

# Gas Laws

One of the most amazing things about gases is that, despite wide differences in *chemical properties*, all the gases more or less obey the *gas laws*. The gas laws deal with how gases behave with respect to pressure, volume, temperature, and amount.

## Pressure

Gases are the only state of matter that can be compressed very tightly or expanded to fill a very large space. *Pressure* is force per unit area, calculated by dividing the force by the area on which the force acts. The earth's gravity acts on air molecules to create a force, that of the air pushing on the earth. This is called *atmospheric pressure*.

The units of pressure that are used are pascal (Pa), standard atmosphere (atm), and torr. 1 atm is the average pressure at sea level. It is normally used as a standard unit of pressure. The SI unit though, is the pascal. 101,325 pascals equals 1 atm.

For laboratory work the atmosphere is very large. A more convenient unit is the torr. 760 torr equals 1 atm. A torr is the same unit as the mmHg (millimeter of mercury). It is the pressure that is needed to raise a tube of mercury 1 millimeter.

## The Gas Laws: Pressure Volume Temperature Relationships

### Boyle's Law: The Pressure-Volume Law



Robert Boyle (1627-1691)

*Boyle's law* or the *pressure-volume law* states that the volume of a given amount of gas held at constant temperature varies inversely with the applied pressure when the temperature and mass are constant.

$$V \propto \frac{1}{P}$$

Another way to describing it is saying that their products are constant.

$$PV = C$$

When pressure goes up, volume goes down. When volume goes up, pressure goes down. From the equation above, this can be derived:

$$P_1V_1 = P_2V_2 = P_3V_3 \text{ etc.}$$

This equation states that the product of the initial volume and pressure is equal to the product of the volume and pressure after a change in one of them under constant temperature. For example, if the initial volume was 500 mL at a pressure of 760 torr, when the volume is compressed to 450 mL, what is the pressure?

Plug in the values:

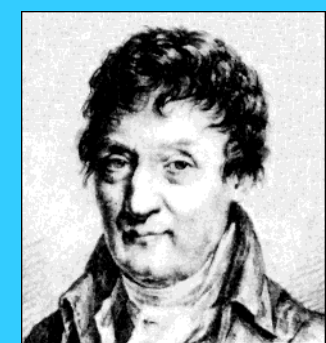
$$P_1V_1 = P_2V_2$$

$$(760 \text{ torr})(500 \text{ mL}) = P_2(450 \text{ mL})$$

$$760 \text{ torr} \times 500 \text{ mL} / 450 \text{ mL} = P_2 \quad 844 \text{ torr} = P_2$$

The pressure is 844 torr after compression.

## Charles' Law: The Temperature-Volume Law



Jacques Charles (1746 - 1823)

This law states that the volume of a given amount of gas held at constant pressure is directly proportional to the Kelvin temperature.

$$V \propto T$$

Same as before, a constant can be put in:

$$V / T = C$$

As the volume goes up, the temperature also goes up, and vice-versa.

Also same as before, initial and final volumes and temperatures under constant pressure can be calculated.

$$V_1 / T_1 = V_2 / T_2 = V_3 / T_3 \text{ etc.}$$

## Gay-Lussac's Law: The Pressure Temperature Law



Joseph Gay-Lussac (1778-1850)

This law states that the pressure of a given amount of gas held at constant volume is directly proportional to the Kelvin temperature.

$$P \propto T$$

Same as before, a constant can be put in:

$$P / T = C$$

As the pressure goes up, the temperature also goes up, and vice-versa.

Also same as before, initial and final volumes and temperatures under constant pressure can be calculated.

$$P_1 / T_1 = P_2 / T_2 = P_3 / T_3 \text{ etc.}$$

## Avogadro's Law: The Volume Amount Law



[Amedeo Avogadro \(1776-1856\)](#)

Gives the relationship between volume and amount when pressure and temperature are held constant. Remember amount is measured in moles. Also, since volume is one of the variables, that means the container holding the gas is flexible in some way and can expand or contract.

If the amount of gas in a container is increased, the volume increases. If the amount of gas in a container is decreased, the volume decreases.

$$V \propto n$$

As before, a constant can be put in:

$$V / n = C$$

This means that the volume-amount fraction will always be the same value if the pressure and temperature remain constant.

$$V_1 / n_1 = V_2 / n_2 = V_3 / n_3 \text{ etc.}$$

## The Combined Gas Law

Now we can combine everything we have into one proportion:

$$V \propto \frac{T}{P}$$

The volume of a given amount of gas is proportional to the ratio of its Kelvin temperature and its

pressure.

