Chapter 12

THERMODYNAMIC PROPERTY RELATIONS

Partial Differentials

$$\left(\frac{\partial z}{\partial x}\right)_y = \lim_{\Delta x \to 0} \left(\frac{\Delta z}{\Delta x}\right)_y = \lim_{\Delta x \to 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x} \qquad \textbf{(12–2)}$$

$$\Delta z = z(x + \Delta x, y + \Delta y) - z(x, y)$$

Adding and subtracting $z(x, y + \Delta y)$, we get

$$\Delta z = z(x + \Delta x, y + \Delta y) - z(x, y + \Delta y) + z(x, y + \Delta y) - z(x, y)$$

or

$$\Delta z = \frac{z(x + \Delta x, y + \Delta y) - z(x, y + \Delta y)}{\Delta x} \Delta x + \frac{z(x, y + \Delta y) - z(x, y)}{\Delta y} \Delta y$$

Taking the limits as $\Delta x \to 0$ and $\Delta y \to 0$ and using the definitions of partial derivatives, we obtain

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \qquad \textbf{(12–3)}$$

Equation 12–3 is the fundamental relation for the total differential of a dependent variable in terms of its partial derivatives with respect to the independent variables. This relation can easily be extended to include more independent variables.

Partial Differential Relations

$$dz = M\,dx + N\,dy \qquad \textbf{(12–4)}$$

$$\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial x\,\partial y} \quad \text{and} \quad \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial y\,\partial x}$$

The order of differentiation is immaterial for properties since they are continuous point functions and have exact differentials. Therefore, the two relations above are identical:

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{12–5}$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz \tag{12–6}$$

Eliminating dx by combining Eqs. 12–3 and 12–6, we have

$$dz = \left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right] dy + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y dz$$

Rearranging,

$$\left[\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x\right] dy = \left[1 - \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y\right] dz \tag{12–7}$$

The variables *y* and *z* are independent of each other and thus can be varied independently. For example, *y* can be held constant (*dy* _ 0), and *z* can be varied over a range of values (*dz* _ 0). Therefore, for this equation to be valid at all times, the terms in the brackets must equal zero, regardless of the values of *y* and *z*. Setting the terms in each bracket equal to zero gives

$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{(\partial z/\partial x)_y} \tag{12–8}$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial y}\right)_x \rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1 \tag{12–9}$$

The first relation is called the **reciprocity relation,** and it shows that the inverse of a partial derivative is equal to its reciprocal (Fig. 12–6). The second relation is called the **cyclic relation,** and it is frequently used in thermodynamics (Fig. 12–7).

Two of the Gibbs relations were derived in Chap. 7 and expressed as

$$du = T\,ds - P\,dv \tag{12–10}$$

$$dh = T\,ds + v\,dP \tag{12–11}$$

The other two Gibbs relations are based on two new combination properties—the **Helmholtz function** a and the **Gibbs function** g, defined as

$$a = u - Ts \tag{12–12}$$

$$g = h - Ts \tag{12–13}$$

Differentiating, we get

$$da = du - T\,ds - s\,dT$$

$$dg = dh - T\,ds - s\,dT$$

Simplifying the above relations by using Eqs. 12–10 and 12–11, we obtain the other two Gibbs relations for simple compressible systems:

$$da = -s\,dT - P\,dv \tag{12–14}$$

$$dg = -s\,dT + v\,dP \tag{12–15}$$

A careful examination of the four Gibbs relations reveals that they are of the form

$$dz = M\,dx + N\,dy \tag{12–4}$$

with

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \tag{12–5}$$

since u, h, a, and g are properties and thus have exact differentials. Applying Eq. 12–5 to each of them, we obtain

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \tag{12–16}$$

$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P \tag{12–17}$$

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v \tag{12–18}$$

$$\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P \tag{12–19}$$

These are called the **Maxwell relations** (Fig. 12–8). They are extremely valuable in thermodynamics because they provide a means of determining the change in entropy, which cannot be measured directly, by simply measuring the changes in properties *P*, *v*, and *T*. Note that the Maxwell relations given above are limited to simple compressible systems. However, other similar relations can be written just as easily for nonsimple systems such as those involving electrical, magnetic, and other effects.

12–3 ▪ THE CLAPEYRON EQUATION

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{Tv_{fg}} \tag{12–22}$$

This is an important thermodynamic relation since it enables us to determine the enthalpy of vaporization h_{fg} at a given temperature by simply measuring the slope of the saturation curve on a *P*-*T* diagram

and the specific volume of saturated liquid and saturated vapor at the given temperature.

The Clapeyron equation is applicable to any phase-change process that occurs at constant temperature and pressure. It can be expressed in a general form as

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{12}}{Tv_{12}} \qquad \textbf{(12–23)}$$

where the subscripts 1 and 2 indicate the two phases.

