# The Gas Laws

Section 1.2 (7th and 8th editions)
Sections 1.1 and 1.2 (9th edition)

*Individual Gases*
>**Boyle's Law**
>**Charles' Law**

**Perfect (Ideal) Gas Equation**

*Mixtures of Gases*
>**Dalton's Law**
>**Mole Fractions**

Last updated: Sept. 14, 2012; minor edit slide 1

# Boyle's Law

Robert Boyle, (1627-91), who was an "experimental philosopher" in the early years of the Royal Society, made a very important contribution in developing a description of the **ideal gas** (also developed ideas about vacuum, atomic nature of matter, etc.)

In 1661, he showed that to a very good approximation that for a constant amount of gas at a fixed temperature:

$$pV = \text{constant} \qquad p \propto \frac{1}{V} , \quad V \propto \frac{1}{p}$$

The pressure of a sample is inversely proportional to its volume, and the volume of a sample is inversely proportional to pressure

# Boyle & Hooke

Boyle did thousands of experiments on air, due to the invention of an **air pump** by his assistant, **Robert Hooke**.
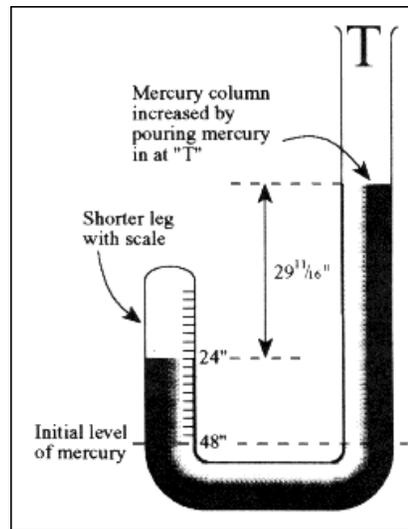


Boyle and Hooke used a **glass J-tube** to examine the properties of air.

Hg was poured into the column (at T) and air was trapped in the sealed end. When the pressure exerted by the Hg was doubled, Boyle found that the volume of trapped air would reduce by half - leading to the discovery of Boyle's (or Mariotte's) Law: $pV = k$ at constant $T$
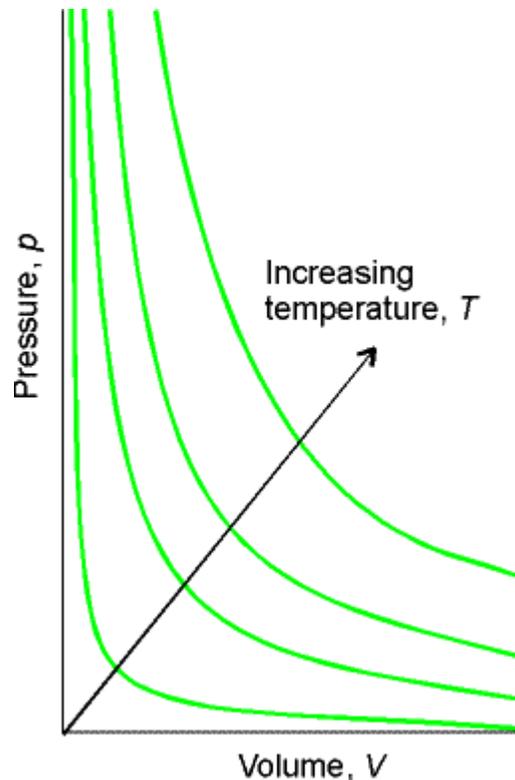
*Boyle was prolific, studying not only the "elastic properties of air," but writing extensively on the existence of vacuum, the necessity of air for burning flames, and the corpuscular nature of matter.*
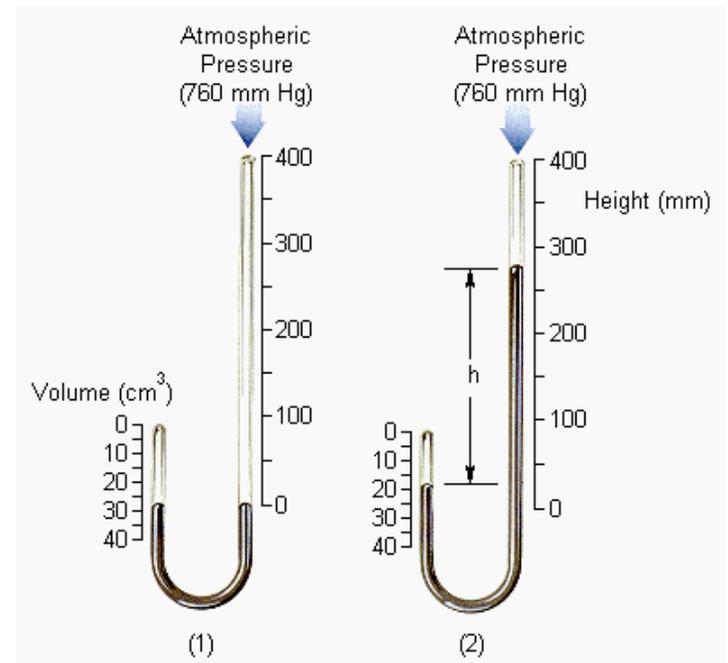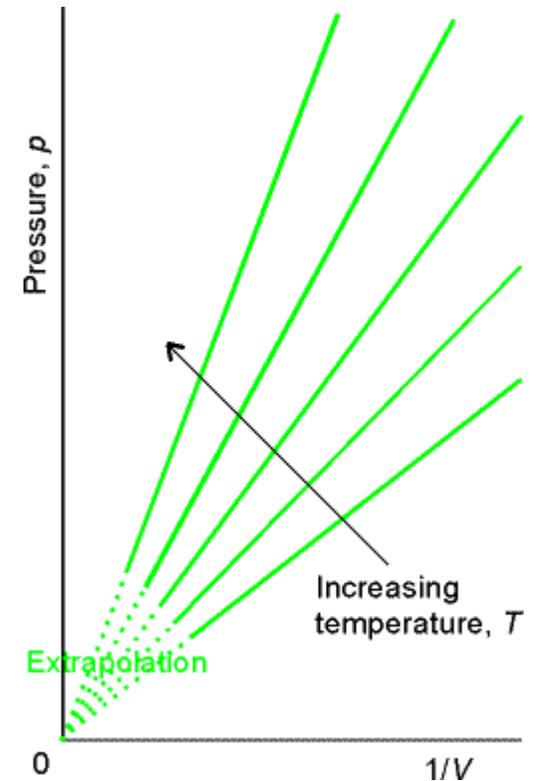
# Isotherms: *p* vs. *V*

