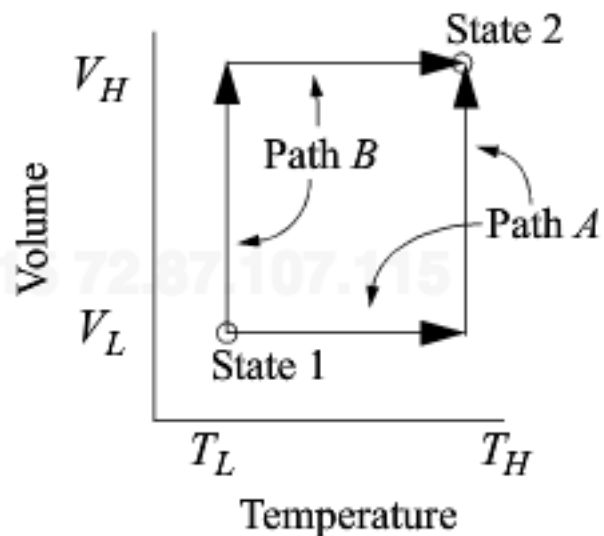


CHAPTER

**8**

**DEPARTURE FUNCTIONS**



**Figure 8.1** Comparison of two alternate paths for calculation of a change of state.

Path A:

$$\Delta U = \int C_V|_{V_L} dT + \int \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] \Big|_{T_H} dV \quad 8.3$$

or Path B:

$$\Delta U = \int C_V|_{V_H} dT + \int \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] \Big|_{T_L} dV \quad 8.4$$

## 7.7 IMPLICATIONS OF REAL FLUID BEHAVIOR

### Example 7.6 Derivatives of the Peng-Robinson equation

Determine  $\left(\frac{\partial P}{\partial T}\right)_V$ ,  $\left(\frac{\partial C_V}{\partial V}\right)_T$ , and  $\left(\frac{\partial U}{\partial V}\right)_T$  for the Peng-Robinson equation.

**Solution:** The derivatives  $(\partial U/\partial V)_T$  and  $(\partial C_V/\partial V)_T$  have been written in terms of measurable properties in Examples 6.6 and 6.9, respectively, and have been evaluated for an ideal gas. The analysis with the Peng-Robinson model provides more realistic representation of the properties of real substances. Beginning with the same analytical expressions set forth in the referenced examples, a key derivative is obtained for the Peng-Robinson equation,

$$P = \frac{RT\rho}{(1-b\rho)} - \frac{a\rho^2}{1+2b\rho-b^2\rho^2}$$

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

$$\alpha \equiv [1 + \kappa(1 - \sqrt{T_r})]^2$$

$$\kappa \equiv 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$b \equiv 0.07779607R \frac{T_c}{P_c}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R\rho}{1-b\rho} - \frac{\rho^2}{1+2b\rho-b^2\rho^2} \frac{da}{dT}$$

which approaches the ideal gas limit:  $\lim_{\rho \rightarrow 0} \left(\frac{\partial P}{\partial T}\right)_V = R\rho = \frac{R}{V}$ . The volume dependence of  $C_V$  is obtained by the second derivative:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V = \frac{-T\rho^2}{1+2b\rho-b^2\rho^2} \frac{d^2 a}{dT^2} = \frac{-\rho^2}{1+2b\rho-b^2\rho^2} \frac{a_c \kappa}{2} \left(\frac{\kappa}{T_c} + \frac{\sqrt{\alpha T_r}}{T}\right)$$

which approaches the ideal gas limit of zero at low density,

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = \frac{\rho^2}{1+2b\rho-b^2\rho^2} \left[a - \frac{da}{dT}\right] = \frac{\rho^2 a_c}{1+2b\rho-b^2\rho^2} [\alpha + \kappa \sqrt{\alpha T_r}],$$

which also approaches the ideal gas limit of zero at low density. We have thus shown that  $C_V$  depends on volume. To calculate a value of  $C_V$ , first we determine  $C_V^ig = C_V^ig - R$ , where  $C_V^ig$  is the heat capacity tabulated in Appendix E. Then, at a given  $\{P, T\}$ , the equation of state is solved for  $\rho$ . The resultant density is used as the limit in the following integrals, noting as  $V \rightarrow \infty$ ,  $\rho \rightarrow 0$ , and  $dV = -d\rho/\rho^2$ : This method is used for departures from ideal gas properties in Chapter 8.

$$C_V - C_V^ig = \int_V^{\infty} \left(\frac{\partial C_V}{\partial V}\right)_T dV = \left(\frac{d^2 a}{dT^2}\right) \int_0^{\rho} \frac{T\rho^2}{1+2b\rho-b^2\rho^2} \frac{d\rho}{\rho^2} = \frac{T}{2\sqrt{2}b} \left(\frac{d^2 a}{dT^2}\right) \ln \left[ \frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho} \right]$$

$$\text{where } \left(\frac{d^2 a}{dT^2}\right) = \frac{a_c \kappa}{2T_c^2 T_r} \left[ \kappa + \frac{\sqrt{\alpha}}{\sqrt{T_r}} \right]$$

### Example 6.6 Accounting for $T$ and $V$ impacts on energy

Derive an expression for  $\left(\frac{\partial U}{\partial V}\right)_T$  in terms of measurable properties. (a) Evaluate for the ideal gas.

(b) Evaluate for the van der Waals equation of state,  $P = RT/(V - b) - a/V$ .

**Solution:** Beginning with the fundamental relation for  $dU$ ,

$$dU = TdS - PdV$$

Applying the expansion rule

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T \quad 6.45$$

Using a Maxwell relation and a basic identity

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \quad 6.46$$

(a) For an ideal gas,  $P = RT/V$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}; \quad \left(\frac{\partial U}{\partial V}\right)_T^{ig} = \frac{RT}{V} - P = 0 \quad (\text{ig})$$

Thus, internal energy of an ideal gas does not depend on volume (or pressure) at a given  $T$ .

(b) For the van der Waals equation,

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}; \quad \left(\frac{\partial U}{\partial V}\right)_T = \frac{RT}{V-b} - \left(\frac{RT}{V-b} - \frac{a}{V^2}\right) = \frac{a}{V^2} \quad (\text{ig})$$

### Example 6.9 Volumetric dependence of $C_V$ for ideal gas

Determine how  $C_V$  depends on volume (or pressure) by deriving an expression for  $(\partial C_V / \partial V)_T$ . Evaluate the expression for an ideal gas.

**Solution:** Following hint #1 and applying Eqn. 4.30:

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

By the chain rule:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial S}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_T + T \frac{\partial}{\partial V} \left[ \left(\frac{\partial S}{\partial T}\right)_V \right]_T$$

Changing the order of differentiation:

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T \frac{\partial}{\partial T} \left[ \left(\frac{\partial S}{\partial T}\right)_V \right] = T \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

For an ideal gas,  $P = RT/V$ , we have  $\left(\frac{\partial P}{\partial T}\right)_V$  in Example 6.6:

$$\frac{\partial}{\partial T} \left[ \left(\frac{\partial P}{\partial T}\right)_V \right]_V = \frac{\partial}{\partial T} \left( \frac{R}{V} \right)_V = 0 \quad (\text{ig}) \quad 6.51$$

Thus, heat capacity of an ideal gas does not depend on volume (or pressure) at a fixed temperature. (We will reevaluate this derivative in Chapter 7 for a real fluid.)

To avoid this calculation, we devise an equivalent pathway of three stages. First, imagine if we had a magic wand to turn our fluid into an ideal gas. Second, the ideal gas state change calculations would be pretty easy. Third, at the final state we could turn our fluid back into a real fluid. **Departure functions** represent the effect of the magic wand to exchange the real fluid with an ideal gas. Being careful with signs of the terms, we may combine the calculations for the desired result:

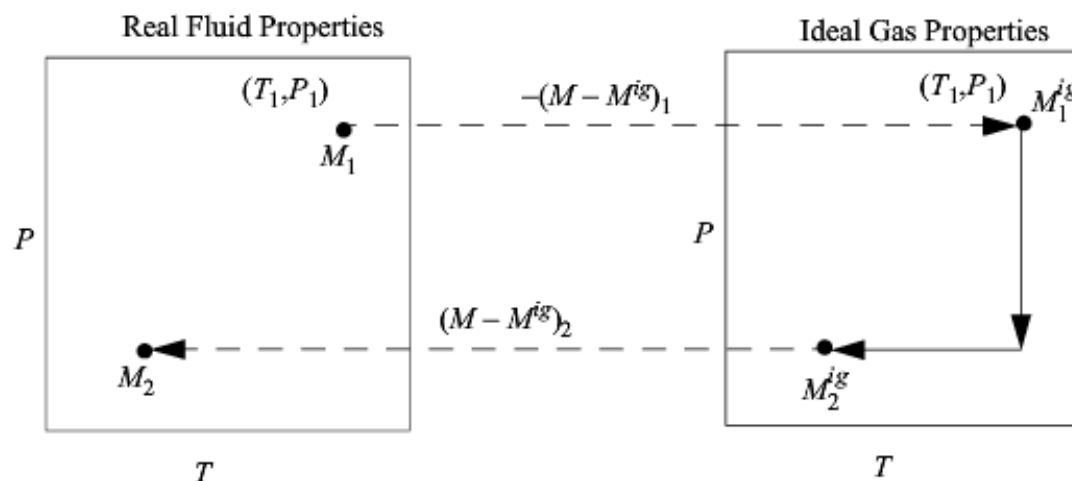
$$\Delta U = U_2 - U_1 = (U_2 - U_2^{ig}) + (U_2^{ig} - U_1^{ig}) - (U_1 - U_1^{ig}) \quad 8.5$$

The calculation can be generalized to any fundamental property from the set  $\{U, H, A, G, S\}$ , using the variable  $M$  to denote the property

$$\Delta M = M_2 - M_1 = (M_2 - M_2^{ig}) + (M_2^{ig} - M_1^{ig}) - (M_1 - M_1^{ig}) \quad 8.6$$

The steps can be seen graphically in Fig. 8.2. Note the dashed lines in the figure represent the calculations from our “magic wand” effect of turning on/off the nonidealities.

! Departure functions permit us to use the ideal gas calculations that are easy, and incorporate a departure property value for the initial and final states.