The Clapeyron equation can be simplified for liquid–vapor and solid–vapor phase changes by utilizing some approximations. At low pressures $v_g \gg v_f$, and thus $v_{fg} \cong v_g$. By treating the vapor as an ideal gas, we have $v_g = RT/P$. Substituting these approximations into Eq. 12–22, we find

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{Ph_{fg}}{RT^2}$$

or

$$\left(\frac{dP}{P}\right)_{\text{sat}} = \frac{h_{fg}}{R}\left(\frac{dT}{T^2}\right)_{\text{sat}}$$

For small temperature intervals h_{fg} can be treated as a constant at some average value. Then integrating this equation between two saturation states yields

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \cong \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{\text{sat}} \qquad \textbf{(12–24)}$$

This equation is called the **Clapeyron–Clausius equation,** and it can be used to determine the variation of saturation pressure with temperature. It can also be used in the solid–vapor region by replacing h_{fg} by h_{ig} (the enthalpy of sublimation) of the substance.

12–4 ▪GENERAL RELATIONS FOR *du*, *dh*, *ds*, c_v, AND c_p

Internal Energy Changes

$$du = c_v\, dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right] dv \qquad \textbf{(12–29)}$$

$$u_2 - u_1 = \int_{T_1}^{T_2} c_v\, dT + \int_{v_1}^{v_2} \left[T\left(\frac{\partial P}{\partial T}\right)_v - P \right] dv \qquad \textbf{(12–30)}$$

Enthalpy Changes

$$dh = c_p\, dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP \qquad \textbf{(12–35)}$$

$$h_2 - h_1 = \int_{T_1}^{T_2} c_p\, dT + \int_{P_1}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right] dP \qquad \textbf{(12–36)}$$

In reality, one needs only to determine either *u*2 -*u*1 from Eq. 12–30 or *h*2 - *h*1 from Eq. 12–36, depending on which is more suitable to the data at hand. The other can easily be determined by using the definition of enthalpy *h* = *u* + *Pv*:

$$h_2 - h_1 = u_2 - u_1 + (P_2 v_2 - P_1 v_1) \qquad \textbf{(12–37)}$$

Entropy Changes

$$ds = \frac{c_v}{T}\, dT + \left(\frac{\partial P}{\partial T}\right)_v dv \qquad \textbf{(12–38)}$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T}\, dT + \int_{v_1}^{v_2} \left(\frac{\partial P}{\partial T}\right)_v dv \qquad \textbf{(12–39)}$$

$$ds = \frac{c_P}{T}\,dT - \left(\frac{\partial v}{\partial T}\right)_P dP \qquad \textbf{(12–40)}$$

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T}\,dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T}\right)_P dP \qquad \textbf{(12–41)}$$

At low pressures gases behave as ideal gases, and their specific heats essentially depend on temperature only. These specific heats are called *zero pressure,* or *ideal-gas, specific heats* (denoted c_{v0} and c_{p0}), and they are relatively easier to determine. Thus it is desirable to have some general relations that enable us to calculate the specific heats at higher pressures (or lower specific volumes) from a knowledge of c_{v0} or c_{p0} and the *P-v-T* behavior of the substance. Such relations are obtained by applying the test of exactness (Eq. 12–5) on Eqs. 12–38 and 12–40, which yields

$$\left(\frac{\partial c_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v \qquad \textbf{(12–42)}$$

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P \qquad \textbf{(12–43)}$$

The deviation of c_p from c_{p0} with increasing pressure, for example, is determined by integrating Eq. 12–43 from zero pressure to any pressure *P* along an isothermal path:

$$(c_p - c_{p0})_T = -T\int_0^P \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP \qquad \textbf{(12–44)}$$

$$c_p - c_v = T\left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v \qquad \textbf{(12–45)}$$

$$c_p - c_v = -T\left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T \qquad \textbf{(12–46)}$$

This relation can be expressed in terms of two other thermodynamic properties called the **volume expansivity β** b and the **isothermal compressibility α**, which are defined as (Fig. 12–10)

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \qquad \textbf{(12–47)}$$

$$\alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \qquad \textbf{(12–48)}$$

$$c_p - c_v = \frac{vT\beta^2}{\alpha} \qquad \textbf{(12–49)}$$

1. The isothermal compressibility α is a positive quantity for all substances in all phases. The volume expansivity could be negative for some substances (such as liquid water below 4°C), but its square is always positive or zero. The temperature *T* in this relation is thermodynamic temperature, which is also positive. Therefore we conclude that *the constant-pressure specific heat is always greater than or equal to the constant-volume specific heat*:

$$c_p \geq c_v \qquad \textbf{(12–50)}$$

2. The difference between c_p and c_v approaches zero as the absolute temperature approaches zero.

3. The two specific heats are identical for truly incompressible substances since *v* = constant. The difference between the two specific heats is very small and is

usually disregarded for substances that are *nearly* incompressible, such as liquids and solids.

