

II. Gaseous State

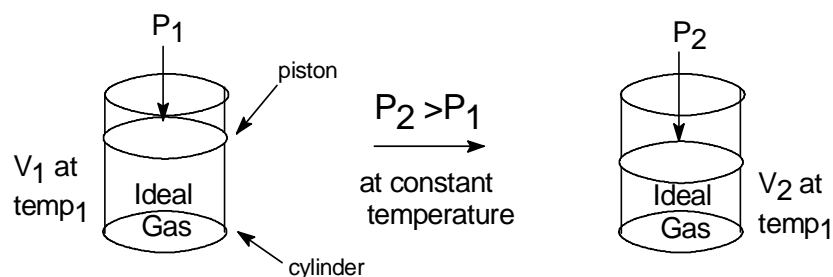
P = pressure in units of atm (atmospheres) or torr. $1.00 \text{ atm} = 760 \text{ torr}$

V = volume in units of L (liters).

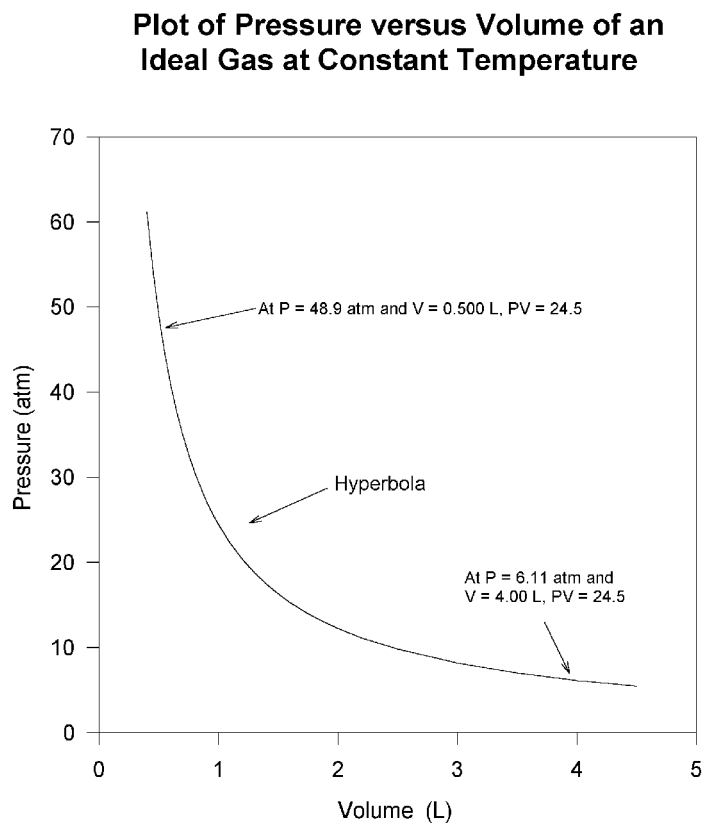
n = moles of the substance

A) Boyle's Law

Consider the change in volume of one mole of an ideal gas with the change in pressure exerted on the gas at constant temperature.



A plot of the volumes at various pressures is seen below.



Note: At any point on the curve the pressure times the volume equals the constant 24.5.

$$PV = \text{constant} \quad \text{when temperature is held fixed}$$

This equation is the mathematical expression of Boyle's law - *at constant temperature the volume occupied by a fixed weight of a gas is inversely proportional to the pressure exerted on it.*

Boyle's law describes the behavior of an ideal gas and approximates the behavior of a real gas. The approximation is very poor at high pressures and low temperatures.

Example: If an 8.00 g sample of a gas occupies 12.3 L at 400 torr, what volume will the gas occupy at the same temperature and 600 torr?

