P-V-T properties of gases

http://eps.mcgill.ca/~courses/c220/
At constant $T$ (for an ideal gas), $V \propto \frac{1}{P}$
or $PV = \text{constant}$
or $P_1V_1 = P_2V_2$

Boyle’s or Mariotte’s law (~1660) does not apply to liquids or solids where no simple relation exists between $V$ and $P$. 
About a century later (1787 & 1808), they demonstrated that, if pressure is kept constant, the volume of a sample of gas varies linearly with the temperature.

\[ T (\text{K}) = t (\degree \text{C}) + 273.15 \]

At constant \( P \) (for an ideal gas), \( V \propto T \)
or \( \frac{V_1}{T_1} = \text{constant} \)
or \( \frac{V_1}{T_1} = \frac{V_2}{T_2} \)
Combining laws (Boyle/Mariotte and Charles/Gay-Lussac) leads to:

\[ V \propto \frac{T}{P} \]

or \[ \frac{PV}{T} = \text{constant} \]

or \[ \frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \]

**Table 1-2** Data for a "model atmosphere"

(Imposing an atmosphere in which the variations with day and night, location, and so forth, are avoided and the data form a self-consistent set)

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Temperature (K)</th>
<th>Pressure (atm)</th>
<th>Density (kg m(^{-3}) = g liter(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>288</td>
<td>1.00</td>
<td>1.22</td>
</tr>
<tr>
<td>20</td>
<td>217</td>
<td>5.4 \times 10^{-2}</td>
<td>8.9 \times 10^{-2}</td>
</tr>
<tr>
<td>40</td>
<td>261</td>
<td>3.0 \times 10^{-3}</td>
<td>4.0 \times 10^{-3}</td>
</tr>
<tr>
<td>60</td>
<td>254</td>
<td>2.5 \times 10^{-4}</td>
<td>3.5 \times 10^{-4}</td>
</tr>
<tr>
<td>80</td>
<td>166</td>
<td>9.9 \times 10^{-6}</td>
<td>2.1 \times 10^{-5}</td>
</tr>
<tr>
<td>100</td>
<td>199</td>
<td>2.1 \times 10^{-7}</td>
<td>3.7 \times 10^{-7}</td>
</tr>
<tr>
<td>200</td>
<td>1404</td>
<td>1.6 \times 10^{-9}</td>
<td>3.7 \times 10^{-10}</td>
</tr>
<tr>
<td>300</td>
<td>1423</td>
<td>2.5 \times 10^{-10}</td>
<td>4.7 \times 10^{-11}</td>
</tr>
<tr>
<td>400</td>
<td>1480</td>
<td>5.6 \times 10^{-11}</td>
<td>9.0 \times 10^{-12}</td>
</tr>
<tr>
<td>500</td>
<td>1576</td>
<td>1.6 \times 10^{-11}</td>
<td>2.2 \times 10^{-12}</td>
</tr>
<tr>
<td>600</td>
<td>1691</td>
<td>5.2 \times 10^{-12}</td>
<td>6.6 \times 10^{-13}</td>
</tr>
<tr>
<td>700</td>
<td>1812</td>
<td>2.0 \times 10^{-12}</td>
<td>2.3 \times 10^{-13}</td>
</tr>
</tbody>
</table>

**Figure 1-5**

Temperature trends in the earth's atmosphere.
We know that the volume of a gas is proportional to the amount of gas present or the number of moles of gas (n), so that:

\[ V \propto n \frac{T}{P} \]

Under standard conditions (T = 273.15K or t = 0°C and P = 1 atm), the volume occupied by one mole of an ideal gas is equal to 22.414 liters, hence,

\[
\frac{PV}{nT} = R = (1 \text{ atm}) (22.414 \text{ liters})/((1 \text{ mol}) (273.15K)) = 0.082056 \text{ liter atm K}^{-1} \text{ mol}^{-1}
\]

Pressure x volume = (force/area) x (area x length) = force x length

Given that 1 liter = 10^{-3} m^3 and 1 atm = 101,325 N m^{-2} = 101,325 Pa
\[ R = 0.082056 \text{ liter atm K}^{-1} \text{ mol}^{-1} \times 1 \text{ m}^3/10^{-3} \text{ L} \times 101,325 \text{ N m}^{-2}/\text{atm} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \] (R = 1.987 cal K^{-1} mol^{-1})

\[ PV = n RT \]
According to Dalton’s law for ideal gases, the total pressure exerted by a mixture of gases is equal to the sum of the pressures which each component would exert if placed separately into a container.

