8 Thermodynamic properties of real gases

Learning Objectives

This chapter will enable readers to

- estimate the thermodynamic properties of an ideal gas in terms of P, v, T and C_p^0;
- define enthalpy, entropy and other departure functions;
- calculate the departure functions from a knowledge of the equation of state of a fluid;
- calculate the departure functions from generalized RK, SRK and PR equations of state;
- calculate the departure functions using Edmister charts;
- extend the Lee–Kesler method for the prediction of departure functions;
- calculate the departure functions using Lee–Kesler data;
- calculate the departure functions from generalized virial coefficient correlation;
- calculate the required thermodynamic properties of a real gas from the ideal gas heat capacity and P–v–T data only; and
- construct thermodynamic property tables and diagrams;

The relationships between the nonmeasurable and measurable properties discussed in Chapter 7 are valid for any substance and the required properties can be estimated in terms of the measurable quantities P, v, T, C_p, C_v, β and κ. In this chapter, the estimation of enthalpy and entropy of a real gas is discussed. Before we discuss the estimation of the properties of a real gas, let us study the properties of an ideal gas.

8.1 Thermodynamic properties of an ideal gas

The change in the internal energy, enthalpy and entropy of a system can be estimated from the relations

$$du = C_v dT + \left(\frac{T\beta}{\kappa} - P\right) dv \tag{7.58}$$

$$dh = C_p dT + v(1 - \beta T)dP \tag{7.64}$$

$$ds = C_v \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_v dv \tag{7.67}$$

or $\quad ds = C_p \dfrac{dT}{T} - \left(\dfrac{\partial v}{\partial T}\right)_P dP \qquad$ [See Example 7.3]

For an ideal gas:

$$\beta = \frac{1}{T}; \quad \kappa = \frac{1}{P}; \quad \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v} \quad \text{and} \quad \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

$$\therefore \quad \left(\frac{\partial u}{\partial v}\right)_T = \frac{T\beta}{\kappa} - 1 = 0 \quad \text{and} \quad \left(\frac{\partial u}{\partial P}\right)_T = \left(\frac{\partial u}{\partial v}\right)_T \left(\frac{\partial v}{\partial P}\right)_T = 0$$

or $u = u(T)$ only. Hence $du = C_v dT$.

$$\left(\frac{\partial h}{\partial P}\right)_T = v(1 - \beta T) = 0 \quad \text{and} \quad \left(\frac{\partial h}{\partial v}\right)_T = \left(\frac{\partial h}{\partial P}\right)_T \left(\frac{\partial P}{\partial v}\right)_T = 0$$

or $h = h(T)$ only. Hence $dh = C_p dT$

$$ds = C_v \frac{dT}{T} + R\frac{dv}{v} = C_p \frac{dT}{T} - R\frac{dP}{P}$$

Thus for an ideal gas

$$u_2^0 - u_1^0 = \int_{T_1}^{T_2} C_v^0 dT \tag{8.1}$$

$$h_2^0 - h_1^0 = \int_{T_1}^{T_2} C_p^0 dT \tag{8.2}$$

$$s_2^0 - s_1^0 = \int_{T_1}^{T_2} C_v^0 \frac{dT}{T} + R\ln\frac{v_2}{v_1} \tag{8.3}$$

or $$s_2^0 - s_1^0 = \int_{T_1}^{T_2} C_p^0 \frac{dT}{T} - R\ln\frac{P_2}{P_1} \tag{8.4}$$

where the superscript zero indicates the ideal gas properties. It can be observed from Eqns.8.1–8.4 that the properties of an ideal gas can be estimated from a knowledge of the heat capacities, and P, v, T data.

8.2   Departure functions

Suppose it is required to estimate the changes in enthalpy or entropy of a real gas when it changes from the initial state P_1, v_1, T_1 to the final state P_2, v_2, T_2. Since the change in the property (h or s) is independent of the path, one can choose a convenient path connecting the given initial and final states to estimate the change in the property. To illustrate the convenient paths, let us consider the evaluation of enthalpy change. We can consider

$$h = h(T, P)$$

Then $dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$ \hfill (7.60)

Equation 7.60 can be integrated from (P_1, T_1) to (P_2, T_2) by two different paths as given below.

