

Tutorial 6**GASES**

Before working with gases some definitions are needed:

PRESSURE: atmospheres or mm Hg; 1 atm = 760 mm Hg

TEMPERATURE: Kelvin, K, which is °C + 273

STP: Standard Iemperature and Pressure: 273 K and 1 atm (or 760 mm Hg)

BOYLE'S LAW (temperature is constant): $PV = \text{constant}$

This is an inverse relationship: if one variable increases the other must decrease.

CHARLES' LAW (pressure is constant): $V = \text{constant} \times T$

This is a direct relationship: if one variable increases so does the other.

GAY-LUSSAC'S LAW (volume is constant): $P = \text{constant} \times T$

This is a direct relationship: if one variable increases so does the other.

IDEAL GAS LAW: $PV = nRT$, where

P = pressure of the gas sample
 V = volume of the gas sample
 T = Kelvin temperature of the gas sample
 n = moles of the gas sample
 R = molar gas constant

AVOGADRO'S LAW: At the same temperature and pressure, equal volumes of all gases have the same number of molecules. At STP one mole of any gas occupies a volume of 22.4 L: this is the molar volume.

PVT CHANGES: These are problems which involve only changes in the variables of Pressure, Volume, and Temperature. The IDEAL GAS LAW can be rearranged to

$$(1) \quad \frac{PV}{T} = nR$$

For a fixed number of moles of gas the right side of this equation is constant. We can then derive:

$$(2) \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

where P_1 , V_1 , T_1 are pressure, volume, and temperature for one set of conditions and P_2 , V_2 , T_2 for another. We use this relationship when changing a gas sample from one P-V-T state to another. Solving equation (2) for the individual variables at the second conditions:

$$(3) \quad V_2 = \frac{P_1 V_1 T_2}{P_2 T_1} = V_1 \times \frac{P_1}{P_2} \times \frac{T_2}{T_1}$$

$$(4) \quad P_2 = \frac{P_1 V_1 T_2}{V_2 T_1} = P_1 \times \frac{V_1}{V_2} \times \frac{T_2}{T_1}$$

$$(5) \quad T_2 = \frac{P_2 V_2 T_1}{P_1 V_1} = T_1 \times \frac{P_2}{P_1} \times \frac{V_2}{V_1}$$

Notice: the second value of the variable is the first value multiplied by fractions of the other two variables.

EXAMPLE: A gas sample occupies a volume of 125 mL at STP. Calculate the volume of the gas at 25°C and 450 mm Hg pressure.

There are two ways of solving this problem: (a) blindly substitute values in equation (3), or (b) reason through. Let us do (b). Equation (3) is given below without numerical subscripts on the P and T fractions: they are considered to be correction fractions: the second volume will be the first volume multiplied by two correction fractions, one for pressure and one for temperature.

The pressure and temperature changes are:

pressure change: 760 mm Hg → 450 mm Hg

temperature change: 273 K → 298 K

The effect of the pressure change alone is to increase the volume, since pressure and volume are inversely related (BOYLE'S LAW). Therefore the correction fraction for pressure must make the volume larger and is 760 mm Hg / 450 mm Hg.

Similarly, the temperature change alone will increase the volume, since volume and temperature are directly proportional (CHARLES' LAW). Therefore, the correction fraction for temperature must make the volume larger and is 298 K / 273 K.

The solved problem looks like this:

$$V_2 = V_1 \times \frac{P}{P} \times \frac{T}{T} = 125 \text{ mL} \times \frac{760 \text{ mm Hg}}{450 \text{ mm Hg}} \times \frac{298 \text{ K}}{273 \text{ K}} = 230 \text{ mL}$$

In many problems only one variable changes; these problems are much easier to solve.

EXAMPLE: A gas sample has a pressure of 742 mm Hg at 25° C. Calculate the pressure of the gas at 100° C.

Instead of blindly substituting in equation (4) let us reason. Equation (4) is given below without numerical subscripts on the V and T fractions: they are simply considered to be correction fractions: the second fraction will be the first multiplied by two correction fractions, one for volume and one for temperature. No mention is made of the gas volume so we assume it is constant and the volume correction fraction is not needed.

