

6.7 GENERALIZED PROPERTY CORRELATIONS FOR GASES

Of the two kinds of data needed for evaluation of thermodynamic properties, heat capacities and PVT data, the latter are most frequently missing. Fortunately, the generalized methods developed in Sec. 3.6 for the compressibility factor are also applicable to residual properties. Equations (6.46) and (6.48) are put into generalized form by substitution of the relationships:

$$\frac{P}{dP} = \frac{P_c P_r}{P_c dP_r} \quad \frac{T}{dT} = \frac{T_c T_r}{T_c dT_r}$$

The resulting equations are:

$$\frac{H^R}{RT_c} = -T_r^2 \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} \quad (6.83)$$

$$\frac{S^R}{R} = -T_r \int_0^{P_r} \left(\frac{\partial Z}{\partial T_r} \right)_{P_r} \frac{dP_r}{P_r} - \int_0^{P_r} (Z - 1) \frac{dP_r}{P_r} \quad (6.84)$$

The correlation for Z is based on Eq. (3.57):

$$Z = Z^0 + \omega Z^1$$

$\frac{H^R}{RT_c} = \frac{(H^R)^0}{RT_c} + \omega \frac{(H^R)^1}{RT_c} \quad (6.85)$	$\frac{S^R}{R} = \frac{(S^R)^0}{R} + \omega \frac{(S^R)^1}{R} \quad (6.86)$
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Calculated values of the quantities above as determined by Lee and Kesler are given as functions of T_r and P_r in Tables E.5 through E.12.

However, the generalized second-virial-coefficient correlation valid at low pressures forms the basis for analytical correlations of the residual properties. The equation relating B to the functions B^0 and B^1 is derived in Sec. 3.6: recall equations (3.62 and 3.63)

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1$$

Since B , B^0 , and B^1 are functions T_r only,

$$\frac{P_c}{RT_c} \frac{dB}{dT_r} = \frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r}$$

Equations (6.55) and (6.56) may be written:

$$\frac{H^R}{R} = \frac{P}{R} \left(B - T_r \frac{dB}{dT_r} \right) \quad \quad \frac{S^R}{R} = \frac{P}{RT_c} \frac{dB}{dT_r}$$

Combining each of these equations with the previous equation yields after reduction:

$$\frac{H^R}{RT_c} = P_r \left[B^0 - T_r \frac{dB^0}{dT_r} + \omega \left(B^1 - T_r \frac{dB^1}{dT_r} \right) \right] \quad (6.87)$$

$$\frac{S^R}{R} = -P_r \left(\frac{dB^0}{dT_r} + \omega \frac{dB^1}{dT_r} \right) \quad (6.88)$$

The dependence of B^0 and B^1 on reduced temperature is given by Eqs. (3.65) and (3.66). Differentiation of these equations provides expressions for dB^0/dT_r and dB^1/dT_r . Thus the equations required for application of Eqs. (6.87) and (6.88) are:

$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (3.65)$	$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad (3.66)$
$\frac{dB^0}{dT_r} = \frac{0.675}{T_r^{2.6}} \quad (6.89)$	$\frac{dB^1}{dT_r} = \frac{0.722}{T_r^{5.2}} \quad (6.90)$

The generalized correlations for H^R and S^R , together with ideal-gas heat capacities, allow calculation of enthalpy and entropy values of gases at any temperature and pressure by Eqs. (6.50) and (6.51). For a change from state 1 to state 2, write Eq. (6.50) for both states:

$$H_2 = H_0^{ig} + \int_{T_0}^{T_2} C_P^{ig} dT + H_2^R \quad H_1 = H_0^{ig} + \int_{T_0}^{T_1} C_P^{ig} dT + H_1^R$$

The enthalpy change for the process, $\Delta H = H_2 - H_1$, is the difference between these two equations:

$$\Delta H = \int_{T_1}^{T_2} C_P^{ig} dT + H_2^R - H_1^R \quad (6.91)$$

Similarly, by Eq. (6.51),

$$\Delta S = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R \quad (6.92)$$

written in alternative form these equations becomes:

$$\Delta H = \langle C_P^{ig} \rangle_H (T_2 - T_1) + H_2^R - H_1^R \quad (6.93)$$

$$\Delta S = \langle C_P^{ig} \rangle_S \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} + S_2^R - S_1^R \quad (6.94)$$

