CHAPTER 7 PROPERTIES OF REAL GASES

• Real gases: finite size of molecules and intermolecular interactions
• Chemical potential defined by fugacity rather than pressure

Real Gases and Ideal Gases

• Ideal Gas
  • molecules are point masses; molecules do not interact
  • Experimental Approximation: low density and high temperature
  • Equation of state \( PV = nRT \)
• Real Gas
  • Van der Waals equation of state
  \[
  P = \frac{RT}{V_m - b} - \frac{a}{V_m (V_m + b)} = \frac{nRT}{V - nb} - \frac{n^2a}{\sqrt{T} V(V + nb)}
  \]
  • Redlich-Kwong equation of state
Isotherms for CO₂ at (a) 426 K and (b) 329 K using the vdW equation (purple curve), the R-K equation (blue curve) and the ideal gas equation (red curve). Black dots are accurate values taken from NIST.

Other Equations of State

- Beattie-Bridgeman equation of state

\[ P = \frac{RT}{V_m^2} \left( 1 - \frac{c}{V_m T^3} \right) (V_m + B) - \frac{A}{V_m^2} \text{ with} \]

\[ A = A_0 \left( 1 - \frac{a}{V_m} \right) \quad \text{and} \quad B = B_0 \left( 1 - \frac{b}{V_m} \right) \]

- Virial equation of state

\[ P = RT \left[ \frac{1}{V_m} + \frac{B(T)}{V_m^2} + \ldots \right] \]
Isotherms for CO$_2$ as a vdW Gas

- Critical temperature ($T_c$): critical constants ($P_c$, $V_c$, $T_c$)

\[ \left( \frac{\partial P}{\partial V_m} \right)_{T=T_c} = 0 \] and \[ \left( \frac{\partial^2 P}{\partial V_m^2} \right)_{T=T_c} = 0 \]

- No clear interface between liquid and gas

Compression Factor

- Definition

\[ z = \frac{V_m}{V_m^{ideal}} = \frac{PV_m}{RT} \]

- $z = 1$: ideal gas
- $z > 1$: real gas exert a greater pressure than ideal gas
- $z < 1$: real gas exert a smaller pressure than ideal gas
Boyle Temperature \( T_B = \frac{a}{Rb} \)

- At Boyle temperature, both \( z \rightarrow 0 \) and \( \left( \frac{\partial z}{\partial P} \right)_T \rightarrow 0 \), which is the behavior of an ideal gas

<table>
<thead>
<tr>
<th>Gas</th>
<th>( T_B ) (K)</th>
<th>Gas</th>
<th>( T_B ) (K)</th>
</tr>
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<tbody>
<tr>
<td>He</td>
<td>23</td>
<td>O₂</td>
<td>400.</td>
</tr>
<tr>
<td>H₂</td>
<td>110.</td>
<td>CH₄</td>
<td>510.</td>
</tr>
<tr>
<td>Ne</td>
<td>122</td>
<td>Kr</td>
<td>575</td>
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<tr>
<td>N₂</td>
<td>327</td>
<td>Ethene</td>
<td>735</td>
</tr>
<tr>
<td>CO</td>
<td>352</td>
<td>H₂O</td>
<td>1250</td>
</tr>
</tbody>
</table>


Law of Corresponding States

- Using the critical constants as a point of reference

\[
P_rP_c = \frac{RT_fT_c}{V_{mr}V_{mc} - b} - \frac{a}{V_{mr}^2V_{mc}^2}
\]

\[
P_c = \frac{a}{27b^2}, \quad V_{mc} = 3b, \quad \text{and} \quad T_c = \frac{8a}{27Rb}
\]

\[
\frac{a P_r}{27b^2} = \frac{8aT_r}{27b(3bV_{mr} - b)} - \frac{a}{9b^2V_{mr}^2}
\]

or

\[
P_r = \frac{8T_r}{3V_{mr} - 1} - \frac{3}{V_{mr}^2}
\]
Fugacity and Equilibrium Constant

- Ideal gas \( \mu(T, P) = \mu^o(T) + RT \ln \frac{P}{P^o} \)
- Real gas \( \mu(T, P) = \mu^o(T) + RT \ln \frac{f}{f^o} \)
- Fugacity \( f \) = effective pressure

Quantification of Fugacity

- For any gas at constant \( T \)

\[
dG_m = V_mD_P \left[ d\mu_{\text{ideal}} = V^\text{ideal}_m dP \right] d\mu_{\text{real}} - d\mu_{\text{ideal}} = (V^\text{real}_m - V^\text{ideal}_m) dP
\]

\[
\int_{P_I}^{P} (d\mu_{\text{real}} - d\mu_{\text{ideal}}) = [\mu_{\text{real}}(P) - \mu_{\text{real}}(P_I)] - [\mu_{\text{ideal}}(P) - \mu_{\text{ideal}}(P_I)]
\]

\[
= \int_{P_I}^{P} (V^\text{real}_m - V^\text{ideal}_m) dP
\]

\[
\mu_{\text{real}}(P) - \mu_{\text{ideal}}(P) = \int_{0}^{P} (V^\text{real}_m - V^\text{ideal}_m) dP'
\]

\[
\ln f = \ln P + \frac{1}{RT} \int_{0}^{P} (V^\text{real}_m - V^\text{ideal}_m) dP'
\]