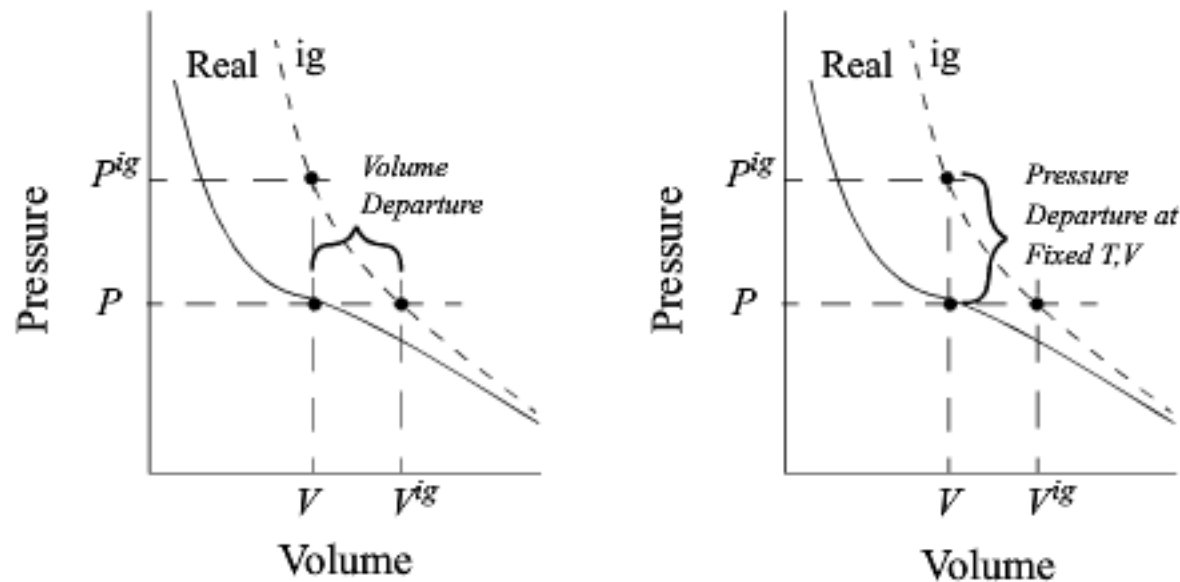


**Figure 8.2** Illustration of calculation of state changes for a generic property  $M$  using departure functions where  $M$  is  $U, H, S, G,$  or  $A$ .

$$C_P^{ig} = C_V^{ig} + R$$
$$dU^{ig} = C_V^{ig} dT \quad dH^{ig} = C_P^{ig} dT \quad dS^{ig} = (C_P^{ig}/T) dT - (R/P) dP$$

8.7

## 8.2 INTERNAL ENERGY DEPARTURE FUNCTION



**Figure 8.3** Comparison of real fluid and ideal gas isotherms at the same temperature, demonstrating the departure function, and the departure function at fixed  $T, V$ .

between the two departure characterizations. When we refer to the departure of the real fluid property and the same ideal gas property at the same  $\{T, P\}$ , we call it simply the **departure function**, and use the notation  $U - U^{ig}$ . When we compare the departure at the same  $\{T, V\}$  we call it the **departure function at fixed  $T, V$** , and designate it as  $(U - U^{ig})_{TV}$ .<sup>1</sup>

$$U(T, V) - U(T, \infty) = \int_{\infty}^V dU = \int_{\infty}^V \left( \frac{\partial U}{\partial V} \right)_T dV \quad 8.8$$

For an ideal gas:

$$U^{ig}(T, V) - U^{ig}(T, \infty) = \int_{\infty}^V dU = \int_{\infty}^V \left( \frac{\partial U}{\partial V} \right)_T^{ig} dV \quad 8.9$$

Since the real fluid approaches the ideal gas at infinite volume, we may take the difference in these two equations to find the departure function at fixed  $T, V$ ,

$$(U - U^{ig})_{TV} - \cancel{(U - U^{ig})_{T, V = \infty}} = \int_{\infty}^V \left[ \left( \frac{\partial U}{\partial V} \right)_T - \left( \frac{\partial U}{\partial V} \right)_T^{ig} \right] dV \quad 8.10$$

$$U - U^{ig} = (U - U^{ig})_{TP} = (U - U^{ig})_{TV} - (U_{TP}^{ig} - U_{TV}^{ig}) = (U - U^{ig})_{TV} - \int_V^{V^{ig}} \left( \frac{\partial U}{\partial V} \right)_T^{ig} dV \quad 8.11$$



$$U - U^{ig} = (U - U^{ig})_{TP} = (U - U^{ig})_{TV} - (U_{TP}^{ig} - U_{TV}^{ig}) = (U - U^{ig})_{TV} - \int_V^{V^{ig}} \left( \frac{\partial U}{\partial V} \right)_T^{ig} dV \quad 8.11$$

We have already solved for  $(\partial U^{ig}/\partial V)_T$  (see Example 6.6 on page 238), and found that it is equal to zero. We are fortunate in this case because the internal energy of an ideal gas does not depend on the volume. When it comes to properties involving entropy, however, the dependency on volume requires careful analysis. Then the systematic treatment developed above is quite valuable.

$$\left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \quad \text{and} \quad \left( \frac{\partial U}{\partial V} \right)_T^{ig} = 0 \quad 8.12$$

Making these substitutions, we have

$$U - U^{ig} = \int_{\infty}^V \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \quad 8.13$$

$$\frac{U - U^{ig}}{RT} = \int_0^\rho \left[ \frac{P}{\rho RT} - \frac{1}{\rho R} \left( \frac{\partial P}{\partial T} \right)_\rho \right] \frac{d\rho}{\rho} = - \int_0^\rho T \left( \frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} \quad 8.14$$

The above equation applies the chain rule in a way that may not be obvious at first:

$$T \left( \frac{\partial Z}{\partial T} \right)_V = T \left( \frac{\partial (P/\rho RT)}{\partial T} \right)_V = \frac{T}{\rho RT} \left( \frac{\partial P}{\partial T} \right)_V - \frac{PT}{R\rho T^2} \left( \frac{\partial T}{\partial T} \right)_V = \frac{1}{\rho R} \left( \frac{\partial P}{\partial T} \right)_V - Z \quad 8.15$$

1. Write the derivative of the property with respect to volume at constant  $T$ . Convert to derivatives of measurable properties using methods from Chapter 6.
2. Write the difference between the derivative real fluid and the derivative ideal gas.
3. Insert integral over  $dV$  and limits from infinite volume (where the real fluid and the ideal gas are the same) to the system volume  $V$ .
4. Add the necessary correction integral for the ideal gas from  $V$  to  $V^{ig}$ . (This will be more obvious for entropy.)
5. Transform derivatives to derivatives of  $Z$ . Evaluate the derivatives symbolically using the equation of state and integrate analytically.
6. Rearrange in terms of density and compressibility factor to make it more compact.

### Example 8.1 Internal energy departure from the van der Waals equation

Derive the internal energy departure function for the van der Waals equation. Suppose methane is compressed from 200 K and 0.1 MPa to 220 K and 60 MPa. Which is the larger contribution in magnitude to  $\Delta U$ , the ideal gas contribution or the departure function? Use  $C_p$  from the back flap and ignore temperature dependence.

$$P = \frac{RT}{V-b} - \frac{a}{V^2} = \frac{\rho RT}{1-b\rho} - a\rho^2 \quad \text{or} \quad Z = \frac{1}{(1-b\rho)} - \frac{a\rho}{RT}$$

= molar density =  $n/V$

**Solution:** For methane,  $a = 230030 \text{ J}\cdot\text{cm}^3/\text{mol}^2$  and  $b = 43.07 \text{ cm}^3/\text{mol}$  were calculated by the critical point criteria in Example 7.7 on page 271. Deriving the departure function,  $-T(dZ/dT)_\rho = -a\rho/RT$ , because the repulsive part is constant with respect to  $T$ . Substituting,

$$\frac{U - U^{ig}}{RT} = -\int_0^\rho T \left( \frac{\partial Z}{\partial T} \right)_\rho \frac{d\rho}{\rho} = -\int_0^\rho \frac{a\rho d\rho}{RT\rho} = -\frac{a}{RT} \int_0^\rho d\rho = -\frac{a\rho}{RT} \Big|_0^\rho = -\frac{a\rho}{RT}$$

Because  $T_r > 1$  there is only one real root. A quick but crude computation of  $\rho$  is to rearrange as  $Zb\rho = bP/RT = b\rho(1 - b\rho) - (a/bRT)(b\rho)^2$ .

At state 2, 220 K and 60 MPa,

$$60 \cdot 43.07 / (8.314 \cdot 220) = b\rho(1 - b\rho) - 230030 / (43.07 \cdot 8.314 \cdot 220) (b\rho)^2.$$

Taking an initial guess of  $b\rho = 0.99$  and solving iteratively gives  $b\rho = 0.7546$ , so

$$(U_2 - U_2^{ig})/RT = -230030 \cdot 0.7546 / (43.07 \cdot 8.314 \cdot 220) = -2.203.$$

At state 1, 200 K and 0.1 MPa,

$$0.1 \cdot 43.07 / (8.314 \cdot 200) = b\rho(1 - b\rho) - 230030 / (43.07 \cdot 8.314 \cdot 200) (b\rho)^2.$$

Taking an initial guess of  $b\rho = 0.99$  and solving iteratively gives  $b\rho = 0.00290$ , so

$$(U_1 - U_1^{ig})/RT = -230030 \cdot 0.00290 / (43.07 \cdot 8.314 \cdot 200) = -0.00931.$$

$$\Delta U = U_2 - U_1 = (U_2 - U_2^{ig}) + (U_2^{ig} - U_1^{ig}) - (U_1 - U_1^{ig})$$

$\Delta U = -2.203(8.314)220 + (4.3 - 1) \cdot 8.314(220 - 200) + 0.00931(8.314)200 = -4030 + 549 + 15 = -3466 \text{ J/mol}$ . The ideal gas part (549) is 14% as large in magnitude as the State 2 departure function (-4030) for this calculation. Clearly, State 2 is not an ideal gas.

### 8.3 ENTROPY DEPARTURE FUNCTION

$$S - S^{ig} = (S - S^{ig})_{TV} - \int_V^{V^{ig}} \left( \frac{\partial S}{\partial V} \right)_T^{ig} dV \quad 8.16$$

$$S - S^{ig} = \int_{\infty}^V \left[ \left( \frac{\partial S}{\partial V} \right)_T - \left( \frac{\partial S}{\partial V} \right)_T^{ig} \right] dV - \int_V^{V^{ig}} \left( \frac{\partial S}{\partial V} \right)_T^{ig} dV = \int_{\infty}^V \left[ \left( \frac{\partial P}{\partial T} \right)_V - \left( \frac{\partial P}{\partial T} \right)_V^{ig} \right] dV - \int_V^{V^{ig}} \left( \frac{\partial P}{\partial T} \right)_V^{ig} dV \quad 8.17$$

Since  $\left( \frac{\partial P}{\partial T} \right)_V^{ig} = \frac{R}{V}$ , we may readily integrate the ideal gas integral (note that this is not zero whereas the analogous equation for energy was zero):

$$S - S^{ig} = \int_{\infty}^V \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{R}{V} \right] dV + R \ln \frac{V}{V^{ig}} \quad 8.18$$

Recognizing  $V^{ig} = RT/P$ ,  $V/V^{ig} = PV/RT = Z$ ,

$$\frac{S - S^{ig}}{R} = \int_{\infty}^V \left[ \frac{1}{R} \left( \frac{\partial P}{\partial T} \right)_V - \frac{1}{V} \right] dV + \ln Z = \int_0^{\rho} \left[ -T \left( \frac{\partial Z}{\partial T} \right)_{\rho} - (Z - 1) \right] \frac{d\rho}{\rho} + \ln Z \quad 8.19$$

$$U - U^{ig} = \int_{\infty}^V \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV \quad 8.13$$

$$\frac{U - U^{ig}}{RT} = \int_0^{\rho} \left[ \frac{P}{\rho RT} - \frac{1}{\rho R} \left( \frac{\partial P}{\partial T} \right)_{\rho} \right] \frac{d\rho}{\rho} = - \int_0^{\rho} T \left( \frac{\partial Z}{\partial T} \right)_{\rho} \frac{d\rho}{\rho} \quad 8.14$$

where Eqn. 8.15 has been applied to the relation for the partial derivative of  $P$ .

! The departures for  $U$  and  $S$  are the building blocks from which the other departures can be written by combining the relations derived in the previous sections.