Thus, in Fig. 6.6, the actual path from state 1 to state 2 (dashed line) is replaced by a three-step calculational path:

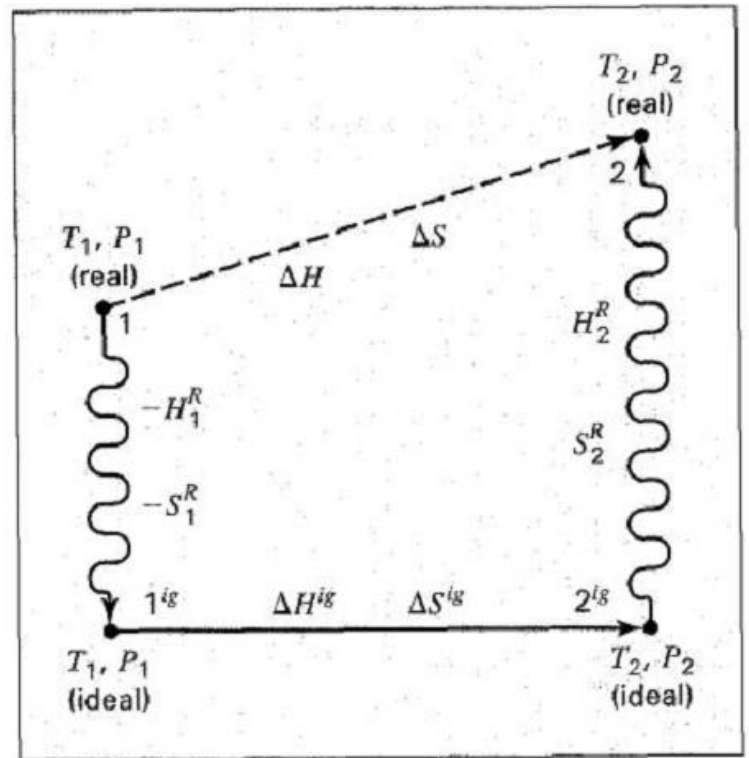


Figure 6.6 Calculational path for property changes ΔH and ΔS

Step 1 \longrightarrow 1^{ig}: A hypothetical process that transforms a real gas into an ideal gas at T_1 and P_1 . The enthalpy and entropy changes for this process are:

$$H_1^{ig} - H_1 = -H_1^R \quad S_1^{ig} - S_1 = -S_1^R$$

Step 1^{ig} \longrightarrow 2^{ig}: Changes in the ideal-gas state from (T_1, P_1) to (T_2, P_2) . For this process,

$$\Delta H^{ig} = H_2^{ig} - H_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} dT \quad (6.95)$$

$$\Delta S^{ig} = S_2^{ig} - S_1^{ig} = \int_{T_1}^{T_2} C_P^{ig} \frac{dT}{T} - R \ln \frac{P_2}{P_1} \quad (6.96)$$

Step 2^{ig} → 2: Another hypothetical process that transforms the ideal gas back into a real gas at T_2 and P_2 . Here,

$$H_2 - H_2^{ig} = H_2^R \quad S_2 - S_2^{ig} = S_2^R$$

Equations (6.91) and (6.92) result from addition of the enthalpy and entropy changes for the three steps.

Example 6.9

Estimate V , U , H , and S for 1-butene vapor at 200°C and 70 bar if H and S are set equal to zero for saturated liquid at 0°C. Assume that the only data available are:

$$T_c = 420.0 \text{ K} \quad P_c = 40.43 \text{ bar} \quad \omega = 0.191$$

$$T_b = 266.9 \text{ K} \quad (\text{normal boiling point})$$

$$C_p^{ig}/R = 1.967 + 31.630 \times 10^{-3}T - 9.837 \times 10^{-6}T^2 \quad (T/\text{K})$$