Here are some plots depicting Boyle's Law.  Each plotted line corresponds to a different temperature, and are known as **isotherms**, as they depict the other variables of the state function at a constant temperature:

For plots of *p* vs. *V*, the isotherms are **hyperbolas** (i.e., plot of y as function of x when xy = constant)

For plots of *p* vs.  1/*V*, the isotherms are **linear**



Pressure, *p*

Increasing temperature, *T*

Volume, *V*



Pressure, *p*

Increasing temperature, *T*

Extrapolation

0

1/*V*

# Rationalizing Boyle's Law

Boyle's law strictly only applies to ideal gases at very low pressures, when there are very few molecular collisions and very few interactions between the molecules.

*How do we rationalize Boyle's law?*

Say we have an ideal gas in a container of volume $V$, and then we reduce the volume of the container by half, to $V/2$. What happens to the pressure?

The pressure doubles, since now twice as many molecules are striking the sides of the container!
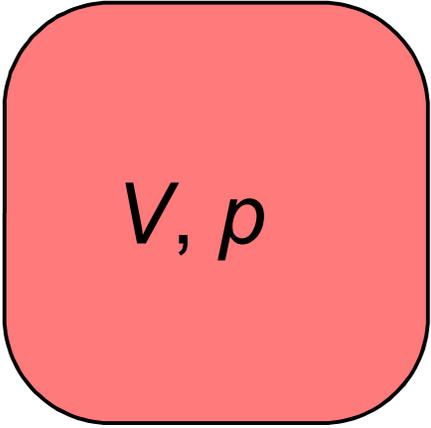
$V, p$

$V/2, 2p$

# Charles' (Gay-Lussac's) Law

Jacques Charles (1746-1823), a French physicist, constructed the first hydrogen balloons, making an ascent to over 3000 meters (1.9 mi) in 1783. His name is chiefly remembered, however, for the discovery of Charles's law, which states that the volume of a fixed quantity of gas at constant pressure is proportional to its temperature. Hence all gases, at the same pressure, expand equally for the same rise in temperature. He communicated his early results to Joseph-Louis Gay-Lussac, who published his own experimental results in 1802, six months after John Dalton had also deduced the law.