Same as before, a constant can be put in:

$$PV/T = C$$

As the pressure goes up, the temperature also goes up, and vice-versa.

Also same as before, initial and final volumes and temperatures under constant pressure can be calculated.

$$P_1V_1/T_1 = P_2V_2/T_2 = P_3V_3/T_3 \text{ etc.}$$

## The Ideal Gas Law

The previous laws all assume that the gas being measured is an *ideal gas*, a gas that obeys them all exactly. But over a wide range of temperature, pressure, and volume, real gases deviate slightly from ideal. Since, according to Avogadro, the same volumes of gas contain the same number of moles, chemists could now determine the formulas of gaseous elements and their formula masses. The ideal gas law is:

$$PV = nRT$$

Where  $n$  is the number of moles of the number of moles and  $R$  is a constant called the *universal gas constant* and is equal to approximately 0.0821 L-atm / mole-K.

### EXAMPLE 1:

The balloon used by Charles in his historic flight in 1783 was filled with about 1300 mole of  $H_2$ . If the outside temperature was 21 °C and the atmospheric pressure was 750 mm Hg, what was the volume of the balloon?

Quantity	Raw data	Conversion	Data with proper units
$P$	750 mm Hg	$\times 1 \text{ atm} / 760 \text{ torr} =$	0.9868 atm
$V$	?		?
$n$	1300 mole $H_2$		1300 mole $H_2$
$R$	0.0821 L-atm / mole-K		0.0821 L-atm / mole-K
$T$	21 °C	$+ 273 =$	294 K

$$V = nRT / P ; V = (1300 \text{ mole})(0.0821 \text{ L-atm/mole-K})(294 \text{ K}) / (0.9868 \text{ atm}) = 31798.358 \text{ L} = \underline{3.2 \times 10^4} \text{ L.}$$

## Other Forms of the Gas Law

If the definition of the mole is included in the equation, the result is:

$$PV = gRT / FW$$

or

$$FW = gRT / PV$$

This equation provides a convenient way of determining the formula weight of a gas if mass, temperature, volume and pressure of the gas are known (or can be determined).

### EXAMPLE 2:

A 0.1000 g sample of a compound with the empirical formula  $\text{CHF}_2$  is vaporized into a 256 mL flask at a temperature of 22.3 °C. The pressure in the flask is measured to be 70.5 torr. What is the molecular formula of the compound?

<i>Quantity</i>	<i>Raw data</i>	<i>Conversion</i>	<i>Data with proper units</i>
<i>P</i>	70.5 torr	x 1 atm / 760 torr =	0.0928 atm
<i>V</i>	256 mL	x 1 L / 1000 mL =	0.256 L
<i>g</i>	0.1000 g sample		0.1000 g
<i>R</i>	0.0821 L-atm / mole-K		0.0821 L-atm / mole-K
<i>T</i>	22.3 °C	+ 273 =	295.3 K
<i>FW</i>	?		?

$$FW = gRT / PV ; V = (0.1000 \text{ g})(0.0821 \text{ L-atm / mole-K})(295.3 \text{ K}) / (0.0928 \text{ atm})(0.256 \text{ L}) = \underline{102} \text{ g / mole}$$

$$FW \text{ of } \text{CHF}_2 = 51.0 \text{ g / mole} ; 102 / 51.0 = 2 ; \text{C}_2\text{H}_2\text{F}_4$$

If the equation above is rearranged further,

$$g / V = P \times FW / RT = \text{density}$$

you get an expression of the *density* of the gas as a function of *T* and *FW*.

### EXAMPLE 3:

Compare the density of He and air (average *FW* = 28 g/mole) at 25.0 °C and 1.00 atm.

$$d_{\text{He}} = (4.003 \text{ g / mole})(1.00 \text{ atm}) / (0.0821 \text{ L-atm / mole-K})(298 \text{ K}) = 0.164 \text{ g / L}$$

$$d_{\text{air}} = (28.0 \text{ g / mole})(1.00 \text{ atm}) / (0.0821 \text{ L-atm / mole-K})(298 \text{ K}) = 1.14 \text{ g / L}$$