## 8.4 OTHER DEPARTURE FUNCTIONS

The remainder of the departure functions may be derived from the first two and the definitions,

$$H = U + PV \Rightarrow \frac{H - H^{ig}}{RT} = \frac{U - U^{ig}}{RT} + \frac{PV - RT}{RT} = \frac{U - U^{ig}}{RT} + Z - 1 \quad 8.20$$

$$A = U - TS \Rightarrow \frac{A - A^{ig}}{RT} = \frac{U - U^{ig}}{RT} - \frac{S - S^{ig}}{R}$$

where we have used  $PV^{ig} = RT$  for the ideal gas in the enthalpy departure. Using  $H - H^{ig}$  just derived,

$$\frac{G - G^{ig}}{RT} = \frac{H - H^{ig}}{RT} - \frac{S - S^{ig}}{R} \quad 8.21$$

## 8.5 SUMMARY OF DENSITY-DEPENDENT FORMULAS

Formulas for departures at fixed  $T, P$  are listed below. These formulas are useful for an equation of state written most simply as  $Z = f(T, \rho)$  such as cubic EOSs. For treating cases where an equation of state is written most simply as  $Z = f(T, P)$  such as the truncated virial EOS, see Section 8.6.

$$\frac{(U - U^{ig})}{RT} = \int_0^\rho -T \left[ \frac{\partial Z}{\partial T} \right]_\rho \frac{d\rho}{\rho} \quad 8.22$$

$$\frac{(S - S^{ig})}{R} = \int_0^\rho \left[ -T \left[ \frac{\partial Z}{\partial T} \right] - (Z - 1) \right] \frac{d\rho}{\rho} + \ln Z \quad 8.23$$

$$\frac{(H - H^{ig})}{RT} = \int_0^\rho -T \left[ \frac{\partial Z}{\partial T} \right]_\rho \frac{d\rho}{\rho} + Z - 1 \quad 8.24$$

$$\frac{(A - A^{ig})}{RT} = \int_0^\rho \frac{(Z - 1)}{\rho} d\rho - \ln Z \quad 8.25$$

$$\frac{(G - G^{ig})}{RT} = \int_0^\rho \frac{(Z - 1)}{\rho} d\rho + (Z - 1) - \ln Z \quad 8.26$$

Useful formulas at fixed  $T, V$  include:

$$\frac{(A - A^{ig})_{TV}}{RT} = \int_0^{\rho} \frac{(Z - 1)}{\rho} d\rho \quad 8.27$$

$$\frac{(S - S^{ig})_{TV}}{R} = \int_0^{\rho} \left[ -T \left[ \frac{\partial Z}{\partial T} \right]_{\rho} - (Z - 1) \right] \frac{d\rho}{\rho} \quad 8.28$$

## 8.6 PRESSURE-DEPENDENT FORMULAS

Occasionally, our equation of state is difficult to integrate to obtain departure functions using the formulas from Section 8.5. This is because the equation of state is more easily arranged and integrated in the form  $Z=f(T,P)$ , such as the truncated virial EOS. For treating cases where an equation of state is written most simply as  $Z=f(T,\rho)$  such as a cubic EOS, see Section 8.5. We adapt the procedures given earlier in Section 8.2.

1. Write the derivative of the property with respect to pressure at constant  $T$ . Convert to derivatives of measurable properties using methods from Chapter 6.
2. Write the difference between the derivative real fluid and the derivative ideal gas.
3. Insert integral over  $dP$  and limits from  $P=0$  (where the real fluid and the ideal gas are the same) to the system pressure  $P$ .
4. Transform derivatives to derivatives of  $Z$ . Evaluate the derivatives symbolically using the equation of state and integrate analytically.
5. Rearrange in terms of density and compressibility factor to make it more compact.

We omit derivations and leave them as a homework problem. The two most important departure functions at fixed  $T,P$  are

$$\left(\frac{H-H^{ig}}{RT}\right) = -\int_0^P T \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \quad 8.29$$

$$\left(\frac{S-S^{ig}}{R}\right) = -\int_0^P \left[ (Z-1) + T \left(\frac{\partial Z}{\partial T}\right)_P \right] \frac{dP}{P} \quad 8.30$$



## 8.7 IMPLEMENTATION OF DEPARTURE FORMULAS

### Example 8.2 Real entropy in a combustion engine

A properly operating internal combustion engine requires a spark plug. The cycle involves adiabatically compressing the fuel-air mixture and then introducing the spark. Assume that the fuel-air mixture in an engine enters the cylinder at 0.08 MPa and 20°C and is adiabatically and reversibly compressed in the closed cylinder until its volume is 1/7 the initial volume. Assuming that no ignition has occurred at this point, determine the final  $T$  and  $P$ , as well as the work needed to compress each mole of air-fuel mixture. You may assume that  $C_V^{ig}$  for the mixture is 32 J/mole-K (independent of  $T$ ), and that the gas obeys the equation of state,

$$PV = RT + aP$$

where  $a$  is a constant with value  $a = 187 \text{ cm}^3/\text{mole}$ . Do not assume that  $C_V$  is independent of  $\rho$ . Solve using density integrals.

**Solution:** The system is taken as a closed system of the gas within the piston/cylinder. Because there is no flow, the system is irreversible, and reversible, the entropy balance becomes

$$\frac{dS}{dt} = \sum_{in} \dot{S}^{in} \dot{m}^{in} - \sum_{out} \dot{S}^{out} \dot{m}^{out} + \frac{\dot{Q}}{T_{sys}} + \dot{S}_{gen} = 0 \quad 8.31$$

showing that the process is isentropic. To find the final  $T$  and  $P$ , we use the initial state to find the initial entropy and molar volume. Then at the final state, the entropy and molar volume are used to determine the final  $T$  and  $P$ .

This example helps us to understand the difference between departure functions at fixed  $T$  and  $V$  and departure functions at fixed  $T$  and  $P$ . The equation of state in this case is simple enough that it can be applied either way. It is valuable to note how the  $\ln(Z)$  term works out. Fixed  $T$  and  $V$  is convenient since the volume change is specified in this example, and we cover this as Method I, and then use fixed  $T$  and  $P$  as Method II.

This EOS is easy to evaluate with either the pressure integrals of Section 8.6 or the density integrals of Section 8.5. The problem statement asks us to use density integrals.<sup>a</sup> First, we need to rearrange our equation of state in terms of  $Z = f(T, \rho)$ . This rearrangement may not be immediately obvious. Note that dividing all terms by  $RT$  gives  $PV/RT = 1 + aP/RT$ . Note that  $V\rho = 1$ . Multiplying the last term by  $V\rho$ ,  $Z = 1 + aZ\rho$  which rearranges to

$$Z = \frac{1}{1 - a\rho} \quad PV = RT + aP$$

Also, we find the density at the two states using the equation of state,

$$\rho = \frac{P}{RT + aP} \Rightarrow \rho_1 = 3.257\text{E-}5 \text{ gmole/cm}^3 \Rightarrow \rho_2 = 2.280\text{E-}4 \text{ gmole/cm}^3$$

**Method I.** In terms of fixed  $T$  and  $V$ ,  $\left(\frac{\partial Z}{\partial T}\right)_\rho = 0$ ;  $Z - 1 = \frac{1}{1 - a\rho} - \frac{1 - a\rho}{1 - a\rho} = \frac{a\rho}{1 - a\rho}$

$$\frac{(S - S^{ig})_{TV}}{R} = \int_0^\rho \left[ -T \left[ \frac{\partial Z}{\partial T} \right] - (Z - 1) \right] \frac{d\rho}{\rho} = -a \int_0^\rho \frac{d\rho}{1 - a\rho} = \ln(1 - a\rho)$$

$dS^{ig} = (C_p^{ig}/T)dT - (R/P)dP$

$$\begin{aligned} S_2 - S_1 &= (S - S^{ig})_{TV,2} + (S_2^{ig} - S_1^{ig}) - (S - S^{ig})_{TV,1} \\ &= R \cdot [\ln(1 - 187 \cdot 2.28\text{E-}4) + \{(C_p/R)\ln(T_2/T_1) + \ln(V_2/V_1)\} - \ln(1 - 187 \cdot 3.257\text{E-}5)] \end{aligned}$$

$$\Delta S/R = 0 = -0.04357 + 32/8.314 \cdot \ln(T_2/293.15) - \ln(7) + 0.00611 = 0 \Rightarrow T_2 = 490.8 \text{ K}$$

## Example 8.2 Real entropy in a combustion engine (Continued)

**Method II.** In terms of  $T$  and  $P$ ,

$$\begin{aligned} \frac{(S - S^{ig})}{R} &= \int_0^{\rho} \left[ -T \left[ \frac{\partial Z}{\partial T} \right] - (Z - 1) \right] \frac{d\rho}{\rho} + \ln Z \\ &= -a \int_0^{\rho} \frac{d\rho}{1 - a\rho} + \ln Z = \ln(1 - a\rho) + \ln \left[ \frac{1}{1 - a\rho} \right] = 0 \end{aligned}$$

Since the departure is zero, it drops out of the calculations.

$S_2 - S_1 = S_2^{ig} - S_1^{ig} = C_p \ln(T_2/T_1) - R \ln(P_2/P_1)$ . However, since we are given the final volume, we need to calculate the final pressure. Note that we cannot insert the ideal gas law into the pressure ratio in the last term even though we are performing an ideal gas calculation; we must use the pressure ratio for the real gas.

$$\Delta S = C_p \ln(T_2/T_1) - R \ln \left[ \frac{RT_2}{V_2 - a} / \frac{RT_1}{V_1 - a} \right] = (C_p - R) \ln(T_2/T_1) - R \ln \left( \frac{V_1 - a}{V_2 - a} \right)$$

Now, if we rearrange, we can show that the result is the same as Method I:

$$\begin{aligned} \Delta S &= C_v \ln(T_2/T_1) + R \ln(V_2/V_1) + R \ln \left( \frac{1 - a\rho_2}{1 - a\rho_1} \right) \\ &= R \ln(1 - a\rho_2) + C_v \ln(T_2/T_1) + R \ln(V_2/V_1) - R \ln(1 - a\rho_1) \end{aligned}$$

This is equivalent to the equation obtained by Method I and  $T_2 = 490.8$  K.

$$\text{Finally, } P_2 = \frac{RT_2}{V_2 - a} = \frac{8.314(490.8)}{1/2.28 \times 10^{-4} - 187} = 0.972 \text{ MPa}$$

$$W = \Delta U = (U - U^{ig})_2 + C_v \Delta T - (U - U^{ig})_1 = 0 + C_v \Delta T - 0 = 6325 \text{ J/mole}$$

a. The solution to the problem using pressure integrals is left as homework problem 8.7.

