, and refers to any gas at 0°C (273.15 K) and 1 atm of pressure (101.325 kPa). The volume occupied by one mole of gas at STP is 22.4 L and is also referred to as molar volume.

### **Solving Gas Law Problems**

Here is a step-by-step process for solving gas law problems:

1. Identify which variables (out of P, V, n, T) are known and which variables are unknown.
2. Make sure all values have the appropriate units, especially T and R. Remember that T must always be expressed in kelvins.
3. Rearrange the ideal-gas law equation to solve for the unknown variable.
4. Plug in values, and solve for unknown variable.
5. Check your work by making sure units cancel to provide the desired unit for the unknown variable.

**Example:**

An aerosol spray can at sea level (1 atm pressure) and room temperature (25.0°C) with a volume of 350.00 mL contains 2.30g of propane gas (C<sub>3</sub>H<sub>8</sub>) as a propellant. A label on the can warns against exposing it to temperatures above 140°F. What would be the pressure (in atm) inside the can at this critical temperature?

1. Identify which variables (P, V, n, T) are known and which variables are unknown.

Known	Unknown
V = 350.00 mL	n
Mass = 2.30g C <sub>3</sub> H <sub>8</sub>	P
T = 140°F	

The number of moles (n) can be found using the provided mass. Convert grams to moles using the molar mass of propane.

$$2.30\text{g C}_3\text{H}_8 \times \frac{1\text{ mol C}_3\text{H}_8}{44.121\text{g C}_3\text{H}_8} = .0521\text{ mol C}_3\text{H}_8$$

2. Make sure all values have appropriate units, especially R and T. Because the problem asks for the pressure in atm,  $0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$  should be the value of R. This means that the given volume needs to be converted from mL to L.

$$350.00\text{ mL} \times \frac{1\text{ L}}{1000\text{ mL}} = .35000\text{ L}$$

Since the temperature was given in Fahrenheit, it needs to be converted to kelvin.

$$T_{\text{Kelvin}} = \left[ (140^\circ\text{F} - 32) \times \frac{5}{9} \right] + 273 = 333\text{ K}$$

3. Rearrange the ideal-gas law to solve for the unknown variable.

$$P = \frac{nRT}{V}$$

4. Plug in values, and solve for P.

$$P = \frac{0.0521 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 333 \text{ K}}{.35000 \text{ L}}$$

$$P = 4.07 \text{ atm}$$

5. Check the answer by making sure units cancel, providing the desired unit for the unknown variable. In this case, after cancelling all units, only atm (a unit of pressure) should be left over. This is why previous steps focused on converting the known values into the proper units.

$$P = \frac{nRT}{V} = \frac{0.0521 \text{ mol} \times 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \times 333 \text{ K}}{.350 \text{ L}}$$

### Van der Waals Equation for Non-Ideal Gases

The van der Waals equation is a more accurate alternative for the ideal-gas law that considers both intermolecular forces and gas molecule volume. The equation combines two new variables, called van der Waals constants ( $a$  and  $b$ ), with familiar values to represent intermolecular forces and volume of molecules. Van der Waals constants are experimentally determined values that can be found in any textbook. The following figure demonstrates how the ideal-gas law equation is modified to account for intermolecular forces and molecule volume:

$$P \cdot V = n \cdot R \cdot T \rightarrow \left( P + \frac{an^2}{V^2} \right) \cdot (V - nb) = nRT$$

### Gas Density and Molar Mass

The ideal-gas law has applications beyond solving for the four variables  $P$ ,  $V$ ,  $n$ , and  $T$ . Gas density can also be found using a form of the ideal-gas law. Incorporating molar mass ( $M_A$ ),

which has units of grams per mole ( $\frac{\text{g}}{\text{mol}}$ ), into the ideal-gas law equation provides the means to solve for the density of a gas. The equation below demonstrates how to find gas density,  $d$ , using the modified form of the ideal-gas law:

$$d = \frac{n \cdot M_A}{V} = \frac{P \cdot M_A}{R \cdot T}$$

### Dalton's Law of Partial Pressures and Mole Fractions

When gases are physically (not chemically) mixed in a container, they all contribute to the container's pressure. Therefore, total pressure on a container caused by a mixture of gases can be isolated into the individual pressures of each gas or their partial pressures.

The equation below shows how individual gas pressures are added to determine the total pressure of the container, where  $P_{\text{total}}$  is the total pressure of the container, and  $P_A$ ,  $P_B$ , etc. are the pressures of individual gases:

$$P_{\text{Total}} = P_A + P_B + P_C + \dots$$

The moles of one gas in a mixture divided by the total number of moles in the same mixture is called a mole fraction. A mole fraction can be used to relate the partial pressure of a gas and the total pressure of a gas mixture. This is demonstrated in the next equation, where  $P_A$  is the partial pressure of gas A,  $P_{\text{Total}}$  is the total pressure of the container,  $X_A$  is the mole fraction of A, and  $n_A$  and  $n_{\text{Total}}$  are the number of moles of gas A and the total moles of gas in the container, respectively.

$$P_A = X_A \cdot P_{\text{total}}, \text{ where } X_A = \frac{n_A}{n_{\text{total}}}$$

#### Example:

At 22.4 L and 0.00°C, assuming the gas behaves ideally, the pressure exerted by 10.00 mol of  $\text{O}_2$  is 10.0 atm.

