States of Matter

Solid

Liquid

Gas

Condensed States
State Functions

The state of a certain amount of gas is specified by three inter-related variables, called **state functions**:  
\[ P - \text{Pressure} \quad V - \text{Volume} \quad T - \text{Temperature} \]

- Values of \( P, V, \) and \( T \) depend on the state of the gas, regardless of how the state was achieved.

- For a given sample, specifying two variables fixes the third.

- Relationships between \( P, V, \) and \( T \) are **equations of state**, commonly called the **gas laws**.
Pressure

Pressure is defined as a force per unit area:

\[ P = \frac{F}{A} = \frac{ma}{A} \]

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

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

\[ P_{\text{cgs}} = \frac{(g)(\text{cm} \cdot \text{s}^{-2})}{\text{cm}^2} = \text{dyne/cm}^2 \]

\[ P_{\text{SI}} = \frac{(kg)(\text{m} \cdot \text{s}^{-2})}{\text{m}^2} = \text{newton/m}^2 = \text{pascal (Pa)} \]
Barometer
Evangelista Torricelli - 1643

Torricelli vacuum

\[ P_{\text{atm}} = P_{\text{Hg}} \]

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.

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 \((h)\):

\[ P_{\text{Hg}} = gdh = P_{\text{atm}} \]

L Both \(g\) and \(d\) are constants, so

\[ P_{\text{atm}} \propto h \]
Pressure Units
Related to the Height
of a Mercury Column

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

\[ \text{mm Hg} \]

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

\[ 1 \text{ mm Hg} / 1 \text{ torr} \]

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

\[ 1 \text{ atm} / 760 \text{ mm Hg} / 760 \text{ torr} \]

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

\[ 1 \text{ atm} / 101,325 \text{ Pa (exactly)} \]

- The SI unit comparable to atm is the bar \( = 10^5 \) Pa:

\[ 1 \text{ atm} / 1.01325 \text{ bar (exactly)} \]
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.

\[ P_{\text{gas}} = gdh \]

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

\[ P_{\text{gas}} = P_{\text{atm}} \pm gdh \]
Closed-Ended Manometer

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

\[ P_{\text{gas}} = gh \]
If the height of the outer arm is higher than the inner arm, \( P_{\text{gas}} > P_{\text{atm}} \) and \( P_{\text{gas}} = P_{\text{atm}} + gh \).

If the height of the inner arm is higher than the outer arm, \( P_{\text{gas}} < P_{\text{atm}} \) and \( P_{\text{gas}} = P_{\text{atm}} - gh \).
Robert Boyle’s Pressure-Volume Experiments

1662

\[ P_1 = P_{\text{atm}} = 760 \text{ torr} \quad P_2 = 1520 \text{ torr} \quad P_3 = 2280 \text{ torr} \]
Historical Data from Boyle's Pressure vs. Volume Experiments
Boyle's Data Replotted as Pressure vs. Reciprocal Volume
Boyle's Law

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

\[ V \propto 1/P \]

\[ V = b/P \]

\[ VP = b \]

\[ b = f(n, T) \]

\[ P_1V_1 = P_2V_2 \]
Jacques Charles’ Temperature-Volume Experiments
1787

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

Temperature (deg C) vs. Volume (L) for 0.5 mol, 1.0 mol, 1.5 mol, and 2.0 mol gas.
Charles' Law

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

\[ V = cT \quad c = f(n, P) \]

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

\[ \frac{V_1}{T_1}, \quad \frac{V_2}{T_2} \]
Combined Gas Law

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

\[ V \% \frac{T}{P} \quad \gamma \quad V' \cdot k \left( \frac{T}{P} \right) \]

\[ \frac{PV}{T} \quad k \quad k' \quad f(n) \]

\[ \frac{P_1V_1}{T_1}, \quad \frac{P_2V_2}{T_2} \]
Combined Gas Law Equation
to
Ideal Gas Equation of State
(Ideal Gas Law Equation)

From the Combined Gas Law:

\[
\frac{PV}{T} = k' \cdot f(n)
\]

If \( k \propto n \), 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

\[
PV = nRT
\]

\( PV = nRT \) is the equation of state of an ideal gas, also called the ideal gas law equation.

\( PV = nRT \) is the most important of all the fundamental gas law equations.
Ideal Gas Law

\[ PV = nRT \]

\[ R = 0.08206 \text{ L@m/K@mol} \]

\[^L\] \( R \), 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.

<table>
<thead>
<tr>
<th>Units</th>
<th>Numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>L@m/K@mol</td>
<td>0.08206</td>
</tr>
<tr>
<td>J/K@mol</td>
<td>8.314</td>
</tr>
<tr>
<td>cal/K·mol</td>
<td>1.987</td>
</tr>
<tr>
<td>L·torr/K·mol</td>
<td>62.36</td>
</tr>
</tbody>
</table>

\[^t\] \( R \) 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

$$n = \frac{m}{M}$$

Substituting into $PV = nRT$ gives

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

Let $d =$ density $= \frac{m}{V}$:

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

$$\gamma \quad d \cdot \frac{PM}{RT}$$
**Law of Amontons**  
Guillaume Amontons (Fr., 1663 - 1705), c. 1703

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., $V, n, \text{ and } R$ are constant. Then from $PV = nRT$, gathering the variables on the left and the constants on the right

$$\frac{T}{P} \cdot \frac{V}{nR} \cdot a \cdot a' = f(n, V)$$

$$\frac{T_1}{P_1}, \frac{T_2}{P_2}$$
Gay-Lussac's Law of Combining Gas Volumes
Joseph Louis Gay-Lussac (Fr., 1778-1850), 1808

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

\[
\begin{align*}
3 \text{vol.} & \quad + \quad 1 \text{vol.} & \quad = \quad 2 \text{vol.} \\
3 \text{H}_2(g) & \quad + \quad \text{N}_2(g) & \quad = \quad 2 \text{NH}_3(g)
\end{align*}
\]
Gay-Lussac's
Law of Combining Gas Volumes
from $PV = nRT$

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

$$V' = n\left(\frac{RT}{P}\right) \quad \gamma \quad V' = gn \quad g' = f(P,T)$$
Avogadro's Hypothesis
Amedeo Avogadro (It., 1776 - 1856), 1811

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 $PV = nRT$:

$$V' = n\left(\frac{RT}{P}\right) \quad \text{and} \quad V' = gn \quad g' = f(P,T)$$
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.

\[ 1 \text{ mol} = 22.4 \text{ L at STP} \]
## Gas Law Summary

\[ PV = nRT \]

### Boyle:
- \( V, P \) variable \( n, T \) constant
- \[ PV = nRT \]
- \( P_1 V_1 = P_2 V_2 \)

### Charles:
- \( V, T \) variable \( n, P \) constant
- \[ PV = nRT \]
- \( \frac{V_1}{T_1}, \frac{V_2}{T_2} \)

### Amontons:
- \( P, T \) variable \( n, V \) constant
- \[ PV = nRT \]
- \( \frac{T_1}{P_1}, \frac{T_2}{P_2} \)

### Gay-Lussac & Avogadro:
- \( V, n \) variable \( P, T \) constant
- \[ PV = nRT \]
- \( \frac{n_1}{V_1}, \frac{n_2}{V_2} \)

### Other:
- \( P, n \) variable \( T, V \) constant
- \[ PV = nRT \]
- \( \frac{n_1}{P_1}, \frac{n_2}{P_2} \)

### General:
- \( P, V, T \) variable \( n \) constant
- \[ PV = nRT \]
- \( \frac{P_1 V_1}{T_1}, \frac{P_2 V_2}{T_2} \)