The temperature changes from 298 K to 373 K; this temperature increase will increase the pressure (GAY-LUSSAC'S LAW). Therefore the correction fraction for temperature must make the pressure larger and is 373 K / 298 K. The solved problem looks like this:

$$P_2 = P_1 \times \frac{V}{V} \times \frac{T}{T} = P_1 \times \frac{T}{T} = 742 \text{ mm Hg} \times \frac{373 \text{ K}}{298 \text{ K}} = 929 \text{ mm Hg}$$

MASS-VOLUME RELATIONSHIPS: PVT problems work for any gas. If we want to know the volume of a given mass of gas, or the mass of a given volume of gas, then we must consider a specific gas; the mass of 100 mL of oxygen is different from the mass of 100 mL of neon.

We must first evaluate R, the molar gas constant. Solve the IDEAL GAS LAW for R and substitute known values for n, P, V, and T: one mole of a gas occupies 22.4 L at 1 atm and 273 K:

$$R = \frac{PV}{nT} = \frac{(1 \text{ atm})(22.4 \text{ L})}{(1 \text{ mol})(273 \text{ K})} = 0.0821 \frac{\text{L-atm}}{\text{mol-K}}$$

or

$$R = \frac{PV}{nT} = \frac{(760 \text{ mm})(22.4 \text{ L})}{(1 \text{ mol})(273 \text{ K})} = 62.4 \frac{\text{mm-L}}{\text{mol-K}}$$

Notice there are four units on this constant.

EXAMPLE: Calculate the volume of 0.250 g of oxygen at 25°C and 742 mm Hg pressure.

First convert the mass of oxygen to moles of oxygen:

$$0.250 \text{ g O}_2 \times \frac{1 \text{ mol O}_2}{32.0 \text{ g O}_2} = 7.81 \times 10^{-3} \text{ mol O}_2$$

Then solve the IDEAL GAS LAW for volume. (The units must correspond to the units of the R that is used.)

$$V = \frac{nRT}{P} = \frac{(7.81 \times 10^{-3} \text{ mol})(62.4 \frac{\text{mm-L}}{\text{mol-K}})(298 \text{ K})}{(742 \text{ mm})} = 0.196 \text{ L}$$

or

$$V = \frac{nRT}{P} = \frac{(7.81 \times 10^{-3} \text{ mol})(0.0821 \frac{\text{L-atm}}{\text{mol-K}})(298 \text{ K})}{(742 \text{ mm} \times \frac{1 \text{ atm}}{760 \text{ mm}})} = 0.196 \text{ L}$$

EXAMPLE: Calculate the mass of 335 mL of sulfur dioxide measured at 37°C and 745 mm Hg pressure.

The IDEAL GAS LAW does not have a mass unit but it has a mass related unit: mol. Therefore, solve for n and subsequently convert to grams:

$$n = \frac{PV}{RT} = \frac{(745 \text{ mm})(0.355 \text{ L})}{(62.4 \frac{\text{mm-L}}{\text{mol-K}})(310 \text{ K})} = 0.0137 \text{ mol SO}_2$$

$$\text{Mass SO}_2 = 0.137 \text{ mol SO}_2 \times \frac{64.1 \text{ g SO}_2}{1 \text{ mol SO}_2} = 0.878 \text{ g SO}_2$$

GAS DENSITY: The density of a gas can be computed from its molar mass and its molar volume under a given set of conditions.

Gases are typically about three orders of magnitude (1000 times) less dense than liquids (at ordinary temperatures and pressures). For convenience, gas density is reported in units of g/L rather than the customary g/mL or g/cm³ unit that is used for liquids and solids.

EXAMPLE: Calculate the density of carbon dioxide at STP.

We know that at STP one mole of any gas occupies 22.4 L (AVOGADRO'S LAW). Thus:

$$D = \frac{\text{molar mass}}{\text{molar volume}} = \frac{44.0 \text{ g CO}_2 / \cancel{\text{mol}}}{22.4 \text{ L CO}_2 / \cancel{\text{mol}}} = 1.96 \text{ g/L}$$

EXAMPLE: Calculate the density of carbon dioxide at 100°C and 850 mm Hg.