### Example 8.3 Compression of methane using the virial equation

Methane gas undergoes a continuous throttling process from upstream conditions of 40°C and 20 bars to a downstream pressure of 1 bar. What is the gas temperature on the downstream side of the throttling device? An expression for the molar ideal gas heat capacity of methane is  $C_p = 19.25 + 0.0523 T + 1.197E-5 T^2 - 1.132E-8 T^3$ ;  $T [≡] K$ ;  $C_p [≡] J/mol-K$

The virial equation of state (Eqns. 7.6–7.10) may be used at these conditions for methane:

$$Z = 1 + BP/RT = 1 + (B^0 + \omega B^1)P_r/T_r$$

$$\text{where } B^0 = 0.083 - 0.422/T_r^{1.6} \text{ and } B^1 = 0.139 - 0.172/T_r^{4.2}$$

**Solution:** Since a throttling process is isenthalpic, the enthalpy departure will be used to calculate the outlet temperature.

$$\Delta H = 0 = H_2 - H_1 = (H_2 - H_2^{ig}) + (H_2^{ig} - H_1^{ig}) - (H_1 - H_1^{ig})$$

The enthalpy departure for the first and third terms in parentheses on the right-hand side can be calculated using Eqn. 8.29. Because  $Z(P, T)$ , we use Eqn. 8.29. For the integrand, the temperature derivative of  $Z$  is required. Recognizing  $B$  is a function of temperature only and differentiating,

$$\left(\frac{H - H^{ig}}{RT}\right) = - \int_0^P T \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P}$$

8.29

$$\left(\frac{\partial Z}{\partial T}\right)_P = 1 + \frac{P}{R} \left[ \frac{\partial (B \cdot (1/T))}{\partial T} \right]_P = \frac{P}{R} \left[ \left(\frac{1}{T}\right) \frac{dB}{dT} - \left(\frac{B}{T^2}\right) \right]$$

Inserting the derivative into Eqn 8.29,

$$\left(\frac{H - H^{ig}}{RT}\right) = \int_0^P \frac{1}{R} \left[ \left(\frac{B}{T}\right) - \frac{dB}{dT} \right] dP$$

$$\left(\frac{H - H^{ig}}{RT}\right) = \frac{P}{R} \left( \frac{B}{T} - \frac{dB}{dT} \right)$$

$$\left(\frac{S - S^{ig}}{R}\right) = - \frac{P}{R} \frac{dB}{dT}$$

$$\left(\frac{S - S^{ig}}{R}\right) = - \int_0^P \left[ (Z - 1) + T \left(\frac{\partial Z}{\partial T}\right)_P \right] \frac{dP}{P}$$

8.30

8.32

We can easily show by differentiating Eqns. 7.8 and 7.9,

$$\frac{dB^0}{dT_r} = \frac{0.6752}{T_r^{2.6}} \quad \frac{dB^1}{dT_r} = \frac{0.7224}{T_r^{5.2}}$$

Substituting the relations for  $B^0$ ,  $B^1$ ,  $dB^0/dT_r$  and  $dB^1/dT_r$  into Eqn. 8.32 for the departure functions for a pure fluid, we get

$$\left( \frac{H - H^{ig}}{RT} \right) = -P_r \left[ \frac{1.0972}{T_r^{2.6}} - \frac{0.083}{T_r} + \omega \left( \frac{0.8944}{T_r^{5.2}} - \frac{0.139}{T_r} \right) \right] \quad 8.33$$

$$\left( \frac{S - S^{ig}}{R} \right) = -P_r \left[ \frac{0.675}{T_r^{2.6}} + \omega \frac{0.722}{T_r^{5.2}} \right] \quad 8.34$$

For the initial state, 1,

$$\left( \frac{H - H^{ig}}{RT} \right) = -0.110 \quad (H - H^{ig})_1 = -287 \text{ J/mole}$$

Assuming a small temperature drop, the heat capacity will be approximately constant over the interval,  $C_p \approx 36 \text{ J/mole-K}$ .

For a throttle,  $\Delta H = 0 \Rightarrow (H - H^{ig})_2 + 36(T_2 - 40) + 287 = 0$ .

Trial and error at state 2 where  $P = 1 \text{ bar}$ ,  $T_2 = 35^\circ\text{C} \Rightarrow -13 + 36(35 - 40) + 287 = 94$ .

$$T_2 = 30^\circ\text{C} \Rightarrow -13 + 36(30 - 40) + 287 = -87$$

Interpolating,  $T_2 = 35 + (35 - 30)/(94 + 87)(-94) = 32.4^\circ\text{C}$ , another trial would show this is close.

### Example 8.4 Computing enthalpy and entropy departures from the Peng-Robinson equation

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy and entropy.

**Solution:** For propane,  $T_c = 369.8$  K;  $P_c = 4.249$  MPa;  $\omega = 0.152$ . The heat capacity coefficients are given by  $A = -4.224$ ,  $B = 0.3063$ ,  $C = -1.586E-4$ ,  $D = 3.215E-8$ . We may use the spreadsheet Preos.xlsx or PreosPropsMenu.m. If we select the spreadsheet, we can use the PROPS page to calculate thermodynamic properties. Using the m-file, we specify the species ID number in the function call to PreosPropsMenu.m and find the departures in the command window. We extract the following results:

**For State 2:**

$$\begin{array}{lll} Z = 0.889058 & V(\text{cm}^3/\text{mol}) = 1369.45 & (H - H^{lg}) (\text{J/mol}) = -1489.87 \\ (U - U^{lg}) (\text{J/mol}) = -1062.65 & & (S - S^{lg}) (\text{J/mol-K}) = -2.29246 \end{array}$$

**For State 1:**

$$\begin{array}{lll} Z = 0.957388 & V(\text{cm}^3/\text{mol}) = 6020.28 & (H - H^{lg}) (\text{J/mol}) = -400.512 \\ (U - U^{lg}) (\text{J/mol}) = -266.538 & & (S - S^{lg}) (\text{J/mol-K}) = -0.708254 \end{array}$$

Ignoring the specification of the reference state for now (refer to Example 8.8 on page 320 to see how to apply the reference state approach), divide the solution into the three stages described in Section 8.1: I. departure Function; II. ideal gas; III. departure function.

The overall solution path for  $H_2 - H_1$  is

$$\Delta H = H_2 - H_1 = (H_2 - H_2^{ig}) + (H_2^{ig} - H_1^{ig}) - (H_1 - H_1^{ig})$$

Similarly, for  $S_2 - S_1 =$

$$\Delta S = S_2 - S_1 = (S_2 - S_2^{ig}) + (S_2^{ig} - S_1^{ig}) - (S_1 - S_1^{ig})$$

The three steps that make up the overall solution are covered individually.

*Step I.* Departures at state 2 from the spreadsheet:

$$(H_2 - H_2^{ig}) = -1490 \text{ J/mol}$$

$$(S_2 - S_2^{ig}) = -2.292 \text{ J/mol-K}$$

*Step II.* State change for ideal gas: The ideal gas enthalpy change has been calculated in Example 2.5 on page 60.

$$H_2^{ig} - H_1^{ig} = 8405 \text{ J/mol}$$

The ideal gas entropy has been calculated in Example 4.6 on page 151:

$$S_2^{ig} - S_1^{ig} = 6.613 \text{ J/mol-K}$$

*Step III.* Departures at state 1 from the spreadsheet:

$$(H_1 - H_1^{ig}) = -401 \text{ J/mole}$$

$$(S_1 - S_1^{ig}) = -0.708 \text{ J/mole-K}$$

The total changes may be obtained by summing the steps of the calculation.

$$\Delta H = -1490 + 8405 + 401 = 7316 \text{ J/mole}$$

$$\Delta S = -2.292 + 6.613 + 0.708 = 5.029 \text{ J/mole-K}$$

### Example 2.5 Enthalpy change of an ideal gas: Integrating $C_p^{ig}(T)$

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy using the ideal gas law.

**Solution:** The ideal gas change is calculated via Eqn. 2.41 and is independent of pressure. The heat capacity constants are obtained from Appendix E.

$$\begin{aligned}H_2^{ig} - H_1^{ig} &= \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} (A + BT + CT^2 + DT^3) dT = \\&= A(T_2 - T_1) + \frac{B}{2}(T_2^2 - T_1^2) + \frac{C}{3}(T_2^3 - T_1^3) + \frac{D}{4}(T_2^4 - T_1^4) \\&= -4.224(463.15 - 378.15) + \frac{0.3063}{2} (463.15^2 - 378.15^2) + \\&\frac{-1.586 \times 10^{-4}}{3} (463.15^3 - 378.15^3) + \frac{3.215 \times 10^{-8}}{4} (463.15^4 - 378.15^4) = 8405 \text{ J/mol}\end{aligned}$$

### Example 4.6 Ideal gas entropy change: Integrating $C_p^{ig}(T)$

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy using the ideal gas law.

**Solution:** Because  $P$  and  $T$  are specified in each state, the ideal gas change is calculated most easily by combining an isobaric temperature step, Eqns. 4.19, and an isothermal pressure change, Eqn. 4.22. The heat capacity constants are obtained from Appendix E.

$$\begin{aligned}S_2^{ig} - S_1^{ig} &= \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} dT - R \ln \frac{P_2}{P_1}; \int_{T_1}^{T_2} \frac{C_p^{ig}}{T} dT = \int_{T_1}^{T_2} \frac{(A + BT + CT^2 + DT^3)}{T} dT \\S_2^{ig} - S_1^{ig} &= A \ln \left( \frac{T_2}{T_1} \right) + B(T_2 - T_1) + \frac{C}{2}(T_2^2 - T_1^2) + \frac{D}{3}(T_2^3 - T_1^3) - R \ln \frac{P_2}{P_1} \\&= -4.224 \ln \frac{463.15}{378.15} + 0.3063(463.15 - 378.15) + \frac{-1.586 \times 10^{-4}}{2} (463.15^2 \\&- 378.15^2) + \frac{3.215 \times 10^{-8}}{3} (463.15^3 - 378.15^3) - 8.314 \ln \frac{25}{5} = 6.613 \text{ J/mol-K}\end{aligned}$$



### Example 8.5 Enthalpy departure for the Peng-Robinson equation

Obtain a general expression for the enthalpy departure function of the Peng-Robinson equation.

**Solution:** Since the Peng-Robinson equation is of the form  $Z(T, \rho)$ , we can only solve with density integrals.

$$Z = \frac{1}{(1 - b\rho)} - \frac{(a\rho)/(RT)}{(1 + 2b\rho + (-b^2\rho^2))}$$

$$-T\left(\frac{\partial Z}{\partial T}\right)_\rho = \frac{(\rho T)/R}{(1 + 2b\rho - b^2\rho^2)} \left[ \frac{-a}{T^2} + \frac{1}{T} \left[ \frac{da}{dT} \right] \right]$$

where  $da/dT$  is given in Eqn. 7.18. Inserting,

$$-T\left(\frac{\partial Z}{\partial T}\right)_\rho = \frac{b\rho}{(1 + 2b\rho - b^2\rho^2)} \left[ \frac{-a}{bRT} - \frac{a_C \kappa \sqrt{\alpha T_r}}{bRT} \right]$$

We introduce  $F(T_r)$  as a shorthand.

$$-T\left(\frac{\partial Z}{\partial T}\right)_\rho \equiv \frac{b\rho}{(1 + 2b\rho - b^2\rho^2)} F(T_r)$$

Also,  $B \equiv bP/RT \Rightarrow b\rho = B/Z$  and  $A \equiv aP/R^2 T^2 \Rightarrow a/bRT = A/B$ . Note that the integration is simplified by integration over  $b\rho$  (see Eqn. B.34).