Solution 6.9

The volume of 1-butene vapor at 200°C and 70 bar is calculated directly from the equation $V = ZRT/P$, where Z is given by Eq. (3.57) with values of Z^0 and Z^1 interpolated in Tables E.3 and E.4. For the reduced conditions,

$$T_r = \frac{200 + 273.15}{420.0} = 1.127 \quad P_r = \frac{70}{40.43} = 1.731$$

the compressibility factor and molar volume are:

$$Z = Z^0 + \omega Z^1 = 0.485 + (0.191)(0.142) = 0.512$$

$$V = \frac{ZRT}{P} = \frac{(0.512)(83.14)(473.15)}{70} = 287.8 \text{ cm}^3 \text{ mol}^{-1}$$

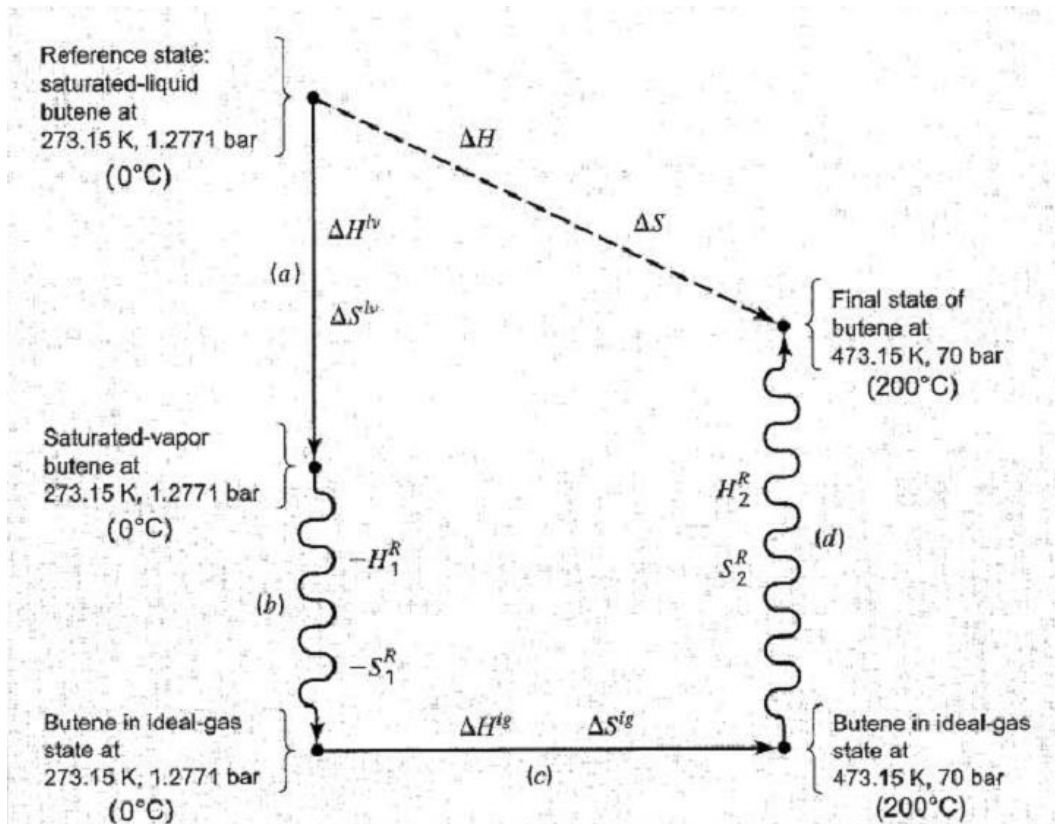


Figure 6.7

For H and S, use a calculational path like that of Fig. 6.6 leading from an initial state of saturated liquid 1-butene at 0 °C where H and S are zero to the final state of interest. In this case, an initial vaporization step is required leading to the four-step path shown by Fig- (6.7). The steps are;

- Vaporization at T_1 and $P_1 = P^{\text{sat}}$
- Transition to the ideal-gas state at (T_1, P_1) .
- Change to (T_2, P_2) in the ideal-gas state,
- Transition to the actual final state at (T_2, P_2) .

