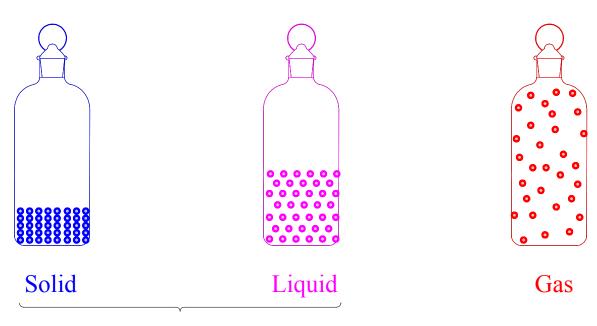
States of Matter

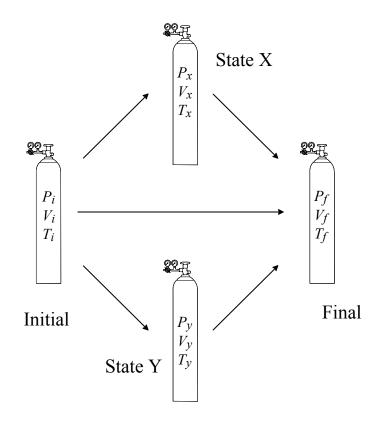


State Functions

The state of a certain amount of gas is specified by three inter-related variables, called **state functions**:

P - Pressure V - Volume T - Temperature

L Values of *P*, *V*, and *T* depend on the state of the gas, regardless of how the state was achieved.



- L For a given sample, specifying two variables fixes the third.
- L Relationships between P, V, and T are equations of state, commonly called the gas laws.

Pressure

L Pressure is defined as a force per unit area:

$$P = F/A = ma/A$$

where F is force, A is area, m is mass, and a is acceleration.

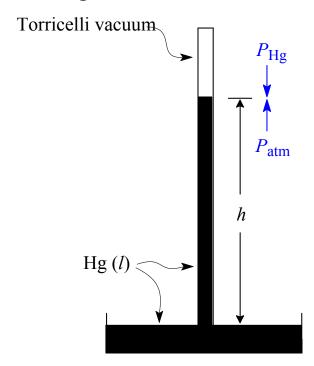
L The units of pressure are a result of this defining equation:

$$P_{\rm cgs} = (g)({\rm cm\cdot s^{-2}})/{\rm cm^2} = {\rm dyne/cm^2}$$

$$P_{\rm SI} = (\text{kg})(\text{m}\cdot\text{s}^{-2})/\text{m}^2 = \text{newton/m}^2 = \text{pascal (Pa)}$$

Barometer

Evangelista Torricelli - 1643



L Liquid mercury in the tube falls to a level at which its downward pressure equals the counter-balancing pressure exerted by the air on the surface of the mercury pool.

$$P_{\rm atm} = P_{\rm Hg}$$

L The pressure of the mercury column is the product of the acceleration of gravity (g), the density of the mercury (d), and the height of the column (h):

$$P_{\rm Hg} = gdh = P_{\rm atm}$$

L Both g and d are constants, so

$$P_{\text{atm}} \% h$$

Pressure Units Related to the Height of a Mercury Column

• The height of the mercury column is usually measured in millimeters, abbreviated

mm Hg

• A pressure equivalent to a millimeter of mercury is called a **torr** (in honor of Torricelli):

1 mm Hg / 1 torr

• Standard atomospheric pressure (abbreviated atm) is the barometric pressure that sustains a mercury column of exactly 760 mm:

• Nowadays, the standard atmosphere has been redefined in terms of the pascal:

• The SI unit comparable to atm is the bar = 10^5 Pa:

1 atm / 1.01325 bar (exactly)

Manometers

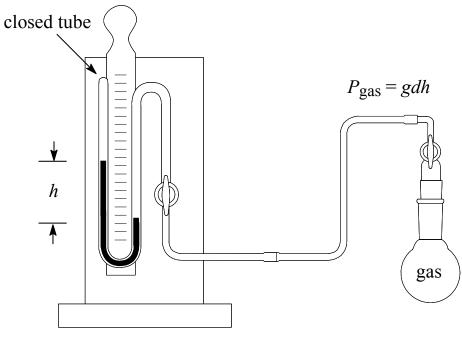
- Pressures of gas samples are routinely measured with a modification of the barometer, called a **manometer**.
 - O Closed-ended manometers measure gas-sample pressure independent of atmospheric conditions.

$$P_{\rm gas} = gdh$$

O Open-ended manometers measure gas-sample pressure relative to the room (ambient) pressure, which must be measured.

$$P_{\rm gas} = P_{\rm atm} \pm gdh$$

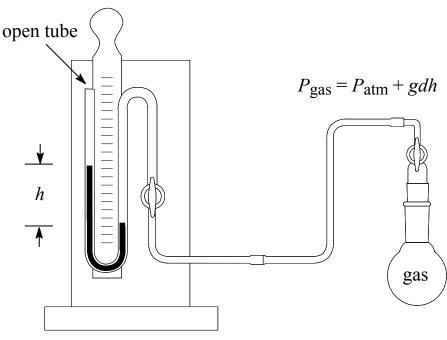
Closed-Ended Manometer



Closed-Ended Manometer

L Difference in height between the two sides indicates the sample gas pressure.