$$\int_0^{b\rho} \left( -T\left(\frac{\partial Z}{\partial T}\right)_\rho \right) \frac{d(b\rho)}{b\rho} = \int_0^{b\rho} \frac{b\rho}{(1 + 2b\rho - b^2\rho^2)} F(T_r) \frac{d(b\rho)}{\rho} =$$

$$\frac{F(T_r)}{\sqrt{8}} \left[ \ln \left( \frac{1 - \sqrt{2}}{1 + \sqrt{2}} \right) \left( \frac{b\rho(1 + \sqrt{2}) + 1}{b\rho(1 - \sqrt{2}) + 1} \right) \right]_0^{b\rho} = \frac{F(T_r)}{\sqrt{8}} \ln \left[ \frac{1 + (1 + \sqrt{2})b\rho}{1 + (1 - \sqrt{2})b\rho} \right]$$

$$\frac{(S - S^{ig})}{R} = \int_0^{\rho} \left[ -T \left[ \frac{\partial Z}{\partial T} \right]_{\rho} - (Z - 1) \right] \frac{d\rho}{\rho} + \ln Z \quad 8.23$$

$$\frac{(H - H^{ig})}{RT} = \int_0^{\rho} -T \left[ \frac{\partial Z}{\partial T} \right]_{\rho} \frac{d\rho}{\rho} + Z - 1 \quad 8.24$$

$$\frac{(A - A^{ig})}{RT} = \int_0^{\rho} \frac{(Z - 1)}{\rho} d\rho - \ln Z \quad 8.25$$

$$\frac{(G - G^{ig})}{RT} = \int_0^{\rho} \frac{(Z - 1)}{\rho} d\rho + (Z - 1) - \ln Z \quad 8.26$$

$$\frac{F(T_r)}{\sqrt{8}} \left[ \ln \left( \frac{1-\sqrt{2}}{1+\sqrt{2}} \right) \left( \frac{b\rho(1+\sqrt{2})+1}{b\rho(1-\sqrt{2})+1} \right) \right]^{b\rho} = \frac{F(T_r)}{\sqrt{8}} \ln \left[ \frac{1+(1+\sqrt{2})b\rho}{1+(1-\sqrt{2})b\rho} \right]$$

$$\frac{B}{Z} = \frac{\frac{bP}{RT}}{\frac{P}{\rho RT}} = b\rho \Rightarrow \int_0^{b\rho} -T \left( \frac{\partial Z}{\partial T} \right)_\rho \frac{d(b\rho)}{b\rho} = \frac{F(T_r)}{\sqrt{8}} \ln \left[ \frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B} \right]$$

$$\frac{(H-H^ig)}{RT} = Z-1 + \frac{1}{\sqrt{8}} \left( \frac{-a}{bRT} - \frac{a_c \kappa \sqrt{\alpha T_r}}{bRT} \right) \ln \left[ \frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B} \right]$$

$$\frac{(H-H^ig)}{RT} = Z-1 - \frac{A}{B\sqrt{8}} \left( 1 + \frac{\kappa \sqrt{T_r}}{\sqrt{\alpha}} \right) \ln \left[ \frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B} \right]$$

8.35

### Example 8.6 Gibbs departure for the Peng-Robinson equation

Obtain a general expression for the Gibbs energy departure function of the Peng-Robinson equation.

$$Z = \frac{1}{(1 - b\rho)} - \frac{a\rho/RT}{(1 + 2b\rho - b^2\rho^2)}$$

**Solution:** The answer is obtained by evaluating Eqn. 8.26. The argument for the integrand is

$$Z - 1 = \frac{1}{1 - b\rho} - \frac{1 - b\rho}{1 - b\rho} - \frac{(a\rho)/RT}{(1 + 2b\rho - b^2\rho^2)} = \frac{b\rho}{(1 - b\rho)} + \frac{a\rho/RT}{(1 + 2b\rho - b^2\rho^2)}$$

Evaluating the integral (similar to the integral in Example 8.5), noting again the change in integration variables,

$$\int_0^{b\rho} (Z - 1) \frac{d(b\rho)}{b\rho} = \int_0^{b\rho} \frac{d(b\rho)}{(1 - b\rho)} + \frac{a}{bRT} \int_0^{b\rho} \frac{d(b\rho)}{(1 + 2b\rho - b^2\rho^2)}$$
$$\frac{(A - A^{ig})_{T,V}}{RT} = -\ln(1 - b\rho) - \frac{a}{bRT\sqrt{8}} \ln \left[ \frac{1 + (1 + \sqrt{2})b\rho}{1 + (1 - \sqrt{2})b\rho} \right]$$

Making the result dimensionless,

$$\boxed{\frac{(G - G^{ig})}{RT} = Z - 1 - \ln(Z - B) - \frac{A}{B\sqrt{8}} \ln \left[ \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right]}$$

8.36

### Example 8.7 $U$ and $S$ departure for the Peng-Robinson equation

Derive the departure functions for internal energy and entropy of the Peng-Robinson equation. Hint: You could start with Eqns. 8.22 and 8.23, or you could use the results of Examples 8.5 and 8.6 without further integration as suggested by Eqn. 8.20 and Eqn. 8.21.

**Solution:** By Eqn. 8.20, the  $U$  departure can be obtained by dropping the “ $Z - 1$ ” term from Eqn. 8.35. We may immediately write:

$$\frac{U - U^{ig}}{RT} = -\frac{A}{B\sqrt{8}} \left( 1 + \frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \right) \ln \left[ \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \quad 8.37$$

By Eqn. 8.21, the entropy departure can be obtained by the difference between the enthalpy departure and Gibbs energy departure, available in Eqns. 8.35 and 8.36. Then, we may immediately write

$$\frac{S - S^{ig}}{R} = \ln(Z - B) - \frac{A}{B\sqrt{8}} \frac{\kappa\sqrt{T_r}}{\sqrt{\alpha}} \ln \left[ \frac{Z + (1 + \sqrt{2})B}{Z + (1 - \sqrt{2})B} \right] \quad 8.38$$

! The departures for  $U$  and  $S$  are the building blocks from which the other departures can be written by combining the relations derived in the previous sections.

## 8.4 OTHER DEPARTURE FUNCTIONS

The remainder of the departure functions may be derived from the first two and the definitions,

$$H = U + PV \Rightarrow \frac{H - H^{ig}}{RT} = \frac{U - U^{ig}}{RT} + \frac{PV - RT}{RT} = \frac{U - U^{ig}}{RT} + Z - 1 \quad 8.20$$

$$A = U - TS \Rightarrow \frac{A - A^{ig}}{RT} = \frac{U - U^{ig}}{RT} - \frac{S - S^{ig}}{R}$$

where we have used  $PV^{ig} = RT$  for the ideal gas in the enthalpy departure. Using  $H - H^{ig}$  just derived,

$$\frac{G - G^{ig}}{RT} = \frac{H - H^{ig}}{RT} - \frac{S - S^{ig}}{R} \quad 8.21$$

## 8.8 REFERENCE STATES

Therefore, to specify a reference state for a real fluid, we need to specify:

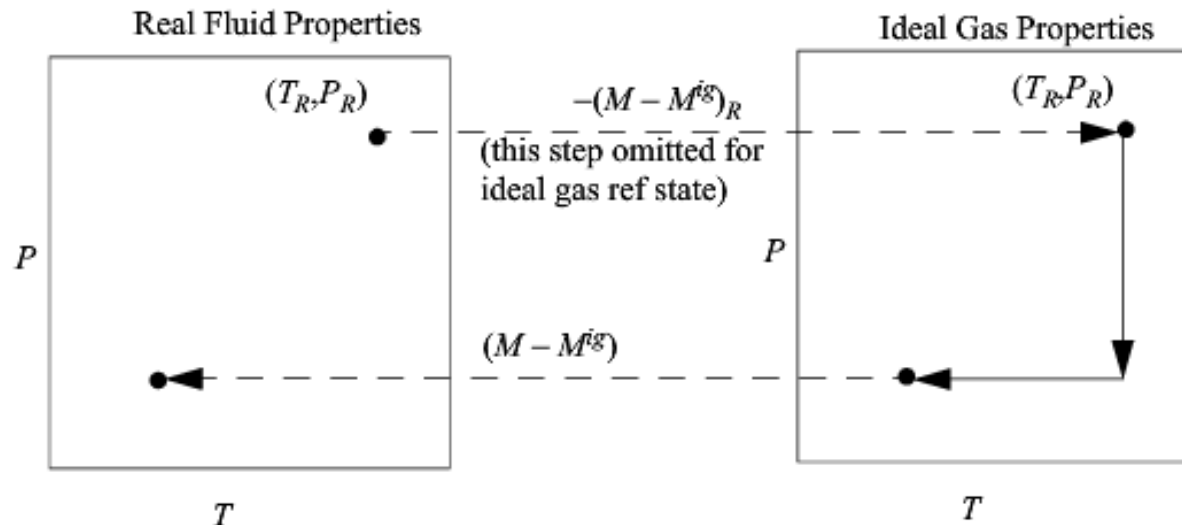
Pressure

Temperature

In addition we must specify the state of aggregation at the reference state from one of the following:

1. Ideal gas
2. Real gas
3. Liquid
4. Solid

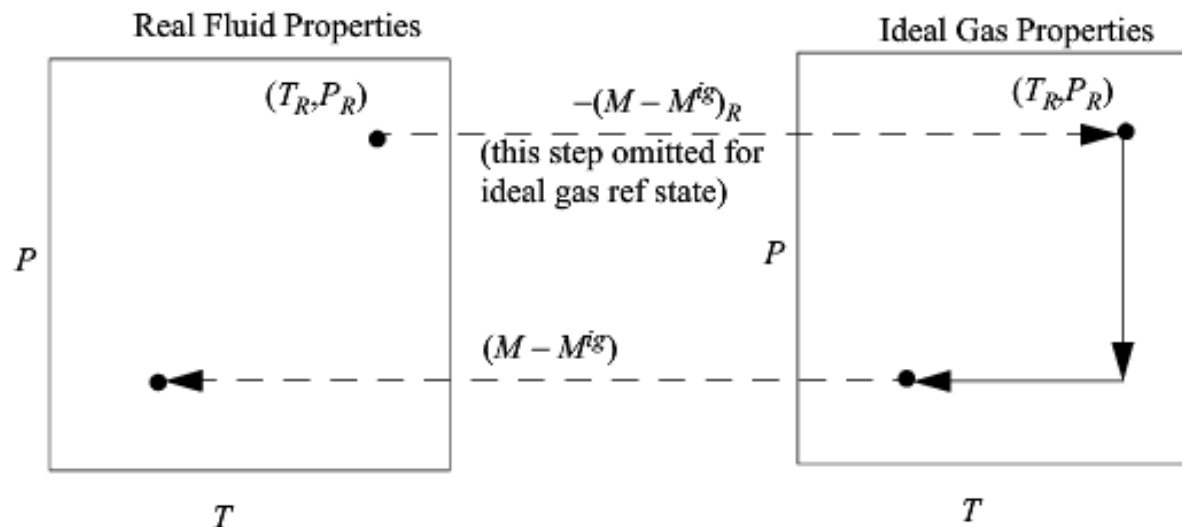
Further, we set  $S_R = 0$ , and either (*but not both*) of  $U_R$  and  $H_R$  to zero. The principle of using a reference state is shown in Fig. 8.4 and is similar to the calculation outlined in Fig. 8.2 on page 303.



**Figure 8.4** Illustration of calculation of state changes for a generic property  $M$  using departure functions where  $M$  is  $U$ ,  $H$ ,  $S$ ,  $G$ , or  $A$ . The calculations are an extension of the principles used in Fig. 8.2 where the initial state is designated as the reference state.

## 8.8 REFERENCE STATES

If we wish to calculate state changes in a property, then the reference state is not important, and all reference state information drops out of the calculation. However, if we wish to generate a chart or table of thermodynamic properties, or compare our calculations to a thermodynamic table/chart, then designation of a reference state becomes essential. Also, if we need to solve unsteady-state problems, the reference state is important because the answer may depend on the reference state as shown in Example 2.15 on page 81. The quantity  $H_R - U_R = (PV)_R$  is non-zero, and although we may substitute  $(PV)_R = RT_R$  for an ideal gas, for a real fluid we must use  $(PV)_R = Z_R RT_R$ , where  $Z_R$  has been determined at the reference state. We also may use a real fluid reference state or an ideal gas reference state. Whenever we compare our calculations with a thermodynamic chart/table, we must take into consideration any differences between our reference state and that of the chart/table.



**Figure 8.4** Illustration of calculation of state changes for a generic property  $M$  using departure functions where  $M$  is  $U$ ,  $H$ ,  $S$ ,  $G$ , or  $A$ . The calculations are an extension of the principles used in Fig. 8.2 where the initial state is designated as the reference state.