Since n and temperature are held fixed,

$$P_1 V_1 = P_2 V_2 = \text{constant}$$

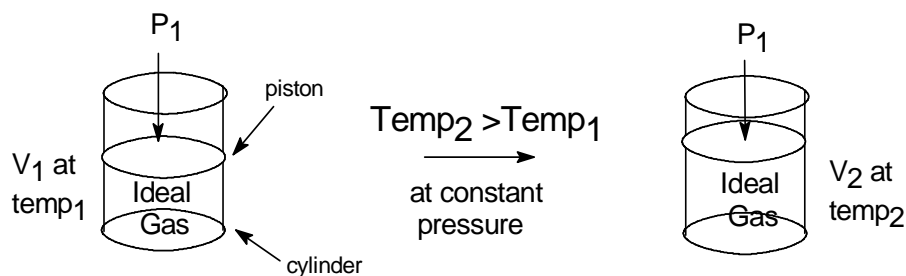
and $V_1 = 12.3 \text{ L}$, $P_1 = 400 \text{ torr}$, $V_2 = ?$, and $P_2 = 600 \text{ torr}$. Substituting

$$P_1 V_1 = (400 \text{ torr})(12.3 \text{ L}) = (600 \text{ torr}) V_2 = P_2 V_2$$

$$V_2 = 8.20 \text{ L}$$

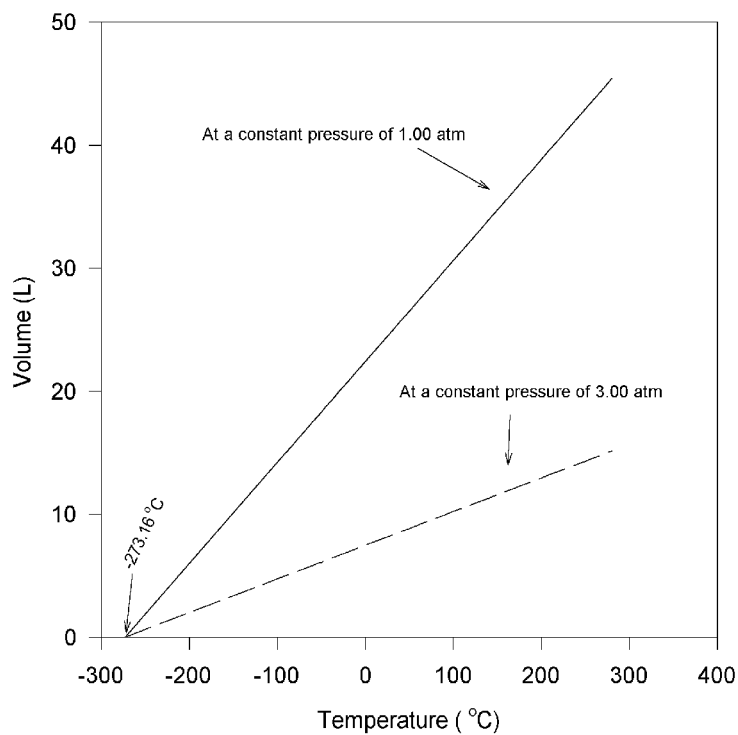
B) Charles' Law

Consider the change in volume of one mole of an ideal gas with the change in temperature when the pressure is held constant.



A plot of the volumes at various temperatures is seen below.