Open-Ended Manometer

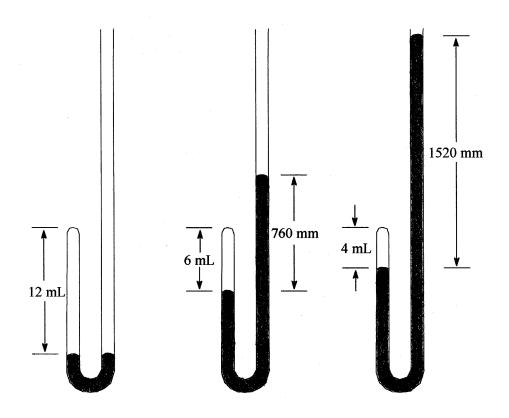


Open-Ended Manometer

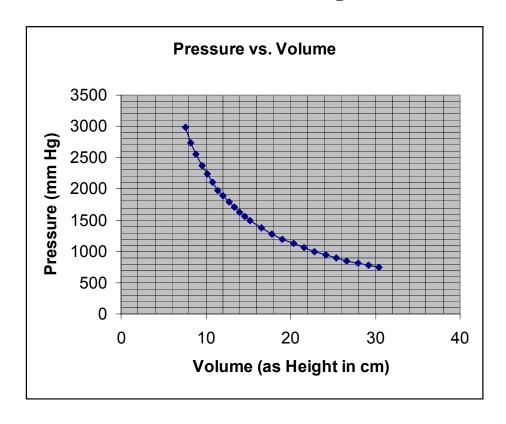
- L If the height of the outer arm is higher than the inner arm, $P_{\text{gas}} > P_{\text{atm}}$ and $P_{\text{gas}} = P_{\text{atm}} + gdh$.
- L If the height of the inner arm is higher than the outer arm, $P_{\text{gas}} < P_{\text{atm}}$ and $P_{\text{gas}} = P_{\text{atm}} gdh$.

Robert Boyle's Pressure-Volume Experiments 1662

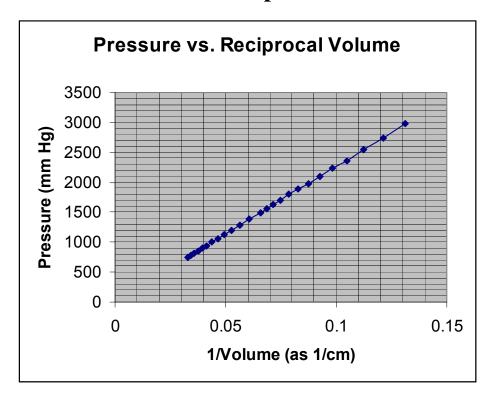
$$P_1 = P_{\text{atm}} = 760 \text{ torr}$$
 $P_2 = 1520 \text{ torr}$ $P_3 = 2280 \text{ torr}$



Historical Data from Boyle's Pressure vs. Volume Experiments



Boyle's Data Replotted as Pressure vs. Reciprocal Volume



Boyle's Law

L For a fixed amount of gas at constant temperature, volume is inversely proportional to pressure.

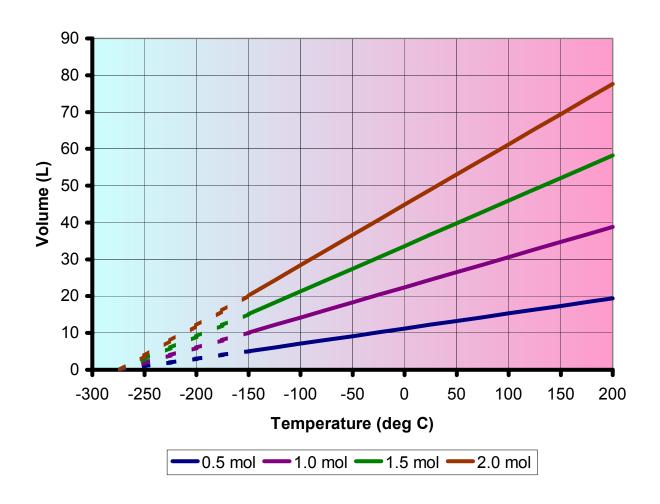
$$V \% 1/P$$

$$V = b/P \qquad VP = b \qquad b = f(n, T)$$

$$P_1V_1 = P_2V_2$$

Jacques Charles' Temperature-Volume Experiments 1787

Volume vs. Temperature for Various Amounts of Gas at 1 atm



Charles' Law

L For a fixed amount of gas at constant pressure, volume is proportional to *absolute* temperature.