Under these P-V-T conditions the molar volume is not 22.4 L. However, we can calculate the molar volume at these conditions. Starting from STP:

pressure change: 760 mm Hg → 850 mm Hg

temperature change: 273 K → 373 K

Setting up the appropriate correction fractions for P and T, the molar volume at the conditions of the problem is:

$$V_{\text{molar}} = 22.4 \text{ L} \times \frac{760 \text{ mm Hg}}{850 \text{ mm Hg}} \times \frac{373 \text{ K}}{273 \text{ K}} = 27.4 \text{ L}$$

The density may now be calculated:

$$D = \frac{\text{molar mass}}{\text{molar volume}} = \frac{44.0 \text{ g CO}_2 / \cancel{\text{mol}}}{27.4 \text{ L CO}_2 / \cancel{\text{mol}}} = 1.61 \text{ g/L}$$

WET GASES: DALTON'S LAW states: in a mixture of gases the total pressure is equal to the sum of the pressures of all gases present:

$$P_{\text{total}} = P_1 + P_2 + P_3 + \dots$$

When a gas is collected over water there is water vapor in the gas volume. According to DALTON'S LAW, the total pressure is:

$$P_{\text{total}} = P_{\text{gas}} + P_{\text{water}}$$

From which,

$$P_{\text{gas}} = P_{\text{total}} - P_{\text{water}}$$

The total pressure, P_{total} , is usually an experimentally determined quantity. The pressure of the water, P_{water} , is the vapor pressure of water. Vapor pressure of water at various temperatures is available in tables, such as Appendix B, p 1018, in your lecture text. (A vapor pressure table is also posted in each lab.) To obtain the gas pressure, subtract the vapor pressure of water from the total pressure.

EXAMPLE: A 325 mL sample of gas is collected over water at 26°C and 742 mm Hg pressure. Calculate the volume of the dry gas at STP. The vapor pressure of water is 25 mm Hg at 25°C.

We first find the pressure due to the gas alone by subtracting the vapor pressure of water:

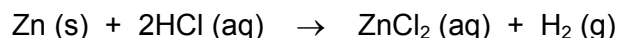
$$P_{\text{gas}} = P_{\text{total}} - P_{\text{water}} = 742 \text{ mm Hg} - 25 \text{ mm Hg} = 717 \text{ mm Hg}$$

We then find the volume at STP by multiplying by appropriate correction fractions:

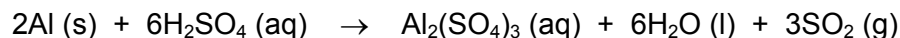
$$V_2 = V_1 \times \frac{P}{P} \times \frac{T}{T} = 325 \text{ mL} \times \frac{717 \text{ mm Hg}}{760 \text{ mm Hg}} \times \frac{273 \text{ K}}{299 \text{ K}} = 280 \text{ mL}$$

- 1) A sample of nitrogen is heated from STP to 100°C at constant pressure. Calculate the volume at 100°C .
- 2) A sample of helium is heated from STP to 100°C at constant volume. Calculate the pressure at 100°C .
- 3) A sample of argon is heated at constant volume from STP until the pressure is 1250 mm Hg. Calculate the temperature.
- 4) A 300-mL sample of sulfur dioxide is cooled from 250°C to 125°C . Calculate the volume.
- 5) A sample of chlorine at 1.25 atm pressure is cooled from 100°C to 0°C . Calculate the pressure.
- 6) A gas is heated at constant pressure from 25°C until its volume increases from 120 mL to 175 mL. Calculate the final temperature.
- 7) A 325-mL sample of nitrogen is at a pressure of 500 mm Hg. The pressure is changed until the volume is 150 mL. Calculate the final pressure.
- 8) A 325-mL sample of nitrogen is cooled from 250°C until its volume is 275 mL. Calculate the final temperature.
- 9) The pressure on a 500-mL sample of gas is changed from 1.25 atm to 5.00 atm. Calculate the volume.
- 10) A sample of oxygen occupies a volume of 437 mL at 25°C and 735 mm Hg pressure. Calculate the volume at STP.
- 11) A gas sample occupies a volume of 125 mL at 100°C and 500 mm Hg pressure. Calculate the volume at 250°C and 1750 mm Hg pressure.
- 12) A 500-mL sample of oxygen has a pressure of 450 mm Hg and a temperature of 100°C . Calculate the pressure when the volume is 700 mL and the temperature is 50°C .
- 13) A gas occupies a volume of 225 mL at STP. Calculate the temperature needed to change the volume to 300 mL and the pressure to 1000 mm Hg.
- 14) A 455-mL sample of gas is obtained at 26°C and 742 mm Hg pressure. What will be the pressure when the volume is 600 mL and the temperature 40°C ?
- 15) A gas occupies a volume of 500 mL at 100°C and 500 mm Hg pressure. What temperature is needed to change the volume to 450 mL and the pressure to 300 mm Hg?
- 16) Calculate the volume of 10.0 g of oxygen at STP.
- 17) Calculate the volume of 25.0 g of chlorine at -32°C and 500 mm Hg.
- 18) Calculate the mass of 155 mL of helium measured at STP.