Plots of Volume versus Temperature of an Ideal Gas at Constant Pressures

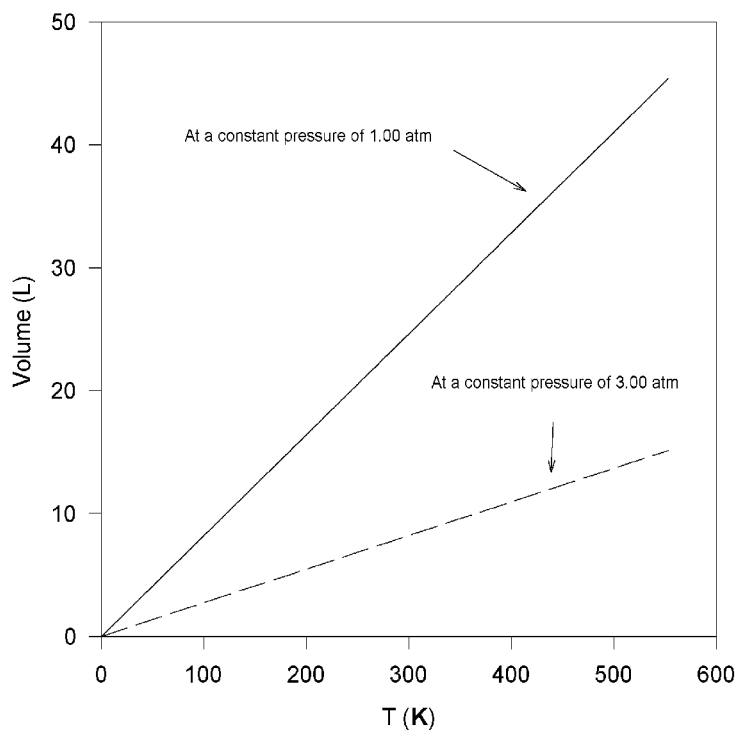


Note: The volume is a linear function of temperature (°C) with $V = 0$ at -273.16°C . If a new temperature scale called the *absolute* or *Kelvin scale* is defined,

$$T(\mathbf{K}) = \text{temp}(^{\circ}\text{C}) + 273.16$$

then the plot of V versus T yields

Plots of Volume versus Absolute Temperature of an Ideal Gas at Constant Pressures



in which the volume is directly proportional to the absolute temperature.

$$V = T \times \text{constant} \quad \text{when pressure is held fixed}$$

This equation is the mathematical expression of Charles' law - *at constant pressure the volume occupied by a fixed weight of a gas is directly proportional to the absolute temperature.*

Charles' law describes the behavior of an ideal gas and approximates the behavior of a real gas. The approximation is very poor at high pressures and low temperatures.

Example: If a 9.3 g sample of a gas occupies 12.3 L at 750 torr and 450 K, what volume will the gas occupy at the same pressure and 25°C?

Since n and P are held fixed,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant}$$

and $V_1 = 12.3 \text{ L}$, $T_1 = 450 \text{ K}$, $V_2 = ?$, and $T_2 = 25^\circ\text{C} + 273 = 298 \text{ K}$. Substituting

$$\frac{V_1}{T_1} = \frac{12.3 \text{ L}}{450 \text{ K}} = \frac{V_2}{298 \text{ K}} = \frac{V_2}{T_2}$$

$$V_2 = 8.20 \text{ L}$$

C) Avogadro's Hypothesis Revisited

At constant pressure and temperature the volume occupied by a gas is directly proportional to the number of moles of the gas.

$$V = n \times \text{constant} \quad \text{when } P \text{ and } T \text{ are held fixed}$$

Note: 1.00 mole of an ideal gas at 1.00 atm and 0°C (Standard Temperature and Pressure, STP) occupies 22.4 L.

D) Ideal Gas Law

Summary:

$$\text{Boyle's:} \quad V \propto \frac{1}{P} \quad \text{when } n \text{ and } T \text{ are held fixed}$$

$$\text{Charles':} \quad V \propto T \quad \text{when } n \text{ and } P \text{ are held fixed}$$

$$\text{Avogadro's:} \quad V \propto n \quad \text{when } P \text{ and } T \text{ are held fixed}$$

$$\text{Summary:} \quad V \propto \frac{1}{P}(T)(n)$$

Replace \propto with = and the proportionality constant R.

$$\text{Ideal Gas Law:} \quad PV = nRT$$

where R is called the *ideal gas constant*.

Example: Evaluate R if 1.00 mole of an ideal gas occupies 22.4 L at 1.00 atm and 0°C.

Given: P = 1.00 atm, V = 22.4 L, n = 1.00 mole, and T = 0°C + 273 = 273 K

$$R = \frac{PV}{nT} = \frac{(1.00 \text{ atm})(22.4 \text{ L})}{(1.00 \text{ mole})(273 \text{ K})} = 0.0821 \frac{\text{L-atm}}{\text{mole-K}}$$

R expressed in other units.

$$R = 0.0821 \frac{\text{L-atm}}{\text{mole-K}} \quad \text{or} \quad 8.314 \frac{\text{J}}{\text{mole-K}} \quad \text{or} \quad 1.987 \frac{\text{cal}}{\text{mole-K}}$$

where J (joules) and cal (calories) are units of energy.

Example: If 1.00 g of an unknown gas occupies 1.575 L at 700 torr and 27°C, what is the MW of the gas?

