## 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
$\mathrm{L} \quad$ 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:

$$
P=F / A=m a / A
$$

where $F$ is force, $A$ is area, $m$ is mass, and $a$ is acceleration.
$L \quad$ The units of pressure are a result of this defining equation:

$$
\begin{gathered}
P_{\mathrm{cgs}}=(\mathrm{g})\left(\mathrm{cm} \cdot \mathrm{~s}^{-2}\right) / \mathrm{cm}^{2}=\text { dyne } / \mathrm{cm}^{2} \\
P_{\mathrm{SI}}=(\mathrm{kg})\left(\mathrm{m} \cdot \mathrm{~s}^{-2}\right) / \mathrm{m}^{2}=\text { newton } / \mathrm{m}^{2}=\text { pascal }(\mathrm{Pa})
\end{gathered}
$$



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.

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

$L$ 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 $(h)$ :

$$
P_{\mathrm{Hg}}=g d h=P_{\mathrm{atm}}
$$

$\mathrm{L} \quad$ Both $g$ and $d$ are constants, so

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

# Pressure Units <br> 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):


## $1 \mathrm{~mm} \mathrm{Hg} / 1$ torr

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

1 atm / $760 \mathrm{~mm} \mathrm{Hg} / 760$ torr

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

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

- The SI unit comparable to atm is the bar $=10^{5} \mathrm{~Pa}$ :

$$
1 \mathrm{~atm} / 1.01325 \text { bar (exactly) }
$$

## 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.

$$
P_{\mathrm{gas}}=g d h
$$

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

$$
P_{\mathrm{gas}}=P_{\mathrm{atm}} \pm g d h
$$

## 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 $P_{\text {gas }}=P_{\text {atm }}+g d h$.

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

Robert Boyle's Pressure-Volume Experiments 1662

$$
P_{1}=P_{\mathrm{atm}}=760 \text { torr } \quad P_{2}=1520 \text { torr } \quad P_{3}=2280 \text { torr }
$$



## Historical Data from Boyle's Pressure vs. Volume Experiments



## Boyle's Data Replotted as Pressure vs. Reciprocal Volume



## Boyle's Law

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

$$
\begin{gathered}
V \% 1 / P \\
V=b / P \quad V P=b \quad b=f(n, T) \\
P_{1} V_{1}=P_{2} V_{2}
\end{gathered}
$$

## 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.

$$
V=c T \quad c=f(n, P)
$$

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:

$$
\begin{aligned}
& V \% \frac{T}{P} \quad Y^{\prime} \quad k\left(\frac{T}{P}\right) \\
& \frac{P V}{T} \cdot k
\end{aligned} k^{\prime} f(n)
$$

$$
\frac{P_{1} V_{1}}{T_{1}}, \frac{P_{2} V_{2}}{T_{2}}
$$

# Combined Gas Law Equation <br> to <br> Ideal Gas Equation of State (Ideal Gas Law Equation) 

From the Combined Gas Law:

$$
\frac{P V}{T}, k \quad k^{\prime} f(n)
$$

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

$$
k=n R
$$

Substituting into $P V / T=k$ gives $P V / T=n R$, or

$$
P V=n R T
$$

$\mathrm{L} \quad P V=n R T$ is the equation of state of an ideal gas, also called the ideal gas law equation.

L $\quad P V=n R T$ is the most important of all the fundamental gas law equations.

## Ideal Gas Law

$$
\begin{gathered}
P V=n R T \\
R=0.08206 \mathrm{~L} @ \mathrm{~m} / \mathrm{K} @ \mathrm{ol}
\end{gathered}
$$

$\mathrm{L} \quad R$, the gas law constant, is a fundamental constant of the Universe and appears in many important physical equations, in addition to $P V=n R T$.
$\mathrm{L} \quad$ The value of $R$ depends upon the units used.

| Units | Numerical value |
| :--- | :--- |
| L@m/K@ol | 0.08206 |
| $\mathrm{~J} / \mathrm{K} @ o l$ | 8.314 |
| cal/K•mol | 1.987 |
| L•torr/K•mol | 62.36 |

$\mathrm{t} \quad R$ values we will use are in blue.

## Variations on $\boldsymbol{P V}=\boldsymbol{n R T}$

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

$$
n=m / M
$$

Substituting into $P V=n R T$ gives

$$
P V^{\prime}\left(\frac{m}{M}\right) R T \quad Y M^{\prime} \frac{m R T}{P V}
$$

Let $d=$ density $=m / V$ :

$$
\begin{gathered}
M^{\prime}\left(\frac{m}{V}\right) \frac{R T}{P}, \frac{d R T}{P} \\
Y d^{\prime} \frac{P M}{R T}
\end{gathered}
$$

## Law of Amontons <br> 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 $P V=n R T$, gathering the variables on the left and the constants on the right

$$
\begin{gathered}
\frac{T}{P} \cdot \frac{V}{n R} \cdot a \quad a{ }^{\prime} f(n, V) \\
\frac{T_{1}}{P_{1}} \cdot \frac{T_{2}}{P_{2}}
\end{gathered}
$$

$$
\begin{gathered}
\text { Gay-Lussac's } \\
\text { Law of Combining Gas Volumes } \\
\text { Joseph Louis Gay-Lussac (Fr., 1778-1850), } 1808
\end{gathered}
$$

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

$$
\begin{array}{cccc}
\begin{array}{ccc}
\mathrm{H}_{2}(g) & + & \mathrm{N}_{2}(g) \\
3 \text { vol. } & & 6
\end{array} \quad \mathrm{NH}_{3}(g) \\
& & & 2 \text { vol. } .
\end{array}
$$

## Gay-Lussac's <br> Law of Combining Gas Volumes from $P V=n R T$

If $P$ and $T$ are held constant, then from $P V=n R T$ :

$$
V^{\prime} n\left(\frac{R T}{P}\right) \quad Y \quad V^{\prime} \quad g n \quad g^{\prime} f(P, T)
$$

## 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 $P V=n R T$ :

$$
V^{\prime} n\left(\frac{R T}{P}\right) \quad Y \quad V^{\prime} \quad g n \quad g^{\prime} f(P, T)
$$

## Standard Temperature ( $0^{\circ} \mathrm{C}$ ) and <br> 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.

$$
1 \mathrm{~mol}=22.4 \mathrm{~L} \text { at STP }
$$

# Gas Law Summary <br> $$
P V=n R T
$$ 

Boyle: $\quad V, P$ variable $n, T$ constant

$$
P V=n R T \quad P_{1} V_{1}=P_{2} V_{2}
$$

Charles: $\quad V, T$ variable $n, P$ constant

$$
P V=n R T \quad \frac{V_{1}}{T_{1}}, \frac{V_{2}}{T_{2}}
$$

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

$$
P V=n R T \quad \frac{T_{1}}{P_{1}}, \frac{T_{2}}{P_{2}}
$$

Gay-Lussac \& Avogadro: $\quad V, n$ variable $\quad P, T$ constant

$$
P V=n R T \quad \frac{n_{1}}{V_{1}}, \frac{n_{2}}{V_{2}}
$$

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

$$
P V=n R T \quad \frac{n_{1}}{P_{1}}, \frac{n_{2}}{P_{2}}
$$

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

$$
P V=n R T \quad \frac{P_{1} V_{1}}{T_{1}}, \frac{P_{2} V_{2}}{T_{2}}
$$