### Example 2.15 Adiabatic expansion of an ideal gas from a leaky tank

An ideal gas is leaking from an insulated tank. Relate the change in temperature to the change in pressure for gas leaking from a tank. Derive an equation for  $\Delta U$  for the tank.

**Solution:** Let us choose our system as the gas in the tank at any time. This will be an open, unsteady-state system. There is no inlet stream and one outlet stream. The mass balance gives  $dn = -dn^{out}$ .

We can neglect kinetic and potential energy changes. Although the gas is expanding, the system size remains unchanged, and there is no expansion/contraction work. The energy balance becomes (on a molar basis):

$$d(nU) = H^{in} dn^{in} - H^{out} dn^{out} + d\dot{Q} + d\dot{W}_{EC} + d\dot{W}_S$$

Since the enthalpy of the exit stream matches the enthalpy of the tank,  $H^{out} = H$ .  $d(nU) = -H^{out} dn^{out} = Hdn$ . Now  $H$  depends on temperature, which is changing, so we are not able to apply hint 4(a) from the problem-solving strategy. It will be necessary to combine terms before integrating. By the product rule of differentiation, the left-hand side expands to  $d(nU) = ndU + Udn$ . Collecting terms in the energy balance,

$$ndU = (H - U)dn$$

Performing some substitutions, the energy balance can be written in terms of  $T$  and  $n$ ,

$$(H - U) = PV = RT; \quad dU = C_V dT; \quad \Rightarrow \frac{C_V}{R} \frac{dT}{T} = \frac{dn}{n} \quad (\text{ig})$$

$$\boxed{\frac{C_V}{R} \ln \frac{T}{T^i} = \ln \frac{n}{n^i}} \quad (\text{*ig})$$

The volume of the tank is constant, ( $V = \text{constant}$ ); therefore,

$$\ln \frac{n}{n^i} = \ln \frac{PT^i}{T^i P^i} = -\ln \frac{T}{T^i} + \ln \frac{P}{P^i} = \frac{C_V}{R} \ln \frac{T}{T^i} \quad (\text{ig})$$

substituting,

$$\left(\frac{C_V}{R} + 1\right) \ln \frac{T}{T^i} = \frac{C_P}{R} \ln \frac{T}{T^i} = \ln \frac{P}{P^i} \quad (\text{*ig})$$

### Example 2.15 Adiabatic expansion of an ideal gas from a leaky tank (Continued)

Recognizing the relation between  $C_V$  and  $C_P$ , defining  $\gamma \equiv C_P/C_V (=1.4$  for an ideal diatomic gas), note  $R/C_P = (C_P - C_V)/C_P = 1 - (1/\gamma) = (\gamma - 1)/\gamma$ :

$$\boxed{\frac{T}{T^i} = \left(\frac{P}{P^i}\right)^{R/C_P} = \left(\frac{P}{P^i}\right)^{(1-(1/\gamma))}} \quad (\text{*ig}) 2.71$$

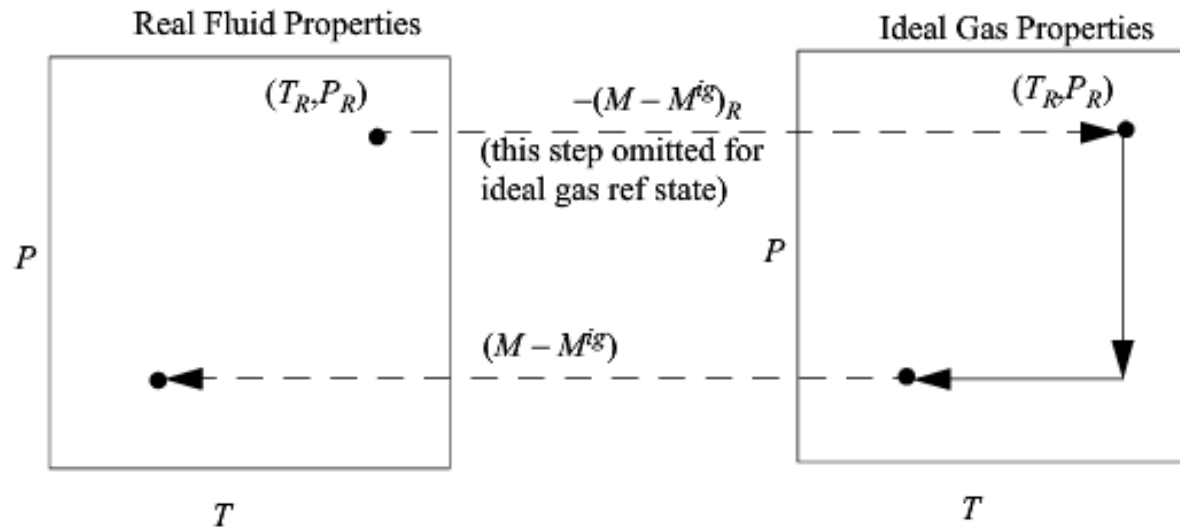
Through the ideal gas law ( $PV = RT$ ), we can obtain other arrangements of the same formula.

$$V/V^i = \left(\frac{P^i}{P}\right)^{1/\gamma}; \quad P^i/P = (V/V^i)^\gamma = (T^i/T)^{(1/\gamma)-1}; \quad T^i/T = (V/V^i)^{\gamma/(\gamma-1)} \quad (\text{*ig}) 2.72$$

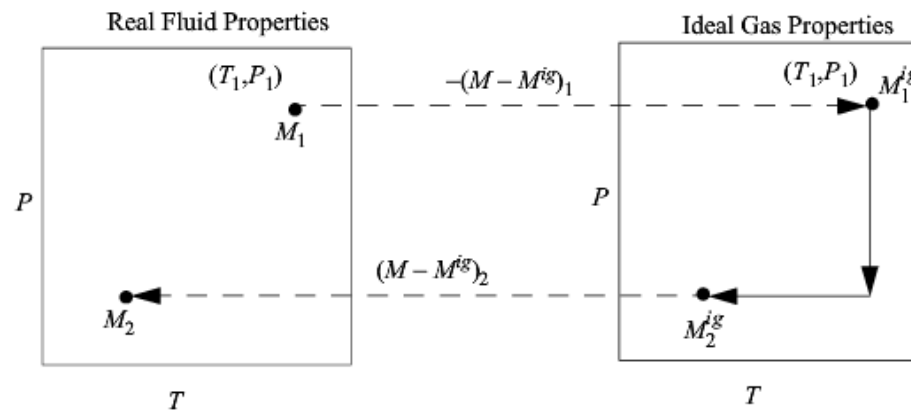
The numerical value for the change in internal energy of the system depends on the reference state because the reference state temperature will appear in the result:

$$\Delta U = n^f(C_V(T^f - T_R) + U_R) - n^i(C_V(T^i - T_R) + U_R) \quad (\text{*ig})$$

## 8.8 REFERENCE STATES



**Figure 8.4** Illustration of calculation of state changes for a generic property  $M$  using departure functions where  $M$  is  $U$ ,  $H$ ,  $S$ ,  $G$ , or  $A$ . The calculations are an extension of the principles used in Fig. 8.2 where the initial state is designated as the reference state.



**Figure 8.2** Illustration of calculation of state changes for a generic property  $M$  using departure functions where  $M$  is  $U$ ,  $H$ ,  $S$ ,  $G$ , or  $A$ .

## Ideal Gas Reference States

For an ideal gas reference state, to calculate a value for enthalpy, we have

$$H = (H - H^{ig})_{T,P} + \int_{T_R}^T C_P dT + H_R^{ig} \quad 8.39$$

$$S = (S - S^{ig})_{T,P} + \int_{T_R}^T \frac{C_P}{T} dT - R \ln \frac{P}{P_R} + S_R^{ig} \quad 8.40$$

where the reference state value,  $S_R^{ig}$ , may be set to zero. From these results we may calculate other

## Real Fluid Reference State

For a real fluid reference state, to calculate a value for enthalpy, we adapt the procedure of Eqn. 8.5:

$$H = (H - H^{ig})_{T,P} + \int_{T_R}^T C_P dT - (H - H^{ig})_R + H_R \quad 8.41$$

For entropy:

$$S = (S - S^{ig})_{T,P} + \int_{T_R}^T \frac{C_P}{T} dT - R \ln \frac{P}{P_R} - (S - S^{ig})_R + S_R \quad 8.42$$

## Changes in State Properties

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$$\Delta H = (H - H^{ig})_{T_2, P_2} + \int_{T_1}^{T_2} C_P dT - (H - H^{ig})_{T_1, P_1} \quad 8.43$$

To calculate entropy changes:

$$\Delta S = (S - S^{ig})_{T_2, P_2} + \int_{T_1}^{T_2} \frac{C_P}{T} dT - R \ln \frac{P_2}{P_1} - (S - S^i)^{ig}_{T_1, P_1} \quad 8.44$$

### Example 8.8 Enthalpy and entropy from the Peng-Robinson equation

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy and entropy. What fraction of the total change is due to the departure functions at 190°C? The departures have been used in Example 8.4, but now we can use the property values directly.

**Solution:** For propane,  $T_c = 369.8$  K;  $P_c = 4.249$  MPa; and  $\omega = 0.152$ . The heat capacity coefficients are given by  $A = -4.224$ ,  $B = 0.3063$ ,  $C = -1.586E-4$ , and  $D = 3.215E-8$ . For Preos.xlsx, we can use the “Props” page to specify the critical constants and heat capacity constants. The reference state is specified on the companion spreadsheet “Ref State.” An arbitrary choice for the reference state is the liquid at 230 K and 0.1 MPa. Returning to the PROPS worksheet and specifying the desired temperature and pressure gives the thermodynamic properties for  $V, U, H$ , and  $S$ .

State	$T$ (K)	$P$ (MPa)	$V$ (cm <sup>3</sup> /mole)	$U$ (J/mole)	$H$ (J/mole)	$S$ (J/mole-K)
2	463.15	2.5	1369	33478	36902	109.15
1	378.15	0.5	6020	26576	29587	104.13

The changes in the thermodynamic properties are  $\Delta H = 7315$  J/mole and  $\Delta S = 5.024$  J/mole-K, identical to the more tediously determined values of Example 8.4 on page 314. The purpose of computing the fractional change due to departure functions is to show that we understand the roles of the departure functions and how they fit into the overall calculation. For the enthalpy, the appropriate fraction of the total change is 20%, for the entropy, 46%.

### Example 8.4 Computing enthalpy and entropy departures from the Peng-Robinson equation

Propane gas undergoes a change of state from an initial condition of 5 bar and 105°C to 25 bar and 190°C. Compute the change in enthalpy and entropy.

**Solution:** For propane,  $T_c = 369.8$  K;  $P_c = 4.249$  MPa;  $\omega = 0.152$ . The heat capacity coefficients are given by  $A = -4.224$ ,  $B = 0.3063$ ,  $C = -1.586E-4$ ,  $D = 3.215E-8$ . We may use the spreadsheet Preos.xlsx or PreosPropsMenu.m. If we select the spreadsheet, we can use the PROPS page to calculate thermodynamic properties. Using the m-file, we specify the species ID number in the function call to PreosPropsMenu.m and find the departures in the command window. We extract the following results:

**For State 2:**

$$\begin{array}{llll} Z = 0.889058 & V(\text{cm}^3/\text{mol}) = 1369.45 & (H - H^{ig})(\text{J/mol}) = & -1489.87 \\ (U - U^{ig})(\text{J/mol}) = & -1062.65 & (S - S^{ig})(\text{J/mol-K}) = & -2.29246 \end{array}$$

**For State 1:**

$$\begin{array}{llll} Z = 0.957388 & V(\text{cm}^3/\text{mol}) = 6020.28 & (H - H^{ig})(\text{J/mol}) = & -400.512 \\ (U - U^{ig})(\text{J/mol}) = & -266.538 & (S - S^{ig})(\text{J/mol-K}) = & -0.708254 \end{array}$$

Ignoring the specification of the reference state for now (refer to Example 8.8 on page 320 to see how to apply the reference state approach), divide the solution into the three stages described in Section 8.1: I. departure Function; II. ideal gas; III. departure function.