Unknown: MW of the gas

Knowns: wt of gas = 1.00 g; V = 1.575 L; P = 700 torr/(760 torr/atm) = 0.921 atm; T = 27°C + 273 = 300 K

Concepts: PV = nRT and MW = wt/mole = wt/n

Relationship: $PV = nRT = \frac{wt}{MW} RT$

Rearranging

$$MW = \frac{(wt)RT}{PV} = \frac{(1.00\text{ g})(0.0821\frac{\text{L}\cdot\text{atm}}{\text{mole}\cdot\text{K}})(300\text{ K})}{(0.921\text{ atm})(1.575\text{ L})} = 17.0\frac{\text{g}}{\text{mole}}$$

The density of a substance is defined as

$$d = \frac{wt}{\text{volume}}$$

For a gas the units of density are g/L.

Example: Calculate the density of a gas (MW = 78.1 g/mole) at 740 torr and 98°C.

Unknown: density (d) of the gas

Knowns: MW of the gas = 78.1 g/mole; P = (740 torr)/(760 torr/atm) = 0.974 atm; T = 98°C + 273 = 371 K

Concepts: PV = nRT; density = d = wt/volume

Relationship: $PV = nRT = \frac{wt}{MW} RT$

Rearranging

$$\frac{wt}{V} = \frac{(MW)P}{RT} = \frac{(78.1\frac{\text{g}}{\text{mole}})(0.974\text{ atm})}{(0.0821\frac{\text{L}\cdot\text{atm}}{\text{mole}\cdot\text{K}})(371\text{ K})} = d$$

$$d = 2.50\frac{\text{g}}{\text{L}}$$

E) Dalton's Law of Partial Pressure

The total pressure exerted by a mixture of gases is the sum of the *partial pressures* of the individual gases. The *partial pressure* of a gas is the pressure that the gas would exert if it were alone in the container at the same temperature.

$$P_T = P_A + P_B + P_C$$

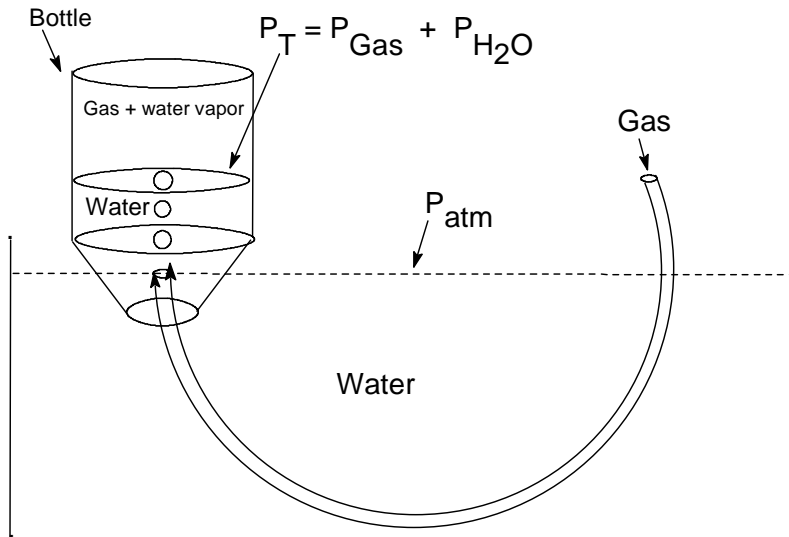
\uparrow Total Pressure \uparrow Partial Pressure of Gas A \uparrow Partial Pressure of Gas B \uparrow Partial Pressure of Gas C

