PROBLEM 11.32

FIND: Derive expressions for \( \beta \) and \( K \) in terms of \( T, p, Z, (\partial Z/\partial T)_p, (\partial Z/\partial p)_T \).

For gas states with \( Pr < 3; T < 2 \), determine the sign of \( K \).

ANALYSIS: From Eqs. 11.62 and 11.63

\[
\beta = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p, \quad K = -\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T
\]

The compressibility factor is

\[
Z(T, p) = \frac{V}{RT}
\]

\[\Rightarrow V = \frac{RT}{p} \cdot Z(T, p)\]

Then

\[
\left( \frac{\partial V}{\partial T} \right)_p = \frac{R}{p} Z + \frac{RT}{p} \left( \frac{\partial Z}{\partial T} \right)_p
\]

and

\[
\left( \frac{\partial V}{\partial p} \right)_T = -\frac{RT}{p^2} Z + \frac{RT}{p} \left( \frac{\partial Z}{\partial p} \right)_T
\]

Accordingly

\[
\beta = \frac{1}{V} \left[ \frac{R}{p} Z + \frac{RT}{p} \left( \frac{\partial Z}{\partial T} \right)_p \right]
\]

\[= \frac{R}{p V} \left( \frac{\partial V}{\partial T} \right)_p + \frac{1}{Z} \left( \frac{\partial Z}{\partial T} \right)_p
\]

\[= \frac{1}{T} + \frac{1}{Z} \left( \frac{\partial Z}{\partial T} \right)_p \]

\[
K = -\frac{1}{V} \left[ -\frac{RT}{p^2} Z + \frac{RT}{p} \left( \frac{\partial Z}{\partial p} \right)_T \right]
\]

\[= \left[ \frac{R}{p V} \cdot Z - \frac{RT}{p V} \left( \frac{\partial Z}{\partial p} \right)_T \right]
\]

\[= \frac{1}{p} - \frac{1}{Z} \left( \frac{\partial Z}{\partial p} \right)_T
\]

Referring to Figure A.2, for \( Pr < 3, T < 0 \) all isotherms have a negative slope: \( (\partial Z/\partial p)_T < 0 \). Thus, it is evident that \( K \)

must be positive at all such states.
PROBLEM 11.36

KNOWN: A gas obeys the van der Waals equation of state.

FIND: (a) Show that \( \left. \frac{\partial V}{\partial P} \right|_T = 0 \). (b) Develop an expression for \( (\gamma - c_v) \).

(c) Develop expressions for \( [u(T_2, v) - u(T_1, v)] \) and \( [P(T_2, v) - P(T_1, v)] \).

(d) Complete the result of (c) if \( c_v = a + bT \) (Note: \( a, b \) are constants, but do not correspond to the constants of the Equation of State.)

ANALYSIS: (a) \( c_v = \frac{\gamma (\partial u)}{\partial T} \). Then

\[
\left( \frac{\partial c_v}{\partial v} \right|_T = \frac{2}{3v} \left( \frac{2a}{3v} \right)_T = \frac{2}{3v} \left[ \frac{2a}{3v} \right]_T
\]

Insert \( \epsilon \) Eq. 11.17

\[
\left( \frac{\partial c_v}{\partial v} \right|_T = \frac{2}{3v} \left[ T \left( \frac{2a}{3v} \right) - b \right] = \frac{2a}{3v(T - 2b)} + \left( \frac{3}{5} \right) - \frac{2b}{v(T - 2b)} = \frac{2a}{3v(T - 2b)}
\]

Using the van der Waals equation

\[
\frac{2b}{v(T - 2b)} = 0 \Rightarrow \left( \frac{\partial c_v}{\partial v} \right|_T = 0.
\]

That is, \( c_v \) is independent of \( v \) and depends only on \( T \): \( c_v = c_v(T) \).

(b) Begin with Eq. 11.15B, and note that \( (\partial u)/(\partial T) \) is evaluated for the van der Waals equation in Ex 11.2. Further,

\[
\left( \frac{\partial P}{\partial V} \right|_T = -\frac{R}{v-b} + \frac{2a}{3v^3}
\]

Thus

\[
c_v - c_p = -T \left[ \frac{R/(v-b)}{2a(v^3 - RT/(v-b))} \right] \left[ \frac{2a}{3v^3} - \frac{RT}{v-b} \right]
\]

\[
= -\frac{R^2 T}{v-b} \left[ \frac{2a}{v^3} - \frac{RT}{v-b} \right]
\]

\[
= \frac{R}{1 - 2a(v-b)/RT v^3}
\]

(c) Using the result of part (a), Eqs. 11.3D and 11.3E give

\[
S(T, v) = S(T, v) = \int_{T_1}^{T_2} \frac{c_v(T)}{T} dT + \int_{v_1}^{v_2} \frac{R}{v-b} dv = \int_{T_1}^{T_2} c_v(T) dT + R \ln \left( \frac{v_2-b}{v_1-b} \right)
\]

\[
\Delta S = \int_{T_1}^{T_2} \left( c_v(T) dT - a \left[ \frac{1}{v_2} - \frac{1}{v_1} \right] \right)
\]

To evaluate these expressions requires only the function \( c_v(T) \).