A. Use the van der Waals equation to determine the pressure of 10.00 mol O<sub>2</sub> at 22.4 L and 0°C. The van der Waals constant *a* for O<sub>2</sub> is 1.36 atm·L<sup>2</sup>/mol<sup>2</sup>. The van der Waals constant *b* for O<sub>2</sub> is 0.0318 L/mol. Does the ideal-gas law over- or underestimate HCN's pressure at the given conditions?

i. Rearrange the van der Waals equation to solve for P.

$$P = \frac{n \cdot R \cdot T}{V - nb} - \frac{an^2}{V^2}$$

ii. Plug in values.

$$P = \frac{10.00 \text{ mol} \cdot 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}} \cdot 273.15 \text{ K}}{22.4 \text{ L} - (10.00 \times 0.0318 \frac{\text{L}}{\text{mol}})} - \frac{1.36 \frac{\text{atm} \cdot \text{L}^2}{\text{mol}^2} \times (10.00 \text{ mol})^2}{(22.4 \text{ L})^2}$$

iii. Solve for P.

$$P = \frac{224.147}{22.082} - \frac{136}{501.76} = 9.88 \text{ atm}$$

iv. Compare values. The answer produced by the van der Waals equation is less than 10.00 atm. Therefore, the ideal-gas law overestimates oxygen's pressure at the given conditions.

B. Find the density of O<sub>2</sub> at the given conditions.

i. Use the number of moles of O<sub>2</sub> (*n*), molar mass of O<sub>2</sub> (*M<sub>A</sub>*), and the volume of the container (*V*) to find density.

$$d = \frac{10.00 \text{ mol} \times 31.998 \frac{\text{g}}{\text{mol}}}{22.4 \text{ L}}$$

ii. Solve for *d*.

$$d = 14.3 \frac{\text{g}}{\text{L}}$$

C. A mixture of 2.00g of O<sub>2</sub> (*g*) and 1.50g of CO<sub>2</sub> (*g*) is placed in a 20.0 L vessel at 0°C. What is the partial pressure of each gas, and what is the total pressure in the vessel?



- i. First, convert grams of each substance to moles.

$$2.00\text{g } O_2 \times \frac{1 \text{ mol}}{31.998\text{g}} = 0.0625 \text{ mol}$$

$$1.50\text{g } CO_2 \times \frac{1 \text{ mol}}{44.009\text{g}} = 0.0341 \text{ mol}$$

- ii. Use ideal-gas law to solve for P, the partial pressure of each gas.

$$P_{O_2} = \frac{nRT}{V} = \frac{(0.0625 \text{ mol})(0.08206 \frac{L \cdot \text{atm}}{\text{mol} \cdot K})(273.15 \text{ K})}{20.0 \text{ L}} = 0.0700 \text{ atm}$$

$$P_{CO_2} = \frac{nRT}{V} = \frac{(0.0341 \text{ mol})(0.08206 \frac{L \cdot \text{atm}}{\text{mol} \cdot K})(273.15 \text{ K})}{20.0 \text{ L}} = 0.0382 \text{ atm}$$

- iii. Add the partial pressures of both gases to obtain the total pressure in the vessel.

$$P_{\text{total}} = 0.0700 \text{ atm} + 0.0382 \text{ atm} = 0.108 \text{ atm}$$

- D. Using answers from the previous question, calculate the mole fraction of  $O_2$ .

- i. A mole fraction is a ratio of the number of moles of one substance to the total number of moles present in the container. Therefore:

$$X_{O_2} = \frac{0.0625 \text{ mol } O_2}{0.0966 \text{ mol total}} = 0.647$$

**Practice:**

1. A 1.35g sample of HCl gas at 30.0°C occupies 550.0 mL. The pressure inside the container is decreased from 610.15 kPa to 310.15 kPa. What volume will the HCl occupy at this new pressure?
2. What will be the pressure (in atm) of a 0.50 mol sample of CO in a 2.0 L container at room temperature (25.0°C)?
3. Find the volume (in liters) of 3.27g of  $N_2$  at 37.0°C and 400.0 kPa.
4. What is the density of a sample of  $NH_3$  at 0.978 atm and 165.5°C?

5. Find the partial pressure of  $N_2$  in a mixture of  $CO_2$ ,  $O_2$ , and  $H_2O$  at 2.5 atm, with partial pressures of 0.10 atm, 0.40 atm, and 0.70 atm, respectively.
6. Earth's atmosphere is composed of 78.0 mol %  $N_2$ , 21.0 mol %  $O_2$ , and 0.90 mol % Ar. The remaining 0.10% is comprised of trace gases like  $CO_2$ . If the atmospheric pressure is 755 torr, what is the partial pressure of  $N_2$  in this mixture?
7. A sample of 0.50 mol sulfur dioxide ( $SO_2$ ) is confined to a 2.0 L container at 20.0°C. Use the van der Waals equation to solve for P, the pressure of  $SO_2$ . The van der Waals constants for  $SO_2$  are:

a.  $a = 6.769 \frac{L^2 \cdot atm}{mol^2}$

b.  $b = 0.05679 \frac{L}{mol}$

**Answers to Practice Problems:**

1. 1082 mL
2. 6.1 atm
3. 0.752 L
4. 0.462 g/L
5. 1.3 atm
6. 589 torr
7. 5.7 atm