Assuming ideal gas behavior

$$P_T = P_A + P_B + P_C = n_A \left[\frac{RT}{V} \right] + n_B \left[\frac{RT}{V} \right] + n_C \left[\frac{RT}{V} \right]$$

$$P_T = (n_A + n_B + n_C) \left[\frac{RT}{V} \right]$$

Collection of a gas over water



When the water level inside the bottle equals the water level outside the bottle, then

$$P_{atm} = P_T = P_{Gas} + P_{H_2O}$$

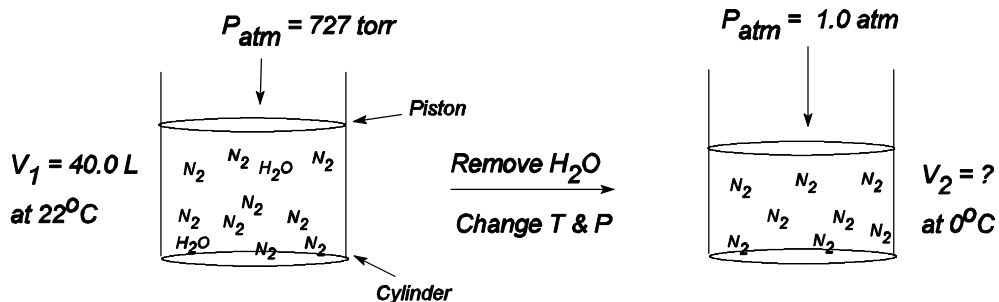
where P_{atm} is the atmospheric pressure, P_T is the total pressure of the gases above the water inside the bottle, P_{Gas} is the partial pressure of the collected gas, and P_{H_2O} is the vapor pressure of water.

Example: A 40.0 L sample of N_2 is collected over water at $22^\circ C$ and an atmospheric pressure of 727 torr. Calculate the volume that the *dry* N_2 will occupy at 1.00 atm and $0^\circ C$. The vapor pressure of water is 20 torr at $22^\circ C$.

Unknown: $V_2 =$ volume of the dry N_2 at 1.00 atm and $0^\circ C$

Knowns: $P_{atm} = 727$ torr, $V_1 = 40.0$ L, $temp_1 = 22^\circ C$, $P_{H_2O} = 20$ torr at $22^\circ C$, and **moles of N_2 are constant**

Concepts: Ideal gas law ($PV = nRT$), Dalton's law of partial pressures



Relationships:

$$P_{atm} = (P_{N_2})_1 + P_{H_2O} \quad ; \quad n_{N_2} = \frac{(P_{N_2})_1 V_1}{RT_1} \quad ; \quad V_2 = \frac{n_{N_2} RT_2}{(P_{N_2})_2}$$

Substituting the center equation for n_{N_2} in the equation on the right

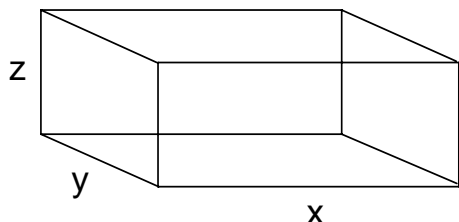
$$V_2 = \left[\frac{(P_{N_2})_1 V_1}{RT_1} \right] \left[\frac{RT_2}{(P_{N_2})_2} \right] = \frac{(P_{N_2})_1 V_1 T_2}{T_1 (P_{N_2})_2} = \frac{(P_{atm} - P_{H_2O}) V_1 T_2}{T_1 (P_{N_2})_2}$$

$$V_2 = \frac{(P_{atm} - P_{H_2O}) V_1 T_2}{T_1 (P_{N_2})_2} = \frac{(727 \text{ torr} - 20 \text{ torr})(40.0 \text{ L})(273 \text{ K})}{(295 \text{ K})(760 \text{ torr})} = 34.4 \text{ L}$$

F) Kinetic Theory of Gases

An *ideal gas* is characterized as a gas that consists of molecules with mass and velocity but no volume. These molecules exhibit no attractive or repulsive forces among themselves or with other matter.

Consider a collection of N identical ideal gas molecules in a container with volume V .



$V = xyz =$ volume of the box
 $N =$ number of identical molecules
 $m =$ mass of one molecule
 $c_i =$ velocity of the i^{th} molecule

N molecules colliding with the yz wall exert a force

$$force = \frac{mN\overline{c^2}}{3x}$$

where

$$\overline{c^2} = \text{mean square velocity} = \frac{c_1^2 + c_2^2 + c_3^2 + \dots + c_i^2 + \dots + c_N^2}{N}$$

(Note: A bar over a symbol, *symbol*, indicates the mean or average value.)