The van der Waals equation of state is

12–5 ▪ THE JOULE-THOMSON COEFFICIENT

The temperature of the fluid may remain unchanged, or it may even increase during a throttling process (Fig. 12–12). The temperature behavior of a fluid during a throttling (h = constant) process is described by the **Joule-Thomson coefficient,** defined as

$$\mu_{JT}\begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

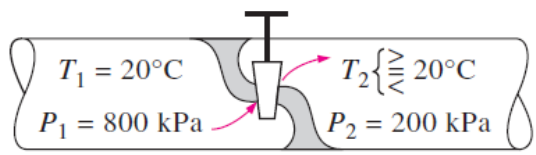

FIGURE 12–12

The temperature of a fluid may increase, decrease, or remain constant during a throttling process.

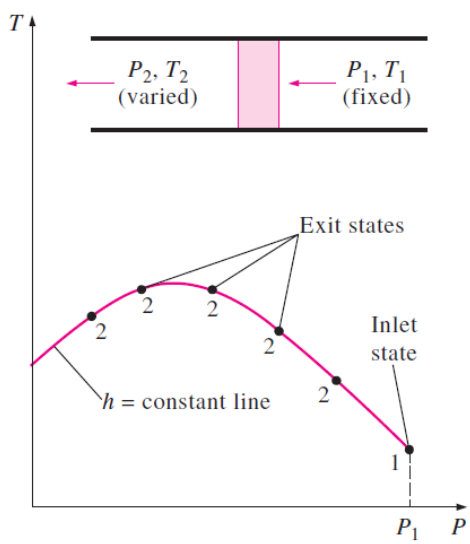

FIGURE 12–13

The development of an h = constant line on a P-T diagram.

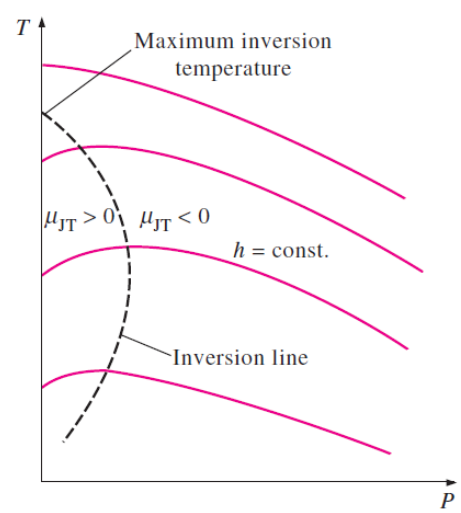

FIGURE 12–14

Constant-enthalpy lines of a substance on a T-P diagram.

It is clear from this diagram that a cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature. This presents a problem for substances whose maximum inversion temperature is well below room temperature.

For hydrogen, for example, the maximum inversion temperature is -68°C. Thus hydrogen must be cooled below this temperature if any further cooling is to be achieved by throttling.

$$dh = c_p\,dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP$$

For an h = constant process we have dh = 0. Then this equation can be rearranged to give

$$-\frac{1}{c_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] = \left(\frac{\partial T}{\partial P}\right)_h = \mu_{JT} \qquad \textbf{(12–52)}$$

12–6 ▪ THE Δ*h*, Δ*u*, AND Δ*s* OF REAL GASES

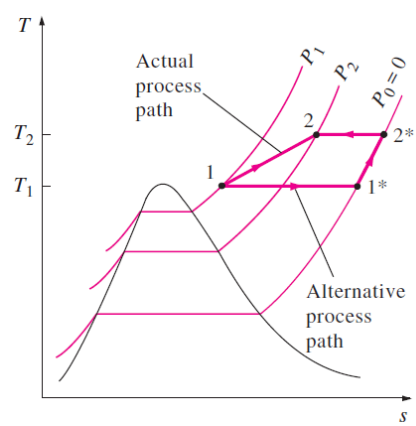

FIGURE 12–16

An alternative process path to evaluate the enthalpy changes of real gases.

$$h_2 - h_1 = (h_2 - h_2^*) + (h_2^* - h_1^*) + (h_1^* - h_1) \quad \textbf{(12–53)}$$

where, from Eq. 12–36,

$$h_2 - h_2^* = 0 + \int_{P_2^*}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_2} dP = \int_{P_0}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_2} dP \quad \textbf{(12–54)}$$

$$h_2^* - h_1^* = \int_{T_1}^{T_2} c_p \, dT + 0 = \int_{T_1}^{T_2} c_{p0}(T) \, dT \quad \textbf{(12–55)}$$

$$h_1^* - h_1 = 0 + \int_{P_1}^{P_1^*} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_1} dP = -\int_{P_0}^{P_1} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_1} dP \quad \textbf{(12–56)}$$