(d) If \( c_v = a + bT \), then

\[
\Delta S = \int_{T_1}^{T_2} \left( a + bT \right) dT + R \ln \left( \frac{v_2-b}{v_1-b} \right) = a \ln \left( \frac{T_2}{T_1} \right) + b(T_2 - T_1) + R \ln \left( \frac{v_2-b}{v_1-b} \right)
\]

\[
\Delta u = \int_{T_1}^{T_2} \left( a + bT \right) dT - a \left[ \frac{1}{v_2} - \frac{1}{v_1} \right] = a(T_2 - T_1) + \frac{b^2 (T_2^2 - T_1^2)}{2} - a \left[ \frac{1}{v_2} - \frac{1}{v_1} \right]
Known: p-v-T data for water are available from the steam tables.

Find: Determine at 50°C, (a) \( h_g - h_f \), (b) \( u_g - u_f \), and (c) \( s_g - s_f \), and compare with table values.

Analysis: The value of \( h_g - h_f \) can be calculated using saturation data and the Clapeyron equation, Eq. 11.40

\[
h_g - h_f = T \left( u_g - u_f \right) \left( \frac{dp}{dt} \right)_{sat}
\]

To obtain the value for \( (dp/dt)_{sat} \), prepare the plot shown below using data from Table A-2

Inserting values into Eq. (1)

\[
h_g - h_f = (50 + 273.15) K (12.032 - 1.021 \times 10^{-3}) \frac{m^3}{kg} (0.00604 \frac{bar}{K}) \left( \frac{10^5 N \cdot m^2}{1 \text{ bar}} \right) \left( \frac{1 \text{ kJ}}{10^3 N \cdot m} \right) = 2348 \text{ kJ/kg}
\]

With Eq. 11.38

\[
s_g - s_f = \frac{h_g - h_f}{T} = \frac{2348}{323.15} = 7.266 \text{ kJ/kg.K}
\]

Further, using \( u = h - pv \)

\[
u_g - u_f = (h_g - h_f) - p (v_g - v_f)
\]

\[
= (2348 \frac{kJ}{kg}) - (0.1235 \text{ bar})(12.032 - 1.021 \times 10^{-3}) \frac{m^3}{kg} \left( \frac{10^5 N \cdot m^2}{1 \text{ bar}} \right) \left( \frac{1 \text{ kJ}}{10^3 N \cdot m} \right) = 2199.4 \text{ kJ/kg}
\]

The respective table values are \( h_g - h_f = 2382.7 \text{ kJ/kg}, s_g - s_f = 7.3725 \text{ kJ/kg.K}, \) and \( u_g - u_f = 2234.2 \text{ kJ/kg}. \) The percent difference between calculated and table values is about 1.5% for all quantities.

An alternative solution using IT follows:
Problem 11.20 (Cont'd.) - Page 2

\textbf{IT Code}

\begin{verbatim}
T = 50 // °C
dT = 0.001
T1 = T - dT
T2 = T + dT

p1 = Psat_T("Water/Steam", T1)
p2 = Psat_T("Water/Steam", T2)
dpdT_sat = ((p2 - p1) / (T2 - T1)) // bar/K
p = Psat_T("Water/Steam", T)
vgs = vsat_Px("Water/Steam", p, 1)
vf = vsat_Px("Water/Steam", p, 0)

hfg = (T + 273.15) * (vgs - vf) * dpdT_sat * 100
sg = ssat_Px("Water/Steam", p, 1)
sf = ssat_Px("Water/Steam", p, 0)
sfg = sg - sf
ufg = hfg - p * (vgs - vf) * 100
\end{verbatim}

\textbf{IT Results}

\begin{itemize}
  \item $(\partial p/\partial T)_{sat} = 0.006127$ bar
  \item $h_g = 2382$ kJ/kg
  \item $s_g = 7.372$ kJ/kg K
  \item $u_f = 2234$ kJ/kg
\end{itemize}

The IT results compare very favorably with the table data.
KNOWN: Two states of ethylene (C₂H₄) are under consideration: T₁ = T₂ = 400 K, P₁ = 1 bar, P₂ = 100 bar.