$$h_2 - h_1 = \int_{T_1}^{T_2} \left(\frac{\partial h}{\partial T}\right)_{P_1} dT + \int_{P_1}^{P_2} \left(\frac{\partial h}{\partial P}\right)_{T_2} dP \tag{8.5}$$

$$h_2 - h_1 = \int_{P_1}^{P_2} \left(\frac{\partial h}{\partial P}\right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial h}{\partial T}\right)_{P_2} dT \tag{8.6}$$

The path followed in Eqn.8.5 is isobaric heating (cooling) from T_1 to T_2 at P_1 followed by isothermal compression (expansion) from P_1 to P_2 at T_2. This path is shown as ABC in Fig.8.1 on the pressure versus temperature diagram. The path followed in Eqn.8.6 is isothermal compression (expansion) from P_1 to P_2 at T_1 followed by isobaric heating (cooling) from T_1 to T_2 at P_2 as shown by ADC in Fig.8.1.
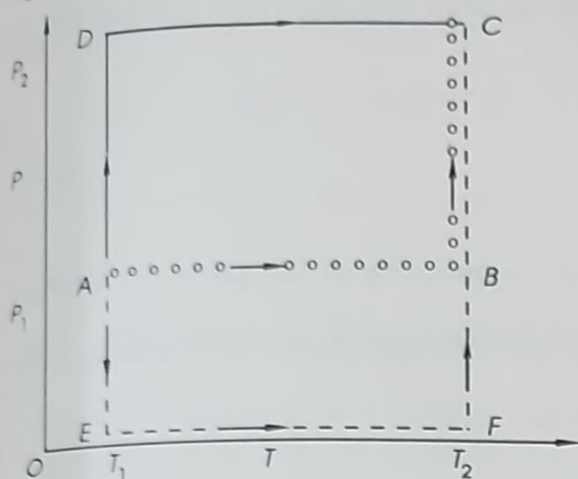

Fig.8.1   *P–T diagram illustrating two different paths of integration.*

Though the two paths ABC and ADC are convenient for integration, we face the practical difficulty regarding the availability of heat capacities $C_{P_1} = (\partial h/\partial T)_{P_1}$ and $C_{P_2} = (\partial h/\partial T)_{P_2}$. Usually, the isobaric heat capacities are measured when the gas is in the ideal gas state $(P \to 0)$. To make use of the available ideal gas state heat capacity data, it is necessary to choose the path $AEFC$ shown by dotted lines in Fig.8.1. That is, $(h_2 - h_1)$ is evaluated from the relation

$$h_2 - h_1 \; = \; \int_{P_1}^{P=0} \left(\frac{\partial h}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} \left(\frac{\partial h}{\partial T} \right)_{P=0} dT + \int_{P=0}^{P_2} \left(\frac{\partial h}{\partial P} \right)_{T_2} dP$$

$$= \; \int_{P_1}^{P=0} \left(\frac{\partial h}{\partial P} \right)_{T_1} dP + \int_{T_1}^{T_2} C_p^0 dT + \int_{P=0}^{P_2} \left(\frac{\partial h}{\partial P} \right)_{T_2} dP$$

or $\;\; h_2 - h_1 = \int_{P_1}^{P=0} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]_{T_1} dP + \int_{T_1}^{T_2} C_p^0 dT + \int_{P=0}^{P_2} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]_{T_2} dP$ (8.7)

For an ideal gas the change in enthalpy is given by Eqn.8.2. Substituting Eqn.8.2 in Eqn.8.7, we get

$$(h_2 - h_2^0) - (h_1 - h_1^0) = \int_{P=0}^{P_2} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]_{T_2} dP - \int_{P=0}^{P_1} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]_{T_1} dP \quad (8.8)$$

From Eqn.8.8 one can write

$$(h - h^0)_{T,P} = \int_{P=0}^{P} \left(\frac{\partial h}{\partial P} \right)_T dP = \int_{P=0}^{P} \left[v - T \left(\frac{\partial v}{\partial T} \right)_P \right]_T dP \quad (8.9)$$

The term $(h - h^0)_{T,P}$ represents the difference between the enthalpies of a real fluid and the fluid in the ideal gas state at the same temperature and pressure, and is called the *enthalpy departure* or *residual enthalpy*.

Similarly one can define the *entropy departure* or *residual entropy* as the difference between the entropies of a real gas and the gas in the ideal gas state at the same temperature and pressure. In general, if M is any extensive thermodynamic property, then the departure function for M or the residual property M is defined as

$$\left.\begin{array}{c} \text{Departure function for } M \\ \text{or} \\ \text{residual property } M \end{array}\right\} = M - M^0 \tag{8.10}$$

where M = property of the real gas at T and P, and M^0 = property of the gas in the ideal-gas state at the same T and P.