The difference between h and h* is called the enthalpy departure, and it represents the variation of the enthalpy of a gas with pressure at a fixed temperature.

using $T = T_{cr} T_R$ and $P = P_{cr} P_R$.

$$Z_h = \frac{(\bar{h}^* - \bar{h})_T}{R_u T_{cr}} = T_R^2 \int_0^{P_R} \left(\frac{\partial Z}{\partial T_R}\right)_{P_R} d(\ln P_R) \quad \textbf{(12–57)}$$

where Z_h is called the **enthalpy departure factor**.

$$\bar{h}_2 - \bar{h}_1 = (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} - R_u T_{cr}(Z_{h_2} - Z_{h_1}) \quad \textbf{(12–58)}$$

or

$$h_2 - h_1 = (h_2 - h_1)_{\text{ideal}} - R T_{cr}(Z_{h_2} - Z_{h_1}) \quad \textbf{(12–59)}$$

Internal Energy Changes of Real Gases

$$\bar{u}_2 - \bar{u}_1 = (\bar{h}_2 - \bar{h}_1) - R_u(Z_2 T_2 - Z_1 T_1) \quad \textbf{(12–60)}$$

Entropy Changes of Real Gases

$$s_2 - s_1 = (s_2 - s_b^*) + (s_b^* - s_2^*) + (s_2^* - s_1^*) + (s_1^* - s_a^*) + (s_a^* - s_1) \quad \textbf{(12–61)}$$

States 1 and 1* are identical (T1 T1* and P1 P1*) and so are states 2 and 2*. The gas is assumed to behave as an ideal gas at the imaginary states 1* and 2* as well as at the states between the two. Therefore, the entropy change during process 1*-2* can be determined from the entropy-change relations for ideal gases. The calculation of entropy change between an actual state and the corresponding imaginary ideal-gas state is more involved, however, and requires the use of generalized entropy departure charts, as explained below.

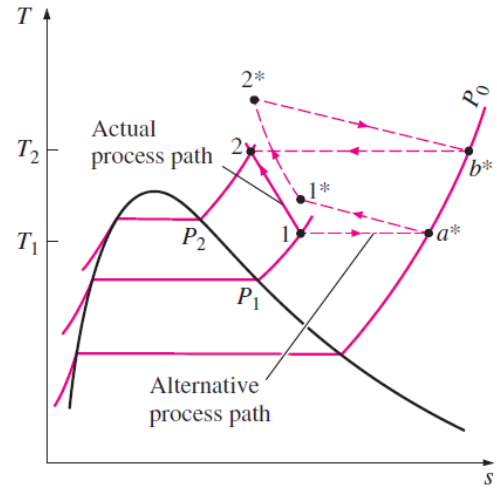

FIGURE 12–17

An alternative process path to evaluate the entropy changes of real gases during process 1-2.

Consider a gas at a pressure P and temperature T. To determine how much different the entropy of this gas would be if it were an ideal gas at the same temperature and pressure, we consider an isothermal process from the actual state P, T to zero (or close to zero) pressure and back to the imaginary ideal gas state P*, T* (denoted by superscript *), as shown in Fig. 12–17. The entropy change during this isothermal process can be expressed as

$$(s_P - s_P^*)_T = (s_P - s_0^*)_T + (s_0^* - s_P^*)_T$$
$$= -\int_0^P \left(\frac{\partial v}{\partial T}\right)_P dP - \int_P^0 \left(\frac{\partial v^*}{\partial T}\right)_P dP$$

where $v = ZRT/P$ and $v^* = v_{\text{ideal}} = RT/P$. Performing the differentiations and rearranging, we obtain

$$(s_P - s_P^*)_T = \int_0^P \left[\frac{(1-Z)R}{P} - \frac{RT}{P}\left(\frac{\partial Zr}{\partial T}\right)_P\right] dP$$

By substituting $T = T_{\text{cr}}T_R$ and $P = P_{\text{cr}}P_R$ and rearranging, the entropy departure can be expressed in a nondimensionalized form as

$$Z_s = \frac{(\bar{s}^* - \bar{s})_{T,P}}{R_u} = \int_0^{P_R} \left[Z - 1 + T_R\left(\frac{\partial Z}{\partial T_R}\right)_{P_R}\right] d(\ln P_R) \qquad \textbf{(12–62)}$$

The difference $(\bar{s}^* - \bar{s})_{T,P}$ is called the entropy departure and Z_s is called the entropy departure factor. The integral in the above equation can be performed by using data from the compressibility charts.

$$\bar{s}_2 - \bar{s}_1 = (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} - R_u(Z_{s_2} - Z_{s_1}) \tag{12–63}$$

$$s_2 - s_1 = (s_2 - s_1)_{\text{ideal}} - R(Z_{s_2} - Z_{s_1}) \tag{12–64}$$