FIND: Using the Redlich-Kwong equation of state, evaluate ΔS and ΔH.

SCHEMATIC & GIVEN DATA:

ENGINEERING MODEL: The Redlich-Kwong equation of state is applicable at these states.

ANALYSIS: The results of Problem 11.49(b) are quoted for present use:

\[
\overline{h}_2 - \overline{h}_1 = p(\overline{V}_2, T) \overline{V}_2 - p(\overline{V}_1, T) \overline{V}_1 - \frac{3}{2} \frac{a}{b} T \ln \left( \frac{\overline{V}_2 + b}{\overline{V}_1 + b} \right)
\]

(1)

\[
\overline{s}_2 - \overline{s}_1 = \overline{R} \ln \left( \frac{\overline{V}_2 - b}{\overline{V}_1 - b} \right) - \frac{a}{2bT^{3/2}} \ln \left( \frac{\overline{V}_2 + b}{\overline{V}_1 + b} \right)
\]

(2)

where the values of a and b are obtained using Eq. 11.8 as

\[
a = 77.76 \text{ bar} \left( \frac{m^3}{\text{kmol}} \right)^2 K^{1/2}, \quad b = 0.03981 \text{ m}^3/\text{kmol}
\]

The values of \(\overline{V}_1\) and \(\overline{V}_2\) can be found using IT to solve the Redlich-Kwong equation knowing the pressure and temperature at each state. The results are

\(\overline{V}_1 = 33.18 \text{ m}^3/\text{kmol}, \quad \overline{V}_2 = 0.2636 \text{ m}^3/\text{kmol}\)

Inserting numerical values into Eq. (2)

\[
\overline{s}_2 - \overline{s}_1 = (8.314 \text{ kJ} / \text{kmol} \cdot K) \ln \left( \frac{223.79}{32.81} \right) - \frac{77.76 \text{ bar} \left( \frac{m^3}{\text{kmol}} \right)^2 K^{1/2}}{2 \times (0.03981 \text{ m}^3/\text{kmol}) (400 K)^{1/2}} \ln \left( \frac{0.30341}{33.21981} \right)
\]

\[
\left[ \frac{10^5 N/m^2}{1 \text{ bar}} \right] \left[ \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}} \right]
\]

\[
\Delta S = -43.20 \text{ kJ/kgmol} \cdot K
\]

\[
\overline{h}_2 - \overline{h}_1 = \left[ (100 \text{ bar}) (0.2636 \text{ m}^3/\text{kmol}) - (1) (33.18) \right] \frac{10^5 \text{ N/m}^2}{1 \text{ bar}} \frac{1 \text{ kJ}}{10^3 \text{ N} \cdot \text{m}}
\]

\[
- \frac{(3) (77.76 \text{ bar} \left( \frac{m^3}{\text{kmol}} \right)^2 K^{1/2})}{(2) (0.03981 \text{ m}^3/\text{kmol}) (400 K)^{1/2}} \ln \left[ \frac{0.30341}{33.21981} \right]
\]

\[
\Delta H = -2270.6 \text{ kJ/kgmol}
\]
PROBLEM 11.48

Known: An expression is provided for the enthalpy departure for use when an equation of state explicit in pressure is in hand.

Find: (a) Derive the expression (b) Using (a) obtain an expression for an enthalpy departure for a gas obeying the Redlich-Kwong equation.
(c) Using (b) evaluate \( \Delta h \) for CO₂ in a process at 300 K from 50 to 20 bar.

Analysis: (a) Beginning with \( h = h(T, v) \), write \( dh = \left( \frac{\partial h}{\partial T} \right)_v dv + \left( \frac{\partial h}{\partial v} \right)_T dv \). Then, at fixed \( T \)

\[
\frac{dh}{dT} = \frac{1}{3V_T} dV \quad \Rightarrow \quad h(T, v) - h(T, v_0) = \int \left( \frac{1}{3V_T} \right) dv
\]  

(1)

with \( h = u + pv \), \( (\partial h/\partial v)_T = (\partial u/\partial v)_T + (\partial (pv)/\partial v)_T \). Introducing Eq. 11.47 this becomes

\[
\left( \frac{\partial h}{\partial v} \right)_T = \left[ \frac{T (\frac{\partial \rho}{\partial T})_V - p}{\frac{v}{3}} \right] + \frac{2pv}{3v_T}
\]  

(2)