At constant pressure: $V = \text{constant} \times (\theta + 273 \ °C)$

Or, on the **thermodynamic temperature scale** devised by Kelvin:

$$V = \text{constant} \times T, \qquad p = \text{constant} \times T$$

# Effects of Changing Temperature

The volume of a gas should extrapolate to zero near -273°C.  Plots of volume and pressure as a function of temperature, at constant pressure and volume, respectively, are shown below:

Lines of constant pressure are known as **isobars**; notice how an infinitely small $V$ implies a temperature near -273°C
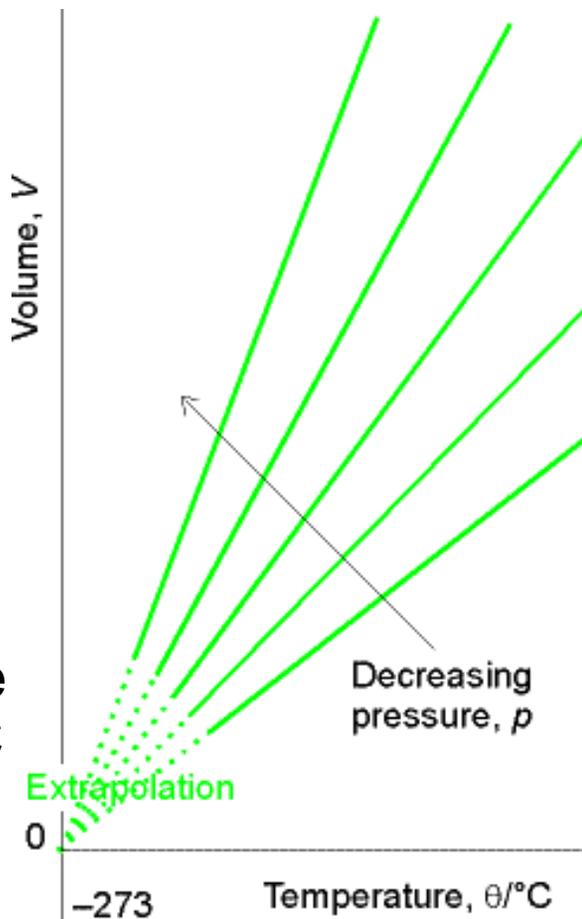
Lines of constant volume are known as **isochors**;

Pressure falls to zero as $T$ approches absolute zero (i.e., no molecular motion)
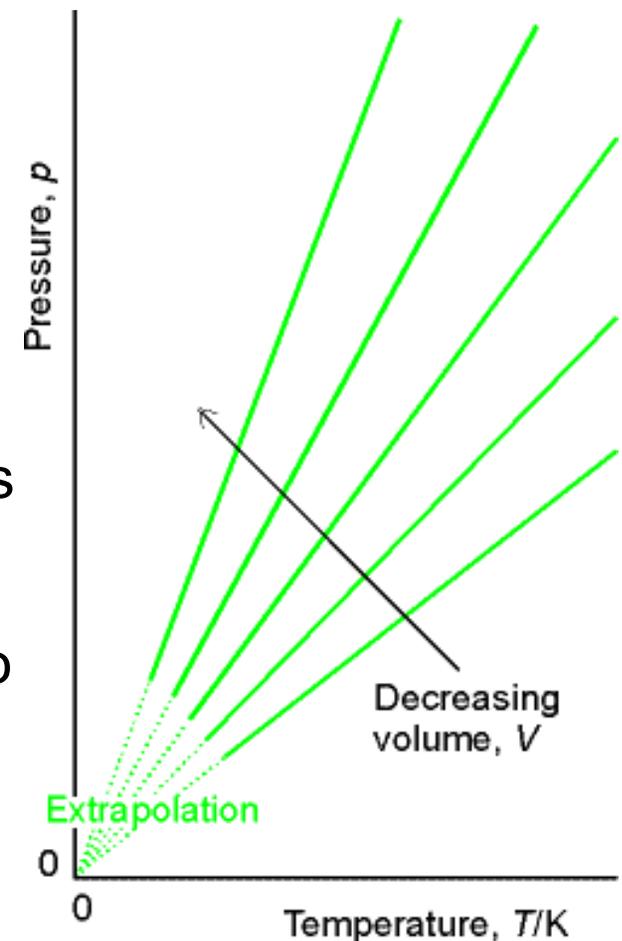
# Rationalizing Charles' Law

As the temperature is increased, the average speed of the molecules increases, thereby increasing the number and force of the collisions that the molecules have with the container's walls (again, this only really applies at **low pressures**)

In order to build up to the ideal gas law, we need to consider the relationship between volume and the number of molecules.