Let us now consider the entropy departure function. The entropy change of a substance can be evaluated by integrating the relation

$$ds = C_p \frac{dT}{T} - \left(\frac{\partial v}{\partial T}\right)_P dP \tag{8.11}$$

along path *AEFC* of Fig.8.1 to get

$$s_2 - s_1 = -\int_{P_1}^{P=0} \left(\frac{\partial v}{\partial T}\right)_{P,T_1} dP + \int_{T_1}^{T_2} \left(\frac{C_p}{T}\right)_{P=0} dT - \int_{P=0}^{P_2} \left(\frac{\partial v}{\partial T}\right)_{P,T_2} dP \tag{8.12}$$

For an ideal gas the change in entropy is given by Eqn.8.4. Substituting Eqn.8.4 in Eqn.8.12, we get

$$(s_2 - s_2^0) - (s_1 - s_1^0) = -\int_{P=0}^{P_2} \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{R}{P}\right]_{T_2} dP - \int_{P=0}^{P_1} - \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{R}{P}\right]_{T_1} dP \tag{8.13}$$

From Eqn.8.13 one can write

$$(s - s^0)_{T,P} = \int_{P=0}^{P} \left[\left(\frac{\partial s}{\partial P}\right)_T + \frac{R}{P}\right] dP = -\int_{P=0}^{P} \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{R}{P}\right]_T dP \tag{8.14}$$

where s = molar entropy of a real gas at T and P, and s^0 = molar entropy of a gas in the ideal gas state at T and P. Equation 8.14 defines the entropy departure or residual entropy. From the enthalpy and entropy departure functions, one can obtain the other departure functions also, by using the relations

$$(u - u^0) = (h - h^0) - P(v - v^0) \tag{8.15}$$

$$(a - a^0) = (u - u^0) - T(s - s^0) \tag{8.16}$$

$$(g - g^0) = (h - h^0) - T(s - s^0) \tag{8.17}$$

The thermodynamic properties of a real gas can be estimated from a knowledge of the departure functions. For example, the change in the enthalpy $(h_2 - h_1)$ and entropy $(s_2 - s_1)$ of a real gas can be expressed as

$$(h_2 - h_1) = (h_2 - h_1) + (h_2^0 - h_1^0) - (h_2^0 - h_1^0) = (h_2 - h_2^0) - (h_1 - h_1^0) + (h_2^0 - h_1^0)$$

or $\quad (h_2 - h_1) = (h_2 - h_2^0) - (h_1 - h_1^0) + \int_{T_1}^{T_2} C_p^0 dT$

$$\tag{8.18}$$

$$(s_2 - s_1) = (s_2 - s_1) + (s_2^0 - s_1^0) - (s_2^0 - s_1^0) = (s_2 - s_2^0) - (s_1 - s_1^0) + (s_2^0 - s_1^0)$$

or $\quad (s_2 - s_1) = (s_2 - s_2^0) - (s_1 - s_1^0) + \int_{T_1}^{T_2} C_p^0 \dfrac{dT}{T} - R \ln \dfrac{P_2}{P_1}$

$$\tag{8.19}$$

8.3 Departure functions from equations of state

The P–v–T behavior of a fluid is conveniently expressed in the form of an equation of state. The equations of state in common use are discussed in Section 3.3. It can be observed that the equations of state in common use are pressure explicit, i.e., volume and temperature appear as independent variables. The evaluation of the enthalpy and entropy departures requires a knowledge of the partial derivative $(\partial v/\partial T)_P$, which cannot be directly obtained from pressure explicit equations of state. In such cases it is useful to develop alternative expressions for the departure functions as shown below.