Inserting Eq. (2) into Eq. (1)

\[
h(T, v) - h(T, v_0) = \int \left[ \frac{T (\frac{\partial \rho}{\partial T})_V - p}{\frac{v}{3}} \right] dv + \left[ pv_0^0(T) \right] - \left[ pv_0^0(T) \right]
\]  

(2)

In the limit as \( p \to 0 \), \( v \to \infty \) and \( (pv)(T, v) \to RT \), \( h(T, v) \to h^*(T) \), so

\[
h(T, v) - h^*(T) = \int \left[ \frac{T (\frac{\partial \rho}{\partial T})_V - p}{\frac{v}{3}} \right] dv + pv - RT
\]  

or

\[
h^*(T) - h(T, v) = RT \left[ 1 - \frac{\rho}{RT} \right] - \frac{1}{\rho} \int \left[ \frac{T (\frac{\partial \rho}{\partial T})_V - p}{\frac{v}{3}} \right] dv
\]

with \( \rho = \rho(T, v) \), \( v \) expressing this on a molar basis

\[
\frac{h^*(T) - h(T, v)}{RT} = \left[ 1 - \frac{1}{\rho} \right] \int \left[ \frac{T (\frac{\partial \rho}{\partial T})_V - p}{\frac{v}{3}} \right] dv
\]  

(3)

(3)

(b) Using the Redlich-Kwong equation of state,

\[
\frac{T (\frac{\partial \rho}{\partial T})_V}{\rho} = \frac{RT}{\rho} + \frac{1}{2 \left( \frac{\rho}{\rho_T} \right)^{\gamma - 1}} = \frac{1}{2 \left( \frac{\rho}{\rho_T} \right)^{\gamma - 1}}
\]

\[
= \frac{2}{3} \left( \frac{\rho}{\rho_T} \right)^{\gamma - 1}
\]

\[
\frac{h^*(T) - h(T, v)}{RT} = \left[ 1 - \frac{1}{\rho} \right] \int \left[ \frac{T (\frac{\partial \rho}{\partial T})_V - p}{\frac{v}{3}} \right] dv
\]

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PROBLEM 11.55

KNOWN: A 0.1-m$^3$ cylinder contains a gaseous mixture with the molar composition $\{97\% \text{CO}, 3\% \text{CO}_2\}$ initially at 30°C and 138 bar. Mixture leaks from the cylinder eventually the cylinder contents are at 129 bar, 30°C.

FIND: Using Kay's rule, estimate the amount of mixture that leaks from the cylinder.

SCHEMATIC & GIVEN DATA:

\[ V = 0.1 \text{ m}^3 \]
\[ T_1 = 30°C, \ P_1 = 138 \text{ bar} \]
\[ T_2 = 30°C, \ P_2 = 129 \text{ bar} \]

ENGINEERING MODEL: The control volume shown on the accompanying sketch is the system.

ANALYSIS: With \( Z = pV/nRT \); \( n = pV/ZRT \). For the control volume, the amount of mixture that leaks out equals \( n \). Thus

\[
n_1 - n_2 = \frac{P_1 V}{Z_1 RT} - \frac{P_2 V}{Z_2 RT} = \frac{V}{RT} \left[ \frac{P_1}{Z_1} - \frac{P_2}{Z_2} \right]
\] (1)

With data from Table A-1

\( \text{CO}: \ T_c = 138 \text{ K}, \ P_c = 135 \text{ bar} \)
\( \text{CO}_2: \ T_c = 304 \text{ K}, \ P_c = 73.9 \text{ bar} \)

Kay's Rule

\[
T_c = 0.97(138) + 0.03(304) = 138.1 \text{ K}
\]
\[
P_c = 0.97(135) + 0.03(73.9) = 129.2 \text{ bar}
\]

Thus

\[
P_{R1} = \frac{138}{36.2} = 3.81, \ T_{R1} = \frac{303}{138.1} = 2.19, \ Z_1 \approx 0.98
\]
\[
P_{R2} = \frac{129}{36.2} = 3.56, \ T_{R2} = \frac{303}{129} = 2.37, \ Z_2 \approx 0.97
\]

Accordingly, Eq. (1) gives

\[
n_1 - n_2 = \frac{0.1 \text{ m}^3}{(514 \text{ kJ/m}^3\text{K})(303 \text{ K})} \left[ \frac{138}{0.98} - \frac{129}{0.97} \right] \text{ bar} \left[ \frac{10^5 \text{ N/m}^2}{1 \text{ bar}} \right]
\]

\[
= 0.031 \text{ kmol}
\]