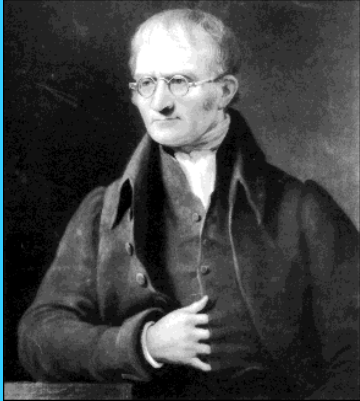
### EXAMPLE 4:

Compare the density of air at 25.0 °C and air at 1807 °C and 1.00 atm.

$$d_{\text{He}} = (28.0 \text{ g / mole})(1.00 \text{ atm}) / (0.0821 \text{ L-atm / mole-K})(298 \text{ K}) = 1.14 \text{ g / L}$$

$$d_{\text{air}} = (28.0 \text{ g / mole})(1.00 \text{ atm}) / (0.0821 \text{ L-atm / mole-K})(2080 \text{ K}) = 0.164 \text{ g / L}$$

## Partial Pressures



**John Dalton (1766-1844)**

**Dalton's Law of Partial Pressures** states that the total pressure of a mixture of nonreacting gases is the sum of their individual partial pressures.

$$P_{\text{total}} = P_a + P_b + P_c + \dots$$

or

$$P_{\text{total}} = n_a RT / V + n_b RT / V + n_c RT / V + \dots$$

or

$$P_{\text{total}} = (n_a + n_b + n_c + \dots) RT / V$$

The pressure in a flask containing a mixture of 1 mole of  $\text{O}_2$  and 0.80 mole  $\text{N}_2$  would be the same as the same flask holding 1 mole of  $\text{O}_2$ .

Partial pressures are useful when gases are collected by bubbling through water (displacement). The gas collected is saturated in water vapor which contributes to the total number of moles of gas in the container.

### EXAMPLE 5:

A sample of  $\text{H}_2$  was prepared in the laboratory by the reaction:



456 mL of gas was collected at 22.0 °C. The total pressure in the flask was 742 torr. How many moles of  $\text{H}_2$  were collected? The vapor pressure of  $\text{H}_2\text{O}$  at 22.0 °C is 19.8 torr.

Quantity	Raw data	Conversion	Data with proper units
$P_{\text{total}}$	742 torr		
$P_{\text{H}_2\text{O}}$	19.8 torr		
$P_{\text{H}_2}$	742 torr - 19.8 torr = 722.2 torr	x 1 atm / 760 torr =	0.9503 atm
$V$	456 mL	x 1 L / 1000 mL =	0.456 L
$n$	?		?
$R$	0.0821 L-atm / mole-K		0.0821 L-atm / mole-K
$T$	22 °C	+ 273 =	295 K

$$n_{\text{H}_2} = P_{\text{H}_2}V / RT ; n_{\text{H}_2} = (0.9503 \text{ atm})(0.456 \text{ L}) / (0.0821 \text{ L-atm} / \text{mole-K})(295 \text{ K}) = \underline{0.0179} \text{ mole H}_2.$$

## Non-Ideal Gases



**Johannes Diderik van der Waals (1837-1923)**

The ideal gas equation ( $PV=nRT$ ) provides a valuable model of the relations between volume, pressure, temperature and number of particles in a gas. As an ideal model it serves as a reference for the behavior of real gases. The ideal gas equation makes some simplifying assumptions which are obviously not quite true. Real molecules do have volume and do attract each other. All gases depart from ideal behavior under conditions of low temperature (when liquefaction begins) and high pressure (molecules are more crowded so the volume of the molecule becomes important). Refinements to the ideal gas equation can be made to correct for these deviations.

In 1873 J. D. van der Waals proposed his equation, known as the van der Waals equation. As there are attractive forces between molecules, the pressure is lower than the ideal value. To account for this the pressure term is augmented by an attractive force term  $a/V^2$ . Likewise real molecules have a volume. The volume of the molecules is represented by the term  $b$ . The term  $b$  is a function of a spherical diameter  $d$  known as the van der Waals diameter. The van der Waals equation for  $n$  moles of gas is:

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

The values for  $a$  and  $b$ , below, are determined empirically:

Molecule	$a$ (liters <sup>2</sup> -atm / mole <sup>2</sup> )	$b$ (liters / mole)
H <sub>2</sub>	0.2444	0.02661
O <sub>2</sub>	1.360	0.03183
N <sub>2</sub>	1.390	0.03913
CO <sub>2</sub>	3.592	0.04267
Cl <sub>2</sub>	6.493	0.05622
Ar	1.345	0.03219
Ne	0.2107	0.01709
He	0.03412	0.02370