The overall solution path for  $H_2 - H_1$  is

$$\Delta H = H_2 - H_1 = (H_2 - H_2^{ig}) + (H_2^{ig} - H_1^{ig}) - (H_1 - H_1^{ig})$$

Similarly, for  $S_2 - S_1 =$

$$\Delta S = S_2 - S_1 = (S_2 - S_2^{ig}) + (S_2^{ig} - S_1^{ig}) - (S_1 - S_1^{ig})$$

The three steps that make up the overall solution are covered individually.

*Step I.* Departures at state 2 from the spreadsheet:

$$(H_2 - H_2^{ig}) = -1490 \text{ J/mol}$$

$$(S_2 - S_2^{ig}) = -2.292 \text{ J/mol-K}$$

*Step II.* State change for ideal gas: The ideal gas enthalpy change has been calculated in Example 2.5 on page 60.

$$H_2^{ig} - H_1^{ig} = 8405 \text{ J/mol}$$

The ideal gas entropy has been calculated in Example 4.6 on page 151:

$$S_2^{ig} - S_1^{ig} = 6.613 \text{ J/mol-K}$$

*Step III.* Departures at state 1 from the spreadsheet:

$$(H_1 - H_1^{ig}) = -401 \text{ J/mole}$$

$$(S_1 - S_1^{ig}) = -0.708 \text{ J/mole-K}$$

The total changes may be obtained by summing the steps of the calculation.

$$\Delta H = -1490 + 8405 + 401 = 7316 \text{ J/mole}$$

$$\Delta S = -2.292 + 6.613 + 0.708 = 5.029 \text{ J/mole-K}$$

### Example 8.9 Liquefaction revisited

Reevaluate the liquefaction of methane considered in Example 5.5 on page 213 utilizing the Peng-Robinson equation. Previously the methane chart was used. Natural gas, assumed here to be pure methane, is liquefied in a simple Linde process. The process is summarized in Fig. 8.5. Compression is to 60 bar, and precooling is to 300 K. The separator is maintained at a pressure of 1.013 bar and unliquefied gas at this pressure leaves the heat exchanger at 295 K. What fraction of the methane entering the heat exchanger is liquefied in the process?

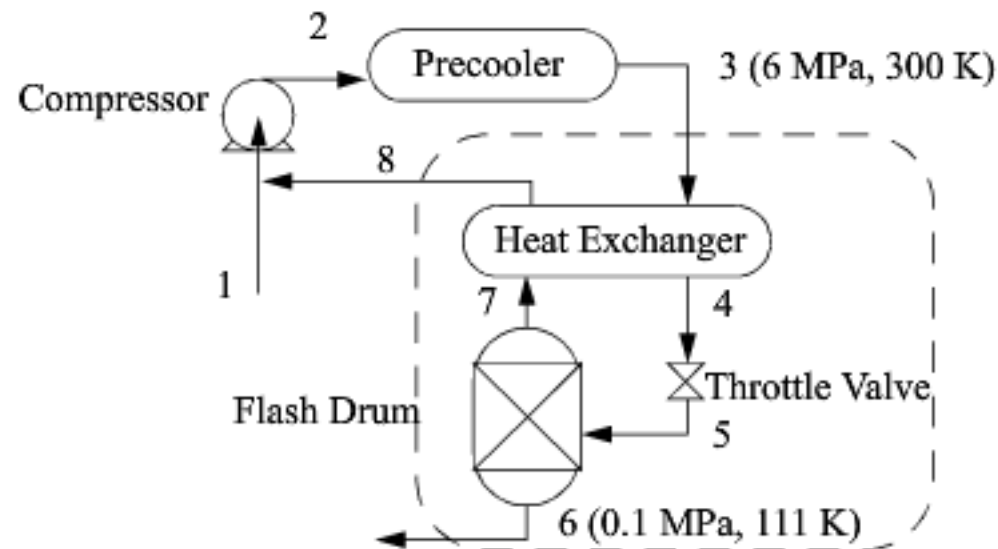


Figure 8.5 Linde liquefaction schematic.

### Example 5.5 Liquefaction of methane by the Linde process

Methane is to be liquefied in a simple Linde process. The feed and recycle are mixed, compressed to 60 bar, and precooled to 300 K. The vapor then passes through a heat exchanger for additional cooling before being throttled to 1 bar. The unliquefied fraction leaves the separator at the saturation temperature, and passes through the heat exchanger, then exits at 295 K. (a) What fraction of the gas is liquefied in the process; and (b) what is the temperature of the high-pressure gas entering the throttle valve?

**Solution:** The schematic is shown in Fig. 5.12. To solve this problem, first recognize that states 3, 6, 7, and 8 are known. State 3 is at 300 K and 60 bar; state 6 is saturated liquid at 1 bar; state 7 is saturated vapor at 1 bar; and state 8 is at 295 K and 1 bar. Use the furnished methane chart from Appendix E.

(a) The System I energy balance is:  $H_3 - [qH_8 + (1 - q)H_6] = 0$

$$\Rightarrow q = \frac{H_3 - H_6}{H_8 - H_6} = \frac{H(60, 300) - H(1, satL)}{H(1, 295) - H(1, satL)} = \frac{1130 - 284}{1195 - 284} = 0.9286 \Rightarrow 7.14\% \text{ liquefied}$$

(b) The energy balance for System II is:  $H_4 - H_3 = -q(H_8 - H_7) = -0.9286(1195 - 796.1)$   
 $= -370.5 \Rightarrow H_4 = 780$

$$\Rightarrow H_4 = 780 @ 60 \text{ bar} \Rightarrow \text{chart gives } -95^\circ\text{F} = 203 \text{ K}$$

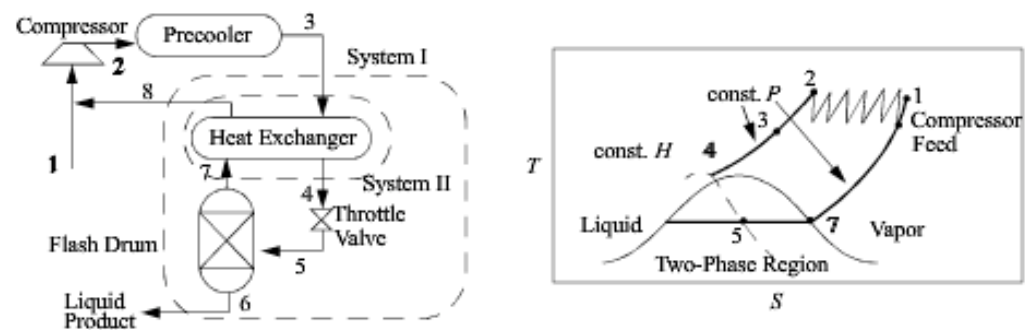


Figure 5.12 Linde liquefaction process schematic. The system boundaries shown on the left are used in Example 5.5.



State 8							
Current State		Roots		Stable Root has a lower fugacity			
T (K)	295	Z	V	fugacity	H	U	S
P (MPa)	0.1013	cm <sup>3</sup> /gmol		MPa	J/mol	J/mol	J/molK
& for 1 root region		0.9976741	24156.607	0.101064	883.5888	-1563.476	35.86881

State 6							
Current State		Roots		Stable Root has a lower fugacity			
T (K)	111	Z	V	fugacity	H	U	S
P (MPa)	0.1013	cm <sup>3</sup> /gmol		MPa	J/mol	J/mol	J/molK
answers for three root region		0.9666276	8806.5826	0.09802	-4736.595	-5628.701	6.759068
		0.0267407	243.62412		-6972.974	-6997.653	-26.6613
		0.0036925	33.640918	0.093712	-12954.48	-12957.88	-66.90221

State 8			
Results			
methane			
T(K)	295	P(MPa)	0.1013
Z			0.997674
V (cm <sup>3</sup> /mol)			24156.1
U (J/mol)			-1563.48
H (J/mol)			883.589
S (J/mol-K)			35.8688
fugacity (MPa)			0.101064

State 6			
Results			
methane			
T(K)	111	P(MPa)	0.1013
Z			0.966628 0.00369249
V (cm <sup>3</sup> /mol)			8806.4 33.6402
U (J/mol)			-5628.7 -12957.9
H (J/mol)			-4736.59 -12954.5
S (J/mol-K)			6.75907 -66.9023
fugacity (MPa)			0.0980197 0.0937095

**Figure 8.6** Summary of enthalpy calculations for methane as taken from the files *Preos.xlsx* (above) and *PreosPropsMenu.m* below.

**Solution:** Before we calculate the enthalpies of the streams, a reference state must be chosen. The reference state is arbitrary. Occasionally, an energy balance is easier to solve by setting one of the enthalpies to zero by selecting a stream condition as the reference state. To illustrate the results let us select a reference state of  $H = 0$  at the real fluid at the state of Stream 3 (6 MPa and 300 K). Because state 3 is the reference state, the  $H_3 = 0$ . The results of the calculations from the Peng-Robinson equation are summarized in Fig. 8.6.

The fraction liquefied is calculated by the energy balance:  $m_3 H_3 = m_8 H_8 + m_6 H_6$ ; then incorporating the mass balance:  $H_3 = (1 - m_6/m_3)H_8 + (m_6/m_3)H_6$ .

The throttle valve is isenthalpic (see Section 2.13). The flash drum serves to disengage the liquid and vapor exiting the throttle valve. The fraction liquefied is  $(1 - q) = m_6/m_3 = (H_3 - H_8)/(H_6 - H_8) = (0 - 883)/(-12,954 - 883) = 0.064$ , or 6.4% liquefied. This is in good agreement with the value obtained in Example 5.5 on page 213.

### Example 8.10 Adiabatically filling a tank with propane

Propane is available from a reservoir at 350 K and 1 MPa. An evacuated cylinder is attached to the reservoir manifold, and the cylinder is filled adiabatically until the pressure is 1 MPa. What is the final temperature in the cylinder?

**Solution:** The critical properties, acentric factor and heat capacity constants, are entered on the “Props” page of Preos.xlsx. On the “Ref State” page, the reference state is arbitrarily selected as the real vapor at 298 K and 0.1 MPa, and  $H_R = 0$ . At the reservoir condition, propane is in the one-root region with  $Z = 0.888$ ,  $H = 3290$  J/mol,  $U = 705$  J/mol, and  $S = -7.9766$  J/mol-K. The same type of problem has been solved for an ideal gas in Example 2.16 on page 82; however, in this example the ideal gas law cannot be used. The energy balance reduces to  $U^f = H^{in}$ , where  $H^{in} = 3290$  J/mol. In Excel, the answer is easily found by using Solver to adjust the temperature on the “Props” page until  $U = 3290$  J/mol. The converged answer is 381 K. In MATLAB, the dialog boxes can be used to match  $U = 3290$  J/mol by adjusting  $T$ . In the MATLAB window, note that the final  $T$  is shown in the “Results” box. The initial guess is preserved in the upper left.