For gas #1  \(-P_1 V = n_1 RT\)
For gas #2  \(-P_2 V = n_2 RT\)
For gas #3  \(-P_3 V = n_3 RT\)
For gas #i  \(-P_i V = n_i RT\)

\[(P_1 + P_2 + P_3 + \ldots + P_i) V = (n_1 + n_1 + n_1 + \ldots + n_i) P\]

\[V \sum P_i = RT \sum n_i\]

where \(\sum n_i = n_{tot}\) and \(\sum P_i = P_{tot}\)

and \(P_i\) is the partial pressure of gas i (pressure exerted by one component of the gas mixture).
Solutions are defined as homogeneous phases formed by dissolving one or more substances (gas, liquid, solid) in another substance.

Whether you consider a gaseous, a liquid or a solid solution, compositional variations within a mixture can be expressed in terms of a number of moles of each species present ($n_1, n_2, n_3, ...$) or as the mole fraction, $X$, defined for the $i$th species as:

$$X_i = \frac{\text{number of moles of } i}{\text{total number of moles}} = \frac{n_i}{\sum n}$$

Therefore, $\sum X_i = 1$
In 1886, Raoult first observed that the vapour pressure (a measure of the escaping velocity) of very similar components in solution (ethylene bromide and propylene bromide) depends only on the mole fraction of each component present in solution at **constant pressure and temperature**.

In other words, if \( P_A = X_A P^\circ_A \)

where \( P_A \) is the vapour pressure of A in the mixture and \( P^\circ_A \) is the vapour pressure of pure A, then

\[
\sum P_i = P_A + P_B + P_C + ... = P_{TOT}
\]

\[
= (X_A + X_B + X_C + ...) P_{TOT}
\]

and \( P_A = X_A P_{TOT} \) or \( P_i = X_i P_{TOT} \)
Vapour pressures in a water-dioxane solution
(the positive deviations from ideality are a macroscopic manifestation of the repulsive forces between water and dioxane molecules)

\[ P_B = h \, \chi_B \], where \( h \) is Henry’s constant (in honour of William Henry, 1774-1836). The value of \( h \) is dependent on the solute and solvent.
One measure of the deviations (f(nature of the gas, T and P)) of a gas from ideal behavior is given by the compressibility factor, $Z$:

$$Z = \frac{PV}{RT}$$

where $V$ is the volume of one mole of a real gas ($V/n$).

Given that:

$V = \frac{RT}{P}$, a gas at 0K would have a null volume!

$\Rightarrow V = \frac{RT}{P} + b$ or $P = \frac{RT}{(V - b)}$

where $b$ is the hypothetical volume of a gas at 0K.

When a gas is on the verge of condensation to a liquid, gas molecules are attracted to each other, resulting in a decrease in pressure. The attractive forces are proportional to the square of their concentration.
Since \( c = n/V = 1/V \), the attractive forces are proportional to \( 1/V^2 \). These attractive forces reduce the total pressure of the gas and, thus (van de Waals equation):

\[
P = \frac{RT}{V - b} - \frac{a}{V^2} \quad \text{(van der Waals equation)}
\]

where \( a \) is a proportionality constant for attraction.

Subsequently, many alternative equations have been proposed that are also based on the sum of repulsive and attractive forces, including the one introduced by Redlich and Kwong in 1949:

\[
P = \frac{RT}{V - b} - \frac{a}{T^{0.5}V(V - b)}
\]

or

\[
P = \frac{RT}{V - b} - \frac{a}{T^{0.5}V(V - b)}
\]

\[
P = \frac{PV}{RT} = 1 + B/V + C/V^2 + D/V^3
\]

where \( B, C, \) and \( D \) are the second, third and fourth virial coefficients (experimentally determined).