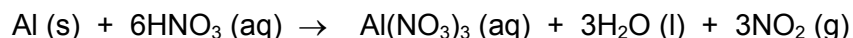
- 19) Calculate the mass of 500 mL of xenon measured at 25°C and 555 mm Hg.
- 20) Calculate the mass of 250 mL of argon measured at -100°C and 10.0 atm.
- 21) What volume of hydrogen, measured at 25°C and 740 mm Hg, will be formed from the reaction of 10.0 g of zinc metal with excess hydrochloric acid?



- 22) What volume of sulfur dioxide, measured at 100°C and 655 mm Hg, will be formed from the reaction of 3.50 g of aluminum metal with excess sulfuric acid?



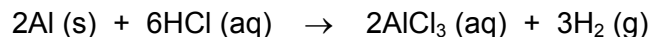
- 23) What volume of nitrogen dioxide, measured at 37°C and 855 mm Hg, will be formed from the reaction of 5.00 g of aluminum metal with excess nitric acid?



- 24) Calculate the density of hydrogen at STP.
- 25) Calculate the density of oxygen at 15°C and 655 mm Hg.
- 26) Calculate the density of sulfur hexafluoride at 150°C and 25.0 atm.

A VAPOR PRESSURE TABLE FOR WATER IS AVAILABLE IN YOUR TEXTBOOK (p. 607).

- 27) A 350-mL sample of hydrogen was collected over water at 25°C at a pressure of 741 mm Hg. Calculate the volume of dry gas at STP.
- 28) A 255-mL sample of nitrogen was collected over water at 21°C at a pressure of 745 mm Hg. Calculate the mass of the gas.
- 29) A dry gas sample measured 253 mL at 30°C and 800 mm Hg. Calculate the volume of the wet gas at 30°C and 800 mm Hg.
- 30) Calculate the volume of 1.25 g of wet oxygen at 25°C and 800 mm Hg.
- 31) A sample of aluminum metal was dissolved in hydrochloric acid. 347 mL of hydrogen gas was collected over water at 25°C and 736 mm Hg. Calculate the mass of the aluminum sample.



- 32) 0.673 g of potassium chlorate was decomposed to produce oxygen. The gas was collected over water at 29°C and 700 mm Hg. Calculate the volume of the collected gas.



Answers to Problems

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|--------------|-------------|----------------|--------------|
| 1) 348 mL | 9) 125 mL | 17) 10.6 L | 25) 1.17 g/L |
| 2) 1040 mm | 10) 387 mL | 18) 0.0277 g | 26) 105 g/L |
| 3) 176°C | 11) 50.1 mL | 19) 1.96 g | 27) 302 mL |
| 4) 228 mL | 12) 278 mm | 20) 7.02 g | 28) 0.283 g |
| 5) 0.915 atm | 13) 206°C | 21) 3.84 L | 29) 264 mL |
| 6) 162°C | 14) 589 mm | 22) 6.89 L | 30) 0.937 L |
| 7) 1080 mm | 15) -72°C | 23) 12.6 L | 31) 0.239 g |
| 8) 170°C | 16) 7.00 L | 24) 0.0902 g/L | 32) 0.231 L |