The **molar volume** is the volume per mole of molecules:

$$V_m = V/n$$

For any gas, the molar volume is the same, regardless of the type of gas. So, **Avogadro's principle** says that the volume of any gas is directly proportional to the number of molecules *at constant temperature and pressure*:

$$V = \text{constant} \times n$$

# Combining the Gas Laws *

**Boyle's Law:** $pV$ = constant, when $n$ and $T$ are constant
**Charles' Law:** $p \propto T$, $V \propto T$, if $n$ and either $V$ or $p$ are held constant
**Avogadro's Principle**: $V \propto n$, at constant $T$ and $p$

Single expression: $$pV \ = \ \text{constant} \times nT \ = \ nRT$$

This is the **perfect gas equation**, which becomes very accurate as the pressure decreases. This is a **limiting law**, which increases in validity as $p \rightarrow 0$. A limiting law is **strictly true at a particular limit**.

A **real gas** behaves like a **perfect gas** in the low pressure limit: at this point, the gas constant, $R$, can be determined very accurately.

**standard ambient pressure and temperature (SATP):**
$T$ = 298.15 K, $p$ = 1 bar, molar volume of gas $V_m$ = 24.790 L mol$^{-1}$
**standard temperature and pressure (STP)**
$T$ = 0 °C, $p$ = 1 atm, molar volume of gas $V_m$ = 22.414 L mol$^{-1}$

Ideal gas law simulation

# The Gas Constant

**$R$ with different units**

| | |
|---|---|
| 8.31451 | J K$^{-1}$ mol$^{-1}$ |
| 8.20578 x 10$^{-2}$ | L atm K$^{-1}$ mol$^{-1}$ |
| 8.31451 x 10$^{-2}$ | L bar K$^{-1}$ mol$^{-1}$ |
| 8.31451 | Pa m$^3$ K$^{-1}$ mol$^{-1}$ |
| 62.364 | L Torr K$^{-1}$ mol$^{-1}$ |
| 1.98722 | cal K$^{-1}$ mol$^{-1}$ |

$R$ is related to the Boltzmann constant, $k$:

$$R = k \cdot N_A$$

where
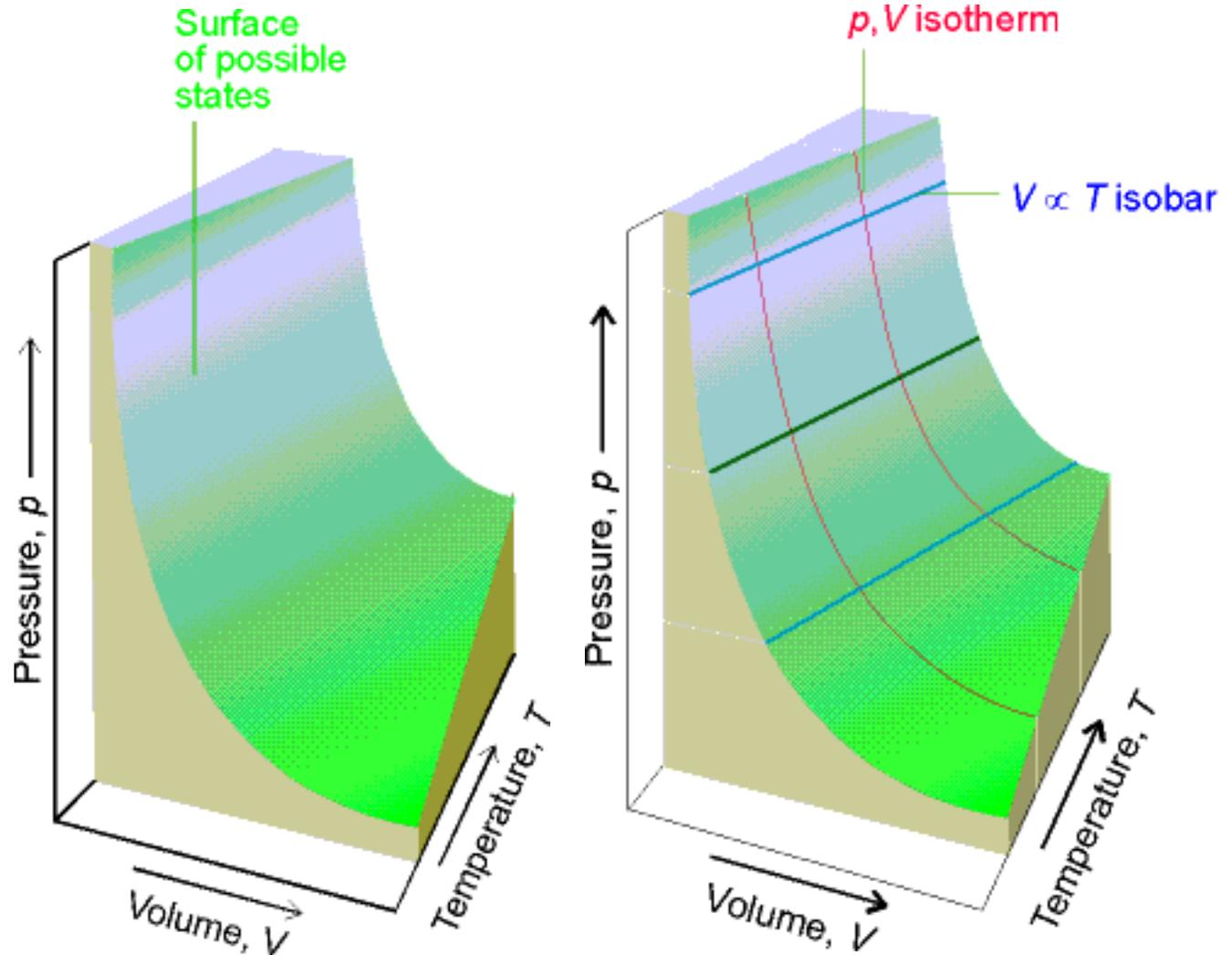
$$k = 1.3806 \times 10^{-23} \text{ J K}^{-1}$$
$$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$$

# Surface of States[†,*]

The perfect gas equation:

$$pV = nRT$$

can be represented as a **three-dimensional surface of possible states**, meaning that the gas cannot exist in states not on the surface



Surface of possible states

Pressure, p

Volume, V

Temperature, T

$p, V$ isotherm

$V \propto T$ isobar

Pressure, p

Volume, V

Temperature, T

*idealgas_2

# John Dalton

John Dalton (1766-1844), an English chemist and physicist, was the first to provide a scientific description of color blindness (1794), a condition from which he suffered and which was long called "Daltonism."

Dalton recorded over 200,000 observations of the atmosphere in his notebooks, and studied mixed gases and the expansion of gases under heat. **Dalton's Law** is still used to describe the law of partial pressures in chemistry.

This work led him to his most important theoretical contribution to chemistry, a scientifically grounded atomic theory of matter. He lectured on his discoveries in 1803, and published them at greater length in *A New System of Chemical Philosophy* in 1808.

# Mixtures of Gases

When we have a mixture of two or more gases, what contribution do each of the member gases make to the overall pressure of the system?

**Dalton's Law**: The total pressure exerted by a homogeneous mixture of gases is equal to the sum of the partial pressures of the individual gases. The **partial pressure** of a gas is the pressure it would exert if all the other gases in the mixture were absent.

If the partial pressure of gas A is $p_A$, and the partial pressure of gas B is $p_B$, etc. then the total pressures for gases in the same vessel is:

$$p_{TOT} = p_A + p_B + \ldots$$

So, for each gas $p_i$:

$$p_i = \frac{n_i RT}{V}$$

# Mole Fractions[†]

For each component of a gaseous mixture J, the mole fraction, $x_J$, is the amount of J expressed as a fraction of the total number of molecules:

$$x_J = \frac{n_J}{n}, \quad \text{where} \quad n = n_A + n_B + \ldots$$

If no J molecules are present: $\qquad x_J = 0$
If only J molecules are present: $\qquad x_J = 1$ $\qquad\qquad\qquad$ thus:

$$x_A + x_B + \ldots = 1$$

The partial pressure of gas J in a mixture is formally defined as:

$$p_J = x_J p$$

where $p$ is total pressure. It follows that for both real and perfect gases:

$$p_A + p_B + \ldots = (x_A + x_B + \ldots)p = p$$