Pressure is force/area

$$P = \frac{force}{area} = \frac{mN\overline{c^2}}{3xyz} = \frac{mN\overline{c^2}}{3V}$$

and rearranging

$$PV = \frac{mN\overline{c^2}}{3} \quad (1)$$

If N is Avogadro's Number, N_A , then $n = 1$ and $PV = RT$. Substituting RT for PV and N_A for N in eq 1.

$$RT = \frac{mN_A \overline{c^2}}{3} \quad (2)$$

Note: If T is increased, then $\overline{c^2}$ will increase and the volume V of the container must increase if P is to remain constant.

G) Graham's Law of Effusion

Rearranging eq 2

$$\overline{c^2} = \frac{3RT}{mN_A} = \frac{3RT}{MW} \quad (3)$$

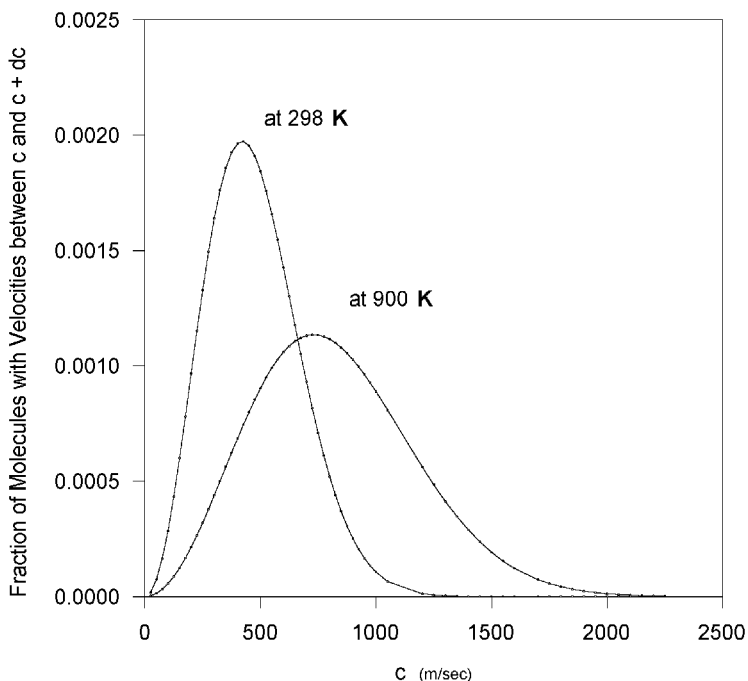
The square root of eq 3 yields the *root mean square velocity*

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{MW}}$$

The *mean velocity* is

$$\bar{c} = \sqrt{\frac{8RT}{\pi MW}}$$

Distribution of Molecular Velocities among Avogadro's Number of N₂ Molecules



Note: c_{mp} is the most probable velocity

Graham's Law: The rate, r , at which a gas effuses through a very small hole is directly proportional to the mean velocity, \bar{c} , of the gas. When the rate of effusion, r_A , of gas A and the rate of effusion, r_B , are measured under the same conditions, then

$$\frac{r_A}{r_B} = \frac{\bar{c}_A}{\bar{c}_B} = \sqrt{\frac{MW_B}{MW_A}}$$

H) Kinetic Energy of Translation

The average kinetic energy of translation per molecule in a collection of Avogadro's Number of molecules is

$$\text{Average Kinetic Energy per Molecule} = \bar{\varepsilon} = \frac{m\overline{c^2}}{2}$$

The kinetic energy of translation for Avogadro's Number of molecules is

$$\text{Kinetic Energy of Translation per Mole} = E_T = N_A \bar{\varepsilon} = \frac{mN_A \overline{c^2}}{2} \quad (4)$$

Substituting $3RT$ for $mN_A \overline{c^2}$ (eq 2) into eq 4 gives

$$E_T = \frac{3RT}{2}$$

The average kinetic energy of translation per molecule is

$$\bar{\varepsilon} = \frac{E_T}{N_A} = \frac{3RT}{2N_A} = \frac{3kT}{2}$$

where k , call Boltzmann's constant, is the ideal gas constant per molecule.