Current State		Roots		Stable Root has a lower fugacity			
T (K)		Z	V	fugacity	H	U	S
P (MPa)		cm <sup>3</sup> /gmol		MPa	J/mol	J/mol	J/molK
	381.365167	0.9153077	2902.3034	0.920298	6192.303	3290	-0.039259
& for 1 root region							

T(K)

P(MPa)

Root to use

large Z

small Z

For Matching U, H, S, or Saturation

adjust T

Value to match:

Run Type

No Matching, use specified T,P

Match U

Match H

Match S

Find Saturation

User Objective, Adjust T and P

The fluid is specified by editing PreosProps.m. Save the file, and then fill in the information here.

Results

propane

T(K)	381.365	P(MPa)	1
Z	0.915308		
V (cm <sup>3</sup> /mol)	2902.24		
U (J/mol)	3290		
H (J/mol)	6192.3		
S (J/mol-K)	-0.0392589		
fugacity (MPa)	0.920298		
User Objective	-6.36649e-012		

### Example 2.16 Adiabatically filling a tank with an ideal gas

Helium at 300 K and 3000 bar is fed into an evacuated cylinder until the pressure in the tank is equal to 3000 bar. Calculate the final temperature of the helium in the cylinder ( $C_p/R = 5/2$ ).

**Solution:** The system will be the gas inside the tank at any time. The system will be an open, unsteady-state system. The mass balance is  $dn = dn^{in}$ . The energy balance becomes:

$$d(nU) = H^{in} dn^{in} - H^{out} dn^{out} + d\dot{Q} + d\dot{W}_{EC} + d\dot{W}_S$$

We recognize that  $H^{in}$  will be constant throughout the tank filling. Therefore, by hint 4a from the problem-solving strategy, we can integrate terms individually. We need to be careful to keep the superscript since the incoming enthalpy is at a different state than the system. The right-hand side of the energy balance can be integrated to give

$$\int_i^f H^{in} dn = H^{in} \int_i^f dn = H^{in} (n^f - n^i) = H^{in} n^f$$

The left-hand side of the energy balance becomes

$$\Delta(U_n) = U^f n^f - U^i n^i = U^f n^f$$

Combining the result with the definition of enthalpy,

$$U^f = H^{in} = U^{in} + PV^{in} = U^{in} + RT^{in} \quad (\text{ig}) \quad 2.73$$

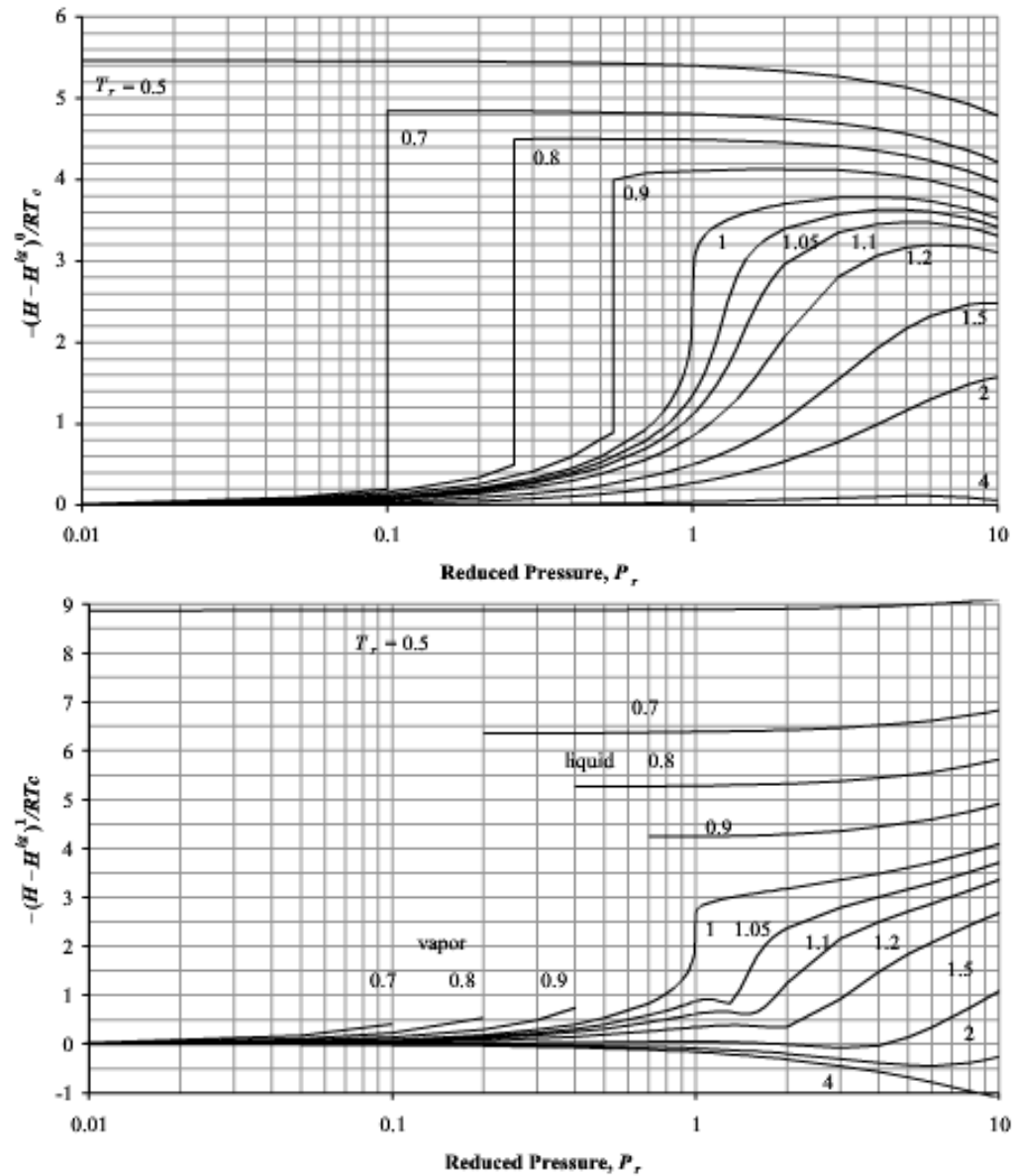
And with our definition of heat capacity, we can find temperatures:

$$\Delta U = C_v(T^f - T^{in}) = RT^{in} \Rightarrow T^f = T^{in}(R + C_v)/C_v = T^{in}C_p/C_v \quad (*\text{ig})$$

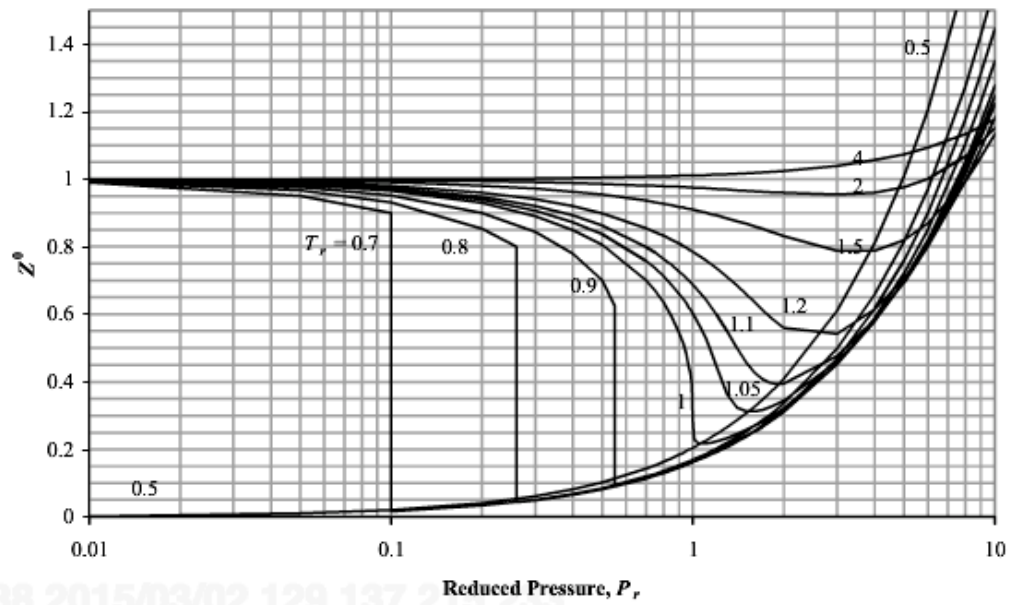
Note that the final temperature is independent of pressure for the case considered here.

## 8.9 GENERALIZED CHARTS FOR THE ENTHALPY DEPARTURE

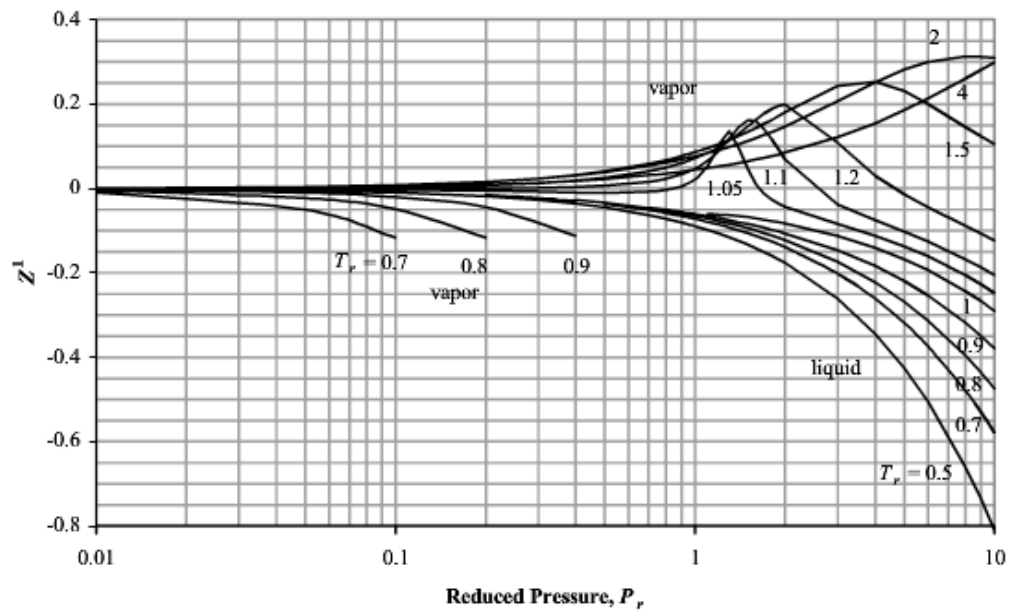
As in the case of the compressibility factor, it is often useful to have a visual idea of how generalized properties behave. Fig. 8.7 on page 324 is analogous to the compressibility factor charts from the previous chapter except that the formula for enthalpy is  $(H - H^{ig}) = (H - H^{ig})^0 + \omega(H - H^{ig})^1$ . Note that one primary influence in determining the liquid enthalpy departure is the heat of vaporization. Also, the subcritical isotherms shift to liquid behavior at lower pressures when the saturation pressures are lower. The enthalpy departure function is somewhat simpler than the compressibility factor in that the isotherms do not cross one another. Note that the temperature used to make the departure dimensionless is  $T_c$ . A sample calculation for propane at 463.15 K and 2.5 MPa gives  $H^{ig} - H = [0.45 + 0.152(0.2)] (8.314) 369.8 = 1480$  J/mole compared to 1489.2 from the Peng-Robinson equation.



**Figure 8.7** Generalized charts for estimating  $(H - H^0)/RT_c$  using the Lee-Kesler equation of state.  $(H - H^0)/RT_c$  uses  $\omega = 0.0$ , and  $(H - H^1)/RT_c$  is the correction factor for a hypothetical compound with  $\omega = 1.0$ . Divide by reduced temperature to obtain the enthalpy departure function.



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**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.