- Step (a) Vaporization of saturated liquid 1-butene at 0 °C. The vapor pressure must be estimated as it is not given. One method is based on the equation:

$$\ln P^{\text{sat}} = A - \frac{B}{T} \quad (6.75)$$

The vapor-pressure curve contains both the normal boiling point, for which $P^{\text{sat}} = 1.0133$ bar at 266.9 K, and the critical point, for which $P^{\text{sat}} = 40.43$ bar at 420.0 K. For these two points,

$$\ln 1.0133 = A - \frac{B}{266.9} \quad \ln 40.43 = A - \frac{B}{420.0}$$

Whence, $A = 10.1260$ $B = 2,699.11$

For 0°C (273.15 K), $P^{\text{sat}} = 1.2771$ bar, a result used in steps (b) and (c). Here, the latent heat of vaporization is required. Equation (4.12) provides an estimate at the normal boiling point, where $T_r = 266.9/420.0 = 0.636$:

$$\frac{\Delta H_n^{lv}}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{rn}} = \frac{1.092(\ln 40.43 - 1.013)}{0.930 - 0.636} = 9.979$$

Whence, $\Delta H_n^{lv} = (9.979)(8.314)(266.9) = 22,137 \text{ J mol}^{-1}$

The latent heat at 273.15 K, or $T_r = 273.15/420.0 = 0.650$, is given by Eq. (4.13):

$$\frac{\Delta H^{lv}}{\Delta H_n^{lv}} = \left(\frac{1 - T_r}{1 - T_{rn}} \right)^{0.38}$$

or $\Delta H^{lv} = (22,137)(0.350/0.364)^{0.38} = 21,810 \text{ J mol}^{-1}$

By Eq. (6.70),

$$\Delta S^{lv} = \Delta H^{lv}/T = 21,810/273.15 = 79.84 \text{ J mol}^{-1} \text{ K}^{-1}$$

- **Step (b):** Transformation of saturated-vapor 1-butene into an ideal gas at the initial conditions (T_1, P_1). Because the pressure is relatively low, the values of H_1^R and S_1^R are estimated by Eqs. (6.87) and (6.88) for the reduced conditions, $T_r = 0.650$ and $P_r = 1.2771/40.43 = 0.0316$. The computational procedure is represented by:

$$\text{HRB}(0.650, 0.0316, 0.191) = -0.0985$$

$$\text{SRB}(0.650, 0.0316, 0.191) = -0.1063$$

Whence, $H_1^R = (-0.0985)(8.314)(420.0) = -344 \text{ J mol}^{-1}$

$$S_1^R = (-0.1063)(8.314) = -0.88 \text{ J mol}^{-1} \text{ K}^{-1}$$

As indicated in Fig. 6.7, the property changes for this step are $-H_1^R$ and $-S_1^R$, because the change is from the real to the ideal-gas state.

- **Step (c):** Changes in the ideal-gas state from (273.15 K, 1.2771 bar) to (473.15 K, 70 bar). Here, ΔH^{ig} and ΔS^{ig} are given by Eqs. (6.95) and (6.96), for which (Secs. 4.1 and 5.5):

$$\begin{aligned} 8.314 \times \text{ICPH}(273.15, 473.15; 1.967, 31.630\text{E-}3, -9.837\text{E-}6, 0.0) \\ = 20,564 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} 8.314 \times \text{ICPS}(273.15, 473.15; 1.967, 31.630\text{E-}3, -9.837\text{E-}6, 0.0) \\ = 55.474 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

Thus, Eqs. (6.95) and (6.96) yield:

$$\Delta H^{ig} = 20,564 \text{ J mol}^{-1}$$

$$\Delta S^{ig} = 55.474 - 8.314 \ln \frac{70}{1.2771} = 22.18 \text{ J mol}^{-1} \text{ K}^{-1}$$

- **Step (d):** Transformation of 1-butene from the ideal-gas state to the real-gas state at T_2 and P_2 . The final reduced conditions are:

$$T_r = 1.127$$

$$P_r = 1.731$$

At the higher pressure of this step, H_2^R and S_2^R are found by Eqs. (6.85) and (6.86), together with the Lee/Kesler correlation. With interpolated values from Tables E.7, E.8, E.11, and E.12, these equations give:

