1) 

\[ 6.6 \text{ Express } (\frac{\partial H}{\partial V})_T \text{ in terms of } \alpha_f \text{ and/or } \kappa_f. \]

(Maxwell & Triple Rule given below.)

2) 

7.1 The compressibility factor chart provides a quick way to assess when the ideal gas law is valid. For the following fluids, what is the minimum temperature in K where the fluid has a gas phase compressibility factor greater than 0.95 at 30 bar?

(a) Nitrogen
(b) Carbon dioxide
(c) Ethanol

(Compressibility charts given below.)

<table>
<thead>
<tr>
<th>Thermodynamic Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc °K</td>
</tr>
<tr>
<td>------</td>
</tr>
<tr>
<td>N2</td>
</tr>
<tr>
<td>CO2</td>
</tr>
<tr>
<td>EtOH</td>
</tr>
</tbody>
</table>

3) 

7.6 N.B. Vargaftik (1975)\(^{23}\) lists the following experimental values for the specific volume of isobutane at 175°C. Compute theoretical values and their percent deviations from experiment by the following:

(a) The generalized charts
(b) The Peng-Robinson equation

Do for Only One Experimental Condition: \( P = 3.5 \text{ MPa}, V = 13.36 \text{ cm}^3/\text{g}. \)

\( P_c=3.648 \text{ MPa}, T_c=408.14°K, \omega=0.177, \text{ MW} = 58.123 \text{ g/mole}, R = 8.314 \text{ cm}^3\text{MPa}/(\text{mole}°\text{K}). \)

Compressibility charts and the Peng-Robinson equation are given below.
Maxwell's Relations

\[
dU = TdS - PdV \Rightarrow -\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial T}{\partial V}\right)_S
\]
\[
dH = TdS + VdP \Rightarrow \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S
\]
\[
dA = -SdT - PdV \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T
\]
\[
dG = -SdT + VdP \Rightarrow -\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T
\]

6.15 Triple product rule.

6.16 Chain rule interposing a variable.

6.17 The expansion rule.

Peng-Robinson Equation:

The Peng-Robinson equation of state (EOS) is given by:

\[
P = \frac{RT\rho}{(1 - b\rho)} - \frac{a\rho^2}{1 + 2b\rho - b^2\rho^2} \text{ or } Z = \frac{1}{(1 - b\rho)} - \frac{a}{bRT} \cdot \frac{b\rho}{1 + 2b\rho - b^2\rho^2}
\]

where \( \rho = \text{molar density} = n/V, \) \( b \) is a constant, and \( a \) depends on temperature and acentric factor,\(^7\)

\[
a \equiv a_c\alpha; \quad a_c \equiv 0.45723553 \frac{R^2 T_c^2}{P_c}
\]

\[
b \equiv 0.07779607R \frac{T_c}{P_c}
\]

\[
\alpha \equiv [1 + \kappa(1 - \sqrt{T_c})]^2 \quad \kappa \equiv 0.37464 + 1.54226\omega - 0.26992\omega^2
\]

7.15

7.16

7.17
\[ Z = 1 + (B^0 + \omega B^1)P_r/T_r \quad \text{or} \quad Z = 1 + BP/RT \quad \text{7.6} \]

where \( B(T) = (B^0 + \omega B^1)RT_c/P_c \quad \text{7.7} \]

\[ B^0 = 0.083 - 0.422/T_r^{1.6} \quad \text{7.8} \]

\[ B^1 = 0.139 - 0.172/T_r^{4.2} \quad \text{7.9} \]

Subject to \( T_r > 0.686 + 0.439P_r \) or \( V_r > 2.0 \) \quad \text{7.10} \]
Figure 7.4 Generalized charts for estimating the compressibility factor. \( Z^0 \) applies the Lee-Kesler equation using \( \omega = 0.0 \), and \( Z^1 \) is the correction factor for a hypothetical compound with \( \omega = 1.0 \). Note the semilog scale.
1) 

6.6 Express \( \left( \frac{\partial H}{\partial V} \right)_T \) in terms of \( \alpha_p \) and/or \( \kappa_T \).

(Maxwell & Triple Rule given below.)

\[
\begin{align*}
(6.06) \text{ Express } (dH/dV)_T \text{ in terms of } \\
&= T \left( \frac{\partial S}{\partial V} \right)_T + V \left( \frac{\partial P}{\partial V} \right)_T \\
&= T \left( \frac{\partial P}{\partial T} \right)_V + V \left( \frac{\partial P}{\partial V} \right)_T \\
&\quad \text{where } \left( \frac{\partial P}{\partial T} \right)_V = - \left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial V} \right)_T = \frac{\alpha_p}{\kappa_T} \\
&= \frac{\alpha_p T - 1}{\kappa_T}
\end{align*}
\]

2) 

7.1 The compressibility factor chart provides a quick way to assess when the ideal gas law is valid. For the following fluids, what is the minimum temperature in K where the fluid has a gas phase compressibility factor greater than 0.95 at 30 bar?

(a) Nitrogen  
(b) Carbon dioxide  
(c) Ethanol

(Compressibility charts given below.)

<table>
<thead>
<tr>
<th>Thermodynamic Parameters</th>
<th>T_c °K</th>
<th>P_c MPa</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>N_2</td>
<td>126</td>
<td>3.41</td>
<td>0.040</td>
</tr>
<tr>
<td>CO_2</td>
<td>304.2</td>
<td>7.32</td>
<td>0.228</td>
</tr>
<tr>
<td>EtOH</td>
<td>513.9</td>
<td>6.38</td>
<td>0.635</td>
</tr>
</tbody>
</table>

(7.01) The compressibility factor chart provides...

- a) \( Pr = 0.88 \), the T limit where \( Z^0 > 0.95 \) is \( Tr = 1.75, T > 220 \) K
- b) \( Pr = 0.41 \), the T limit where \( Z^0 > 0.95 \) is \( Tr = 1.4, T > 425 \) K
- c) \( Pr = 0.47 \), the T limit where \( Z^0 > 0.95 \) is \( Tr = 1.5, T > 775 \) K

Therefore, it can be seen that there isn’t any single temperature above which the ideal gas law is valid for all fluids; the temperature depends on the fluid.
7.6 N.B. Vargaftik (1975) lists the following experimental values for the specific volume of isobutane at 175°C. Compute theoretical values and their percent deviations from experiment by the following:

(a) The generalized charts
(b) The Peng-Robinson equation

Do for Only One Experimental Condition: $P = 3.5 \text{ MPa}, V = 13.36 \text{ cm}^3/\text{g}$.

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Compressibility charts and the Peng-Robinson equation are given below.