We know that $d(Pv) = Pdv + vdP$

or $\quad vdP = d(Pv) - Pdv$

$$\tag{8.20}$$

and the cyclic relation among the three variables P, v and T is given by

$$\left(\frac{\partial P}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_v = -1 \quad \text{or} \quad \left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial v}{\partial P}\right)_T$$

or $\quad \left[\left(\frac{\partial v}{\partial T}\right)_P dP\right]_T = -\left[\left(\frac{\partial P}{\partial T}\right)_v dv\right]_T$

$$\tag{8.21}$$

Substituting Eqns.8.20 and 8.21 in Eqns.8.9 and 8.14, we get

$$(h - h^0)_{T,P} = \int_{P=0}^{P} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right]_T dP$$

$$= \int_{P=0}^{P} d(Pv) + \int_{v=\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]_T dv \quad \text{(since } v = \infty \text{ as } P = 0)$$

$$= Pv - (Pv)_{P=0} + \int_{v=\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]_T dv$$

$$= Pv - RT + \int_{v=\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right]_T dv$$

or $(h - h^0)_{T,P} = RT(Z - 1) + \int_{v=\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right]_T dv$ (8.22)

$$(s - s^0)_{T,P} = -\int_{P=0}^{P} \left[\left(\frac{\partial v}{\partial T}\right)_P - \frac{R}{P}\right]_T dP = \int_{v=\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv + \int_{P=0}^{P} R\frac{dP}{P}$$

$$= \int_{v=\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv + \int \left[R\frac{d(Pv)}{Pv} - R\frac{dv}{v}\right]$$

$$= \int_{v=\infty}^{v} \left(\frac{\partial P}{\partial T}\right)_v dv + R\int_{Pv=RT}^{Pv} d\ln(Pv) - \int_{v=\infty}^{v} R\frac{dv}{v}$$

$$= R\ln\left(\frac{Pv}{RT}\right) + \int_{v=\infty}^{v} \left[\left(\frac{\partial P}{\partial T}\right)_v - \frac{R}{v}\right] dv$$

or $(s - s^0)_{T,P} = R\ln Z + \int_{v=\infty}^{v} \left[\left(\frac{\partial P}{\partial T}\right)_v - \frac{R}{v}\right]_T dv$ (8.23)

Example 8.1 Evaluate the enthalpy and entropy departures for a van der Waals gas.

Solution The van der Waals equation of state is given by

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \quad \text{or} \quad \left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v-b}$$

Then

$$(h - h^0) = RT(Z - 1) + \int_{v=\infty}^{v} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv$$

$$= RT(Z - 1) + \int_{v=\infty}^{v} \left[\frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2}\right] dv = RT\left(\frac{Pv}{RT} - 1\right) - \frac{a}{v} = Pv - RT - \frac{a}{v}$$

$$(s - s^0) = R\ln Z + \int_{v=\infty}^{v} \left[\left(\frac{\partial P}{\partial T}\right)_v - \frac{R}{v}\right]_T dv$$

$$= R\ln Z + \int_{v=\infty}^{v} \left(\frac{R}{v-b} - \frac{R}{v}\right)_T dv = R\ln Z + R\ln\frac{v-b}{v^\infty-b} - R\ln\frac{v}{v^\infty}$$

where v^∞ = volume as $P \to 0$, or ideal gas volume. Therefore,

$$s - s^0 = R\ln Z + R\ln\frac{v-b}{v^\infty-b} - R\ln\frac{ZRT}{P}\left(\frac{P^0}{RT}\right)$$

or $s - s^0 = R\ln\frac{v-b}{v^\infty-b} + R\ln\frac{P}{P^0} = R\ln\frac{P(v-b)}{P^0(v^\infty-b)} = R\ln\frac{P(v-b)}{RT}$

Example 8.2 Assuming that n-octane obeys the van der Waals equation of state, calculate the enthalpy and entropy departure for n-octane vapor at 427.85 K and 0.215 MPa.

Solution We have $v = 15.675 \times 10^{-3}$ m³/mol (see Example 3.8). The van der Waals constants of n-octane are given by $a = 3.789$ Pa (m³/mol)²; $b = 2.37 \times 10^{-4}$ m³/mol [see Appendix Table A.2].

$$h - h^0 = Pv - RT - \frac{a}{v}$$

$$= (0.215 \times 10^6 \times 15.675 \times 10^{-3}) - (8.314 \times 427.85) - \frac{3.789}{15.675 \times 10^{-3}}$$

$$= -428.74 \text{ J/mol}$$

$$s - s^0 = R \ln \frac{P(v - b)}{RT}$$

$$= 8.314 \ln \left\{ \frac{0.215 \times 10^6 \times (15.675 \times 10^{-3} - 2.37 \times 10^{-4})}{8.314 \times 427.85} \right\} = -0.5757 \text{ J/mol K}$$