$$\frac{H_2^R}{RT_c} = -2.294 + (0.191)(-0.713) = -2.430$$

$$\frac{S_2^R}{R} = -1.566 + (0.191)(-0.726) = -1.705$$

Whence, $H_2^R = (-2.430)(8.314)(420.0) = -8,485 \text{ J mol}^{-1}$

$$S_2^R = (-1.705)(8.314) = -14.18 \text{ J mol}^{-1} \text{ K}^{-1}$$

The sums of the enthalpy and entropy changes for the four steps give the total changes for the process leading from the initial reference state (where H and S are set equal to zero) to the final state:

$$H = \Delta H = 21,810 - (-344) + 20,564 - 8,485 = 34,233 \text{ J mol}^{-1}$$

$$S = \Delta S = 79.84 - (-0.88) + 22.18 - 14.18 = 88.72 \text{ J mol}^{-1} \text{ K}^{-1}$$

The internal energy is:

$$U = H - PV = 34,233 - \frac{(70)(287.8)}{10 \text{ cm}^3 \text{ bar J}^{-1}} = 32,218 \text{ J mol}^{-1}$$

These results are in far better agreement with experimental values than would have been the case had we assumed 1-butene vapor an ideal gas.

Extension to Gas Mixtures

Although no theoretical basis exists for extension of generalized correlations to mixtures, approximate results for mixtures can often be obtained with pseudocritical parameters resulting from simple linear mixing rules according to the definitions:

$$\omega \equiv \sum_i y_i \omega_i \quad (6.88)$$

$$T_{pc} \equiv \sum_i y_i T_{c_i} \quad (6.89)$$

$$P_{pc} \equiv \sum_i y_i P_{c_i} \quad (6.90)$$

The values so obtained are the mixture ω and pseudocritical temperature and pressure, T_{pc} and P_{pc} which replace T_c and P_c , to define pseudoreduced parameters:

$$T_{pr} = \frac{T}{T_{pc}} \quad (6.91)$$

$$P_{pr} = \frac{P}{P_{pc}} \quad (6.92)$$

These replace T , and P , for reading entries from the tables of App. E,

Example 6.10

Estimate V , H^R , and S^R for an equimolar mixture of carbon dioxide(1) and propane(2) at 450 K and 140 bar by the Lee/Kesler correlations.

Solution 6.10

The pseudocritical parameters are found by Eqs. (6.97) through (6.99) with critical constants from Table B.1 of App. B:

$$\omega = y_1\omega_1 + y_2\omega_2 = (0.5)(0.224) + (0.5)(0.152) = 0.188$$

$$T_{pc} = y_1T_{c1} + y_2T_{c2} = (0.5)(304.2) + (0.5)(369.8) = 337.0 \text{ K}$$

$$P_{pc} = y_1P_{c1} + y_2P_{c2} = (0.5)(73.83) + (0.5)(42.48) = 58.15 \text{ bar}$$

$$\text{Whence, } T_{pr} = \frac{450}{337.0} = 1.335 \quad P_{pr} = \frac{140}{58.15} = 2.41$$

Values of Z^0 and Z^1 from Tables E.3 and E.4 at these reduced conditions are:

$$Z^0 = 0.697 \quad \text{and} \quad Z^1 = 0.205$$

$$\text{By Eq. (3.57), } Z = Z^0 + \omega Z^1 = 0.697 + (0.188)(0.205) = 0.736$$

$$\text{Whence, } V = \frac{ZRT}{P} = \frac{(0.736)(83.14)(450)}{140} = 196.7 \text{ cm}^3 \text{ mol}^{-1}$$

Similarly, from Tables E.7 and E.8, with substitution into Eq. (6.85):

$$\left(\frac{H^R}{RT_{pc}}\right)^0 = -1.730 \quad \left(\frac{H^R}{RT_{pc}}\right)^1 = -0.169$$

$$\frac{H^R}{RT_{pc}} = -1.730 + (0.188)(-0.169) = -1.762$$

$$\text{Whence, } H^R = (8.314)(337.0)(-1.762) = -4,937 \text{ J mol}^{-1}$$

From Tables E.11 and E.12 and substitution into Eq. (6.86),

$$\frac{S^R}{R} = -0.967 + (0.188)(-0.330) = -1.029$$

$$\text{Whence, } S^R = (8.314)(-1.029) = -8.56 \text{ J mol}^{-1} \text{ K}^{-1}$$