$$k = 1.38 \cdot 10^{-23} \frac{J}{\text{molecule-K}}$$

I) van der Waals Equation

Example: A 1.00 mole sample of argon exerts a pressure of 64.02 atm in a 0.250 L container at 223 K (-50°C). Calculate the pressure, P_{ideal} , assuming ideal gas behavior.

$$P_{\text{ideal}} = \frac{n_{\text{Ar}} RT}{V} = \frac{(1.00 \text{ mole})(0.0821 \frac{\text{L-atm}}{\text{mole-K}})(223 \text{ K})}{(0.250 \text{ L})} = 73.2 \text{ atm}$$

Note: The pressure calculated with the ideal gas law (73.2 atm) is 14% larger than the true (measured) pressure (64.02 atm).

We need an equation that is similar to the ideal gas law but gives a better approximation of the behavior of a real gas than $PV = nRT$. To derive such an equation, consider how a real gas differs from an ideal gas.

1) Real gas molecules have attractive forces.

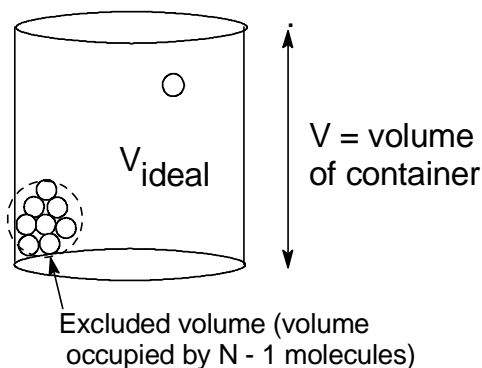
Since real gas molecules have intermolecular forces of attraction, the force exerted when these molecules collide with the wall is less than the force exerted by ideal gas molecules. The intermolecular force of attraction increases with a decrease in distance between neighboring molecules and thus pressure exerted by the real gas decrease as the volume decreases.

$$P_{ideal} > P$$

$$P_{ideal} = P + \frac{a}{V^2} \quad (5)$$

where a/V^2 is the correction for the intermolecular forces of attraction and a is a constant called the van der Waals constant. The magnitude of a depends on the nature of the gas.

2) Real gas molecules have volume.



V_{ideal} is the volume available to a gas molecule. For an ideal gas $V_{ideal} = V$. For a real gas

$$V_{ideal} < V$$

$$V_{ideal} = V - b \quad (6)$$

where b is call a van der Waals constant and is a correction for the excluded volume. The magnitude of b is dependent on the nature of the gas.

For 1.00 mole of a gas

$$P_{ideal} V_{ideal} = R T \quad (7)$$

Substituting eqs 5 and 6 into eq 7

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

For n moles of a gas

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

This equation is called the *van der Waals equation*.

Example: Use the van der Waals equation to calculate the pressure of the Argon gas in the previous example. The van der Waals constants for Ar are $a = 1.35 \text{ atm}\cdot\text{L}^2/\text{mole}^2$ and $b = 0.0322 \text{ L/mole}$.

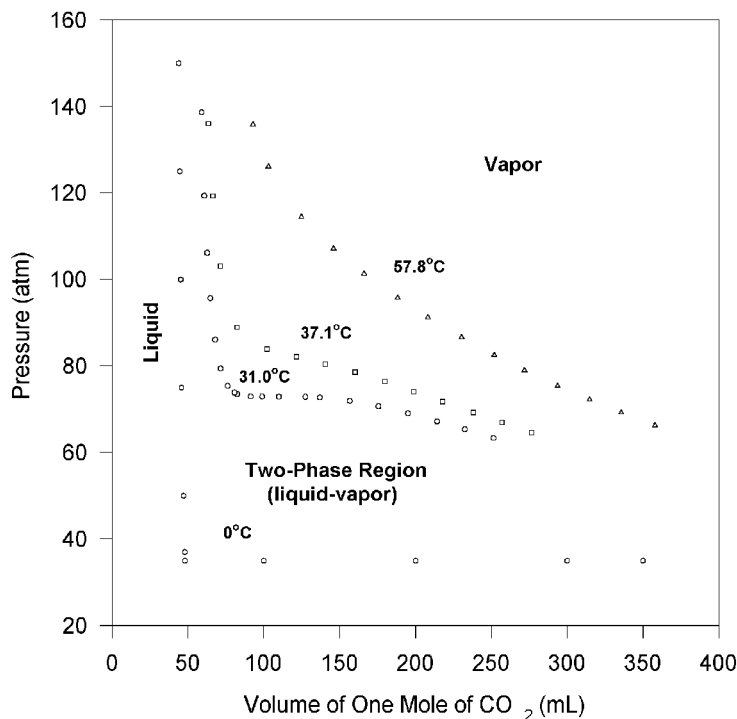
$$P = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2} = \frac{(1.00 \text{ mole})(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mole}\cdot\text{K}})(223 \text{ K})}{(0.250 \text{ L}) - (1.00 \text{ mole})(0.0322 \frac{\text{L}}{\text{mole}})} - \frac{(1.00 \text{ mole})^2 (1.35 \frac{\text{atm}\cdot\text{L}^2}{\text{mole}^2})}{(0.250 \text{ L})^2}$$