$$V = cT$$
 $c = f(n, P)$

K Note: Temperature must be in Kelvin (K)!

$$\frac{V_1}{T_1}$$
 $\frac{V_2}{T_2}$

Combined Gas Law

L Combining Boyle's and Charles' Laws for a fixed amount of gas:

$$V \% \frac{T}{P}$$
 $Y V k \left(\frac{T}{P}\right)$

$$\frac{PV}{T}$$
 ' k k ' $f(n)$

$$\frac{P_1V_1}{T_1} - \frac{P_2V_2}{T_2}$$

Combined Gas Law Equation to Ideal Gas Equation of State (Ideal Gas Law Equation)

From the Combined Gas Law:

$$\frac{PV}{T}$$
 ' k k ' $f(n)$

If k % n, then we can write an equation for k by inserting a proportionality constant, which we will call R:

$$k = nR$$

Substituting into PV/T = k gives PV/T = nR, or

$$PV = nRT$$

- L PV = nRT is the **equation of state of an ideal gas**, also called the **ideal gas law** equation.
- L PV = nRT is the most important of all the fundamental gas law equations.

Ideal Gas Law

$$PV = nRT$$

$R = 0.08206 \, \text{L@tm/K@nol}$

- L R, the **gas law constant**, is a fundamental constant of the Universe and appears in many important physical equations, in addition to PV = nRT.
- L The value of *R* depends upon the units used.

Units	Numerical value
L@tm/K@nol	0.08206
J/K@nol	8.314
cal/K·mol	1.987
L·torr/K·mol	62.36

t R values we will use are in blue.

Variations on PV = nRT

Let m = mass of sample and M = molecular weight. Then the number of moles of gas is

$$n = m/M$$

Substituting into PV = nRT gives

$$PV \cdot \left(\frac{m}{M}\right) RT \quad Y \quad M \cdot \frac{mRT}{PV}$$

Let d = density = m/V:

$$M \cdot \left(\frac{m}{V}\right) \frac{RT}{P} \cdot \frac{dRT}{P}$$

$$Y d \cdot \frac{PM}{RT}$$

Law of Amontons

Guillaume Amontons (Fr., 1663 - 1705), c. 1703

L For a sample of gas in a fixed volume, the pressure is directly proportional to the absolute temperature.

Let the volume for a certain gas sample be fixed; i.e., V, n, and R are constant. Then from PV = nRT, gathering the variables on the left and the constants on the right

$$\frac{T}{P}$$
 $\frac{V}{nR}$ a a $f(n,V)$

$$\frac{T_1}{P_1}$$
 $\frac{T_2}{P_2}$

Gay-Lussac's Law of Combining Gas Volumes

Joseph Louis Gay-Lussac (Fr., 1778-1850), 1808

L In reactions between gases at constant temperature and pressure, the volumes that react are in the ratios of small whole numbers.

$$H_2(g) + N_2(g) - 6 NH_3(g)$$

3 vol. 1 vol. 2vol.

$$3H_2(g) + N_2(g) 6 2NH_3(g)$$

Gay-Lussac's Law of Combining Gas Volumes from PV = nRT

If *P* and *T* are held constant, then from PV = nRT:

$$V' n \left(\frac{RT}{P}\right)$$
 Y $V' gn g' f(P,T)$

Avogadro's Hypothesis

Amedeo Avogadro (It., 1776 - 1856), 1811

L Equal volumes of all gases at the same temperature and pressure contain the same number of molecules.

If P and T are held constant, then from PV = nRT:

$$V' n \left(\frac{RT}{P}\right)$$
 Y $V' gn g' f(P,T)$

Standard Temperature (0 °C) and Pressure (1.00 atm) (STP)

At STP one mole of ideal gas occupies 22.4 L called the *molar volume* of an ideal gas at STP.

1 mol = 22.4 L at STP

Gas Law Summary PV = nRT

$$PV = nRT$$

$$\overline{V}$$
, P variable n , T constant

$$P_1V_1 = P_2V_2$$

$$PV = nRT$$

$$V$$
, T variable n , P constant

$$\frac{V_1}{T_1} \cdot \frac{V_2}{T_2}$$

Amontons:

$$PV = nRT$$

$$P, T$$
 variable

$$P$$
, T variable n , V constant

$$\frac{T_1}{P_1}$$
 $\frac{T_2}{P_2}$

$$PV = nRT$$

$$\frac{n_1}{V_1} - \frac{n_2}{V_2}$$

Other:

$$P$$
, n variable T , V constant

$$PV = nRT$$

$$\frac{n_1}{P_1}$$
 $\frac{n_2}{P_2}$

General:

$$PV = nRT$$

$$P, V, T$$
 variable n constant

$$\frac{T_1}{T_1}$$

$$\frac{P_1V_1}{T_1} - \frac{P_2V_2}{T_2}$$