Real Gas Behavior

The ideal gas law is only approximate. See examples. As pressures increase, particles begin to feel the presence of one another.

- **Virial Equation**

\[
\frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots \quad \begin{cases} 
B \\ C \\ D \end{cases} \text{ different for each gas}
\]

- **van der Waals (VDW) equation**

\[
P = \frac{RT}{V - b} - \frac{a}{V^2} \quad \begin{cases} 
V \text{ different for each gas} \\
a \\
b \end{cases}
\]

Practice with this equation using chlorine gas parameters. How do these differ in philosophy? Can you justify the form of the VDW equation? Can you manipulate VDW equation to show \( P \) is cubic in \( V \) (use common denominator)?

**Example: methane**

<table>
<thead>
<tr>
<th>( V ) [L/mol]</th>
<th>( P ) [bar]</th>
<th>( V ) [L/mol]</th>
<th>( P ) [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.7859</td>
<td>1/7</td>
<td>142.411</td>
</tr>
<tr>
<td>1/2</td>
<td>45.8040</td>
<td>1/8</td>
<td>161.873</td>
</tr>
<tr>
<td>1/3</td>
<td>66.4155</td>
<td>1/9</td>
<td>182.470</td>
</tr>
<tr>
<td>1/4</td>
<td>85.9918</td>
<td>1/10</td>
<td>204.825</td>
</tr>
<tr>
<td>1/5</td>
<td>104.9110</td>
<td>1/11</td>
<td>229.688</td>
</tr>
<tr>
<td>1/6</td>
<td>123.5850</td>
<td>1/12</td>
<td>257.950</td>
</tr>
</tbody>
</table>


Can we compute VDW constants and virial constants from this data? Use **LINEST** in Excel. More instructions for LINEST [here](#).
A plot of $P$ versus $V$ for a given temperature is an isotherm.

**Critical point on a phase diagram**

**Critical point from a series of PV isotherms**

VDW gas example:

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \quad \frac{\partial P}{\partial V} = 0 \quad \frac{\partial^2 P}{\partial V^2} = 0$$

Solve these equations treating $R$ as a constant:

$$a = \frac{27R^2T_c^2}{64P_c} \quad b = \frac{RT_c}{8P_c}$$

**Other important concepts:**

1. How do we measure pressure? What is the SI unit and how is it derived? $1.0 \text{ atm} = 760 \text{ mm Hg}$ equals …

$$P = h \rho g$$

$$P = (.76m)(13.5951 \times 10^3 \text{ kg} \cdot \text{m}^{-3})(9.8 \text{ m} \cdot \text{s}^{-2})$$

$$P = 101325 \text{ N} \cdot \text{m}^{-2} \text{ or Pa}$$

$$P = 1.01325 \text{ bar}$$

Related to this is the idea that the Ideal Gas Constant can be expressed in two different units:

$$R = 8.314 \frac{J}{K \cdot \text{mol}} = 0.08314 \frac{L \cdot \text{bar}}{K \cdot \text{mol}} \quad (L \cdot \text{bar} = 100J)$$
2. What is the Boyle Temperature of a gas?

\[ z = \frac{P V}{RT} \]  
\[ \left( \frac{\partial z}{\partial P} \right)_T = 0 \text{ at the Boyle Temperature} \]

Examine the **compressibility (z) of Nitrogen**. For an ideal gas, the derivative of z is 0 for all temperatures. For a real gas …

for \( T > T_{Boyle} \): \[ \left( \frac{\partial z}{\partial P} \right)_T > 0 \text{ as } P \to 0 \]

for \( T < T_{Boyle} \): \[ \left( \frac{\partial z}{\partial P} \right)_T < 0 \text{ as } P \to 0 \]

3. How are the van der Waals parameters related to the second virial coefficient? How does this show the temperature dependence of B?

\[ B(T) = b - \frac{a}{RT} \]

derived from \( \frac{1}{1 - x} = 1 + x + x^2 + \ldots \)

From this, we can estimate Boyle temperature of a VDW gas as:

\[ b - \frac{a}{RT_{Boyle}^{VDW}} = 0 \]

\[ T_{Boyle}^{VDW} = \frac{a}{bR} \]
4. Derive the Boyle Temperature of a Berthelot Gas:

\[ \overline{V} = \frac{RT}{P} + b - \frac{a}{RT^2} \]

by equating the derivative of \( z \) with respect to \( P \) to zero.

5. Fugacity (\( f \)) and fugacity coefficient (\( \gamma \)):

\[ \ln f = \ln P + \int_{0}^{P} \frac{z-1}{P'} dP' \]

\[ \gamma = \frac{f}{P} \quad f = \gamma P \quad \gamma \text{ depends on } P \text{ and } T \]

(fugacity represents the pressure like quantity of a real gas, whereas for an ideal gas it would be the pressure)

6. Solving for Volume using van der Waals equation requires finding the roots of a 3rd-order polynomial. Use Newton-Raphson technique to iterate to a solution.

\[ \overline{V}^3 - \left( \frac{RT}{P} + b \right) \overline{V}^2 + \frac{a}{P} \overline{V} - \frac{ab}{P} = 0 \]

\[ \overline{V}_{n+1} = \overline{V}_n - \frac{f(\overline{V}_n)}{f''(\overline{V}_n)} \]

Practice using this approach to obtain volume of chlorine gas treated as a VDW gas.