$$P = 62.5 \text{ atm}$$

I) Pressure-Volume Plots at Constant Temperature

1) Real Gas: CO₂

Isotherms - Plots of Pressure versus Volume at Constant Temperature - of CO₂



As the pressure exerted on one mole of CO₂ at 31.0°C increases, the volume of the gas decreases (see the isotherm at 31.0°C). When the pressure reaches 72.9 atm, the volume

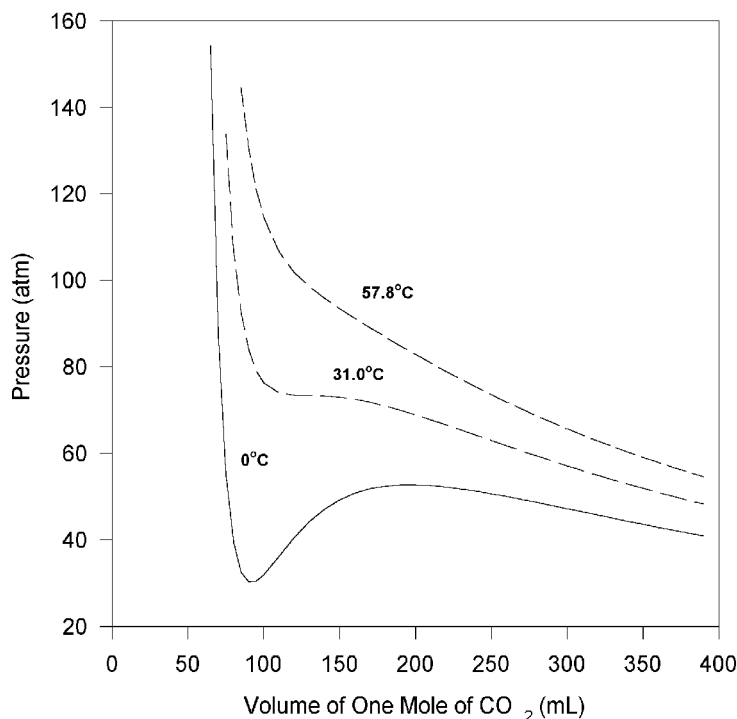
of the gas will be 94.2 mL and liquefaction will occur. The 31.0°C temperature required for liquefaction is called the critical temperature of CO₂. *The critical temperature is the temperature above which liquefaction of the gas is not possible regardless of the magnitude of the pressure.* Additional increases in the pressure at 31.0°C will produce only small decreases in the volume of the **liquid** CO₂.

Note: The isotherm at 37.1°C does not have the hyperbolic character indicative of an ideal gas and thus CO₂ does not exhibit ideal gas behavior at this temperature.

2) van der Waals Gas

The pressures of one mole of CO₂ at 0, 31.0, and 57.8°C and at volumes of 55 to 390 mL were calculated with van der Waals equation. A plot of these pressures as a function of volume is found below.

Isotherms of CO₂ : Pressures Calculated with van der Waals Equation



Note: The van der Waals equation gives a good approximation of the behavior of CO₂ at 31.0 and 57.8°C.