

Chapter 12

THERMODYNAMIC PROPERTY RELATIONS

In the preceding chapters we made extensive use of the property tables. We tend to take the property tables for granted, but thermodynamic laws and principles are of little use to engineers without them. In this chapter, we focus our attention on how the property tables are prepared and how some unknown properties can be determined from limited available data.

It will come as no surprise that some properties such as temperature, pressure, volume, and mass can be measured directly. Other properties such as density and specific volume can be determined from these using some simple relations. However, properties such as internal energy, enthalpy, and entropy are not so easy to determine because they cannot be measured directly or related to easily measurable properties through some simple relations. Therefore, it is essential that we develop some fundamental relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties.

By the nature of the material, this chapter makes extensive use of partial derivatives. Therefore, we start by reviewing them. Then we develop the Maxwell relations, which form the basis for many thermodynamic relations. Next we discuss the Clapeyron equation, which enables us to determine the enthalpy of vaporization from P , v , and T measurements alone, and we develop general relations for c_v , c_p , du , dh , and ds that are valid for all pure substances under all conditions. Then we discuss the Joule-Thomson coefficient, which is a measure of the temperature change with pressure during a throttling process. Finally, we develop a method of evaluating the Δh , Δu , and Δs of real gases through the use of generalized enthalpy and entropy departure charts.

Objectives

The objectives of Chapter 12 are to:

- Develop fundamental relations between commonly encountered thermodynamic properties and express the properties that cannot be measured directly in terms of easily measurable properties.
- Develop the Maxwell relations, which form the basis for many thermodynamic relations.
- Develop the Clapeyron equation and determine the enthalpy of vaporization from P , v , and T measurements alone.
- Develop general relations for c_v , c_p , du , dh , and ds that are valid for all pure substances.
- Discuss the Joule-Thomson coefficient.
- Develop a method of evaluating the Δh , Δu , and Δs of real gases through the use of generalized enthalpy and entropy departure charts.

12-1 ■ A LITTLE MATH—PARTIAL DERIVATIVES AND ASSOCIATED RELATIONS

Many of the expressions developed in this chapter are based on the state postulate, which expresses that the state of a simple, compressible substance is completely specified by any two independent, intensive properties. All other properties at that state can be expressed in terms of those two properties. Mathematically speaking,

$$z = z(x, y)$$

where x and y are the two independent properties that fix the state and z represents any other property. Most basic thermodynamic relations involve differentials. Therefore, we start by reviewing the derivatives and various relations among derivatives to the extent necessary in this chapter.

Consider a function f that depends on a single variable x , that is, $f = f(x)$. Figure 12-1 shows such a function that starts out flat but gets rather steep as x increases. The steepness of the curve is a measure of the degree of dependence of f on x . In our case, the function f depends on x more strongly at larger x values. The steepness of a curve at a point is measured by the slope of a line tangent to the curve at that point, and it is equivalent to the **derivative** of the function at that point defined as

$$\frac{df}{dx} = \lim_{\Delta x \rightarrow 0} \frac{\Delta f}{\Delta x} = \lim_{\Delta x \rightarrow 0} \frac{f(x + \Delta x) - f(x)}{\Delta x} \quad (12-1)$$

Therefore, *the derivative of a function $f(x)$ with respect to x represents the rate of change of f with x .*

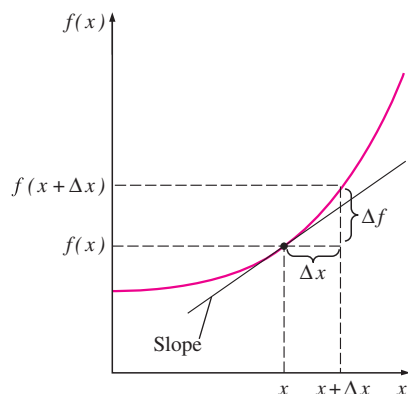


FIGURE 12-1

The derivative of a function at a specified point represents the slope of the function at that point.

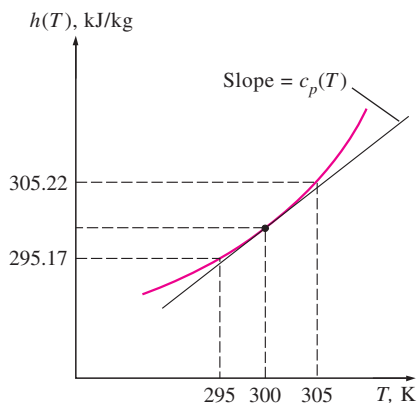


FIGURE 12-2

Schematic for Example 12-1.

EXAMPLE 12-1 Approximating Differential Quantities by Differences

The c_p of ideal gases depends on temperature only, and it is expressed as $c_p(T) = dh(T)/dT$. Determine the c_p of air at 300 K, using the enthalpy data from Table A-17, and compare it to the value listed in Table A-2b.

Solution The c_p value of air at a specified temperature is to be determined using enthalpy data.

Analysis The c_p value of air at 300 K is listed in Table A-2b to be 1.005 kJ/kg · K. This value could also be determined by differentiating the function $h(T)$ with respect to T and evaluating the result at $T = 300$ K. However, the function $h(T)$ is not available. But, we can still determine the c_p value approximately by replacing the differentials in the $c_p(T)$ relation by differences in the neighborhood of the specified point (Fig. 12-2):

$$\begin{aligned} c_p(300 \text{ K}) &= \left[\frac{dh(T)}{dT} \right]_{T=300 \text{ K}} \cong \left[\frac{\Delta h(T)}{\Delta T} \right]_{T \cong 300 \text{ K}} = \frac{h(305 \text{ K}) - h(295 \text{ K})}{(305 - 295) \text{ K}} \\ &= \frac{(305.22 - 295.17) \text{ kJ/kg}}{(305 - 295) \text{ K}} = \mathbf{1.005 \text{ kJ/kg} \cdot \text{K}} \end{aligned}$$

Discussion Note that the calculated c_p value is identical to the listed value. Therefore, differential quantities can be viewed as differences. They can

even be replaced by differences, whenever necessary, to obtain approximate results. The widely used finite difference numerical method is based on this simple principle.

Partial Differentials

Now consider a function that depends on two (or more) variables, such as $z = z(x, y)$. This time the value of z depends on both x and y . It is sometimes desirable to examine the dependence of z on only one of the variables. This is done by allowing one variable to change while holding the others constant and observing the change in the function. The variation of $z(x, y)$ with x when y is held constant is called the **partial derivative** of z with respect to x , and it is expressed as

$$\left(\frac{\partial z}{\partial x}\right)_y = \lim_{\Delta x \rightarrow 0} \left(\frac{\Delta z}{\Delta x}\right)_y = \lim_{\Delta x \rightarrow 0} \frac{z(x + \Delta x, y) - z(x, y)}{\Delta x} \quad (12-2)$$

This is illustrated in Fig. 12-3. The symbol ∂ represents differential changes, just like the symbol d . They differ in that the symbol d represents the *total* differential change of a function and reflects the influence of all variables, whereas ∂ represents the *partial* differential change due to the variation of a single variable.

Note that the changes indicated by d and ∂ are identical for independent variables, but not for dependent variables. For example, $(\partial x)_y = dx$ but $(\partial z)_y \neq dz$. [In our case, $dz = (\partial z)_x + (\partial z)_y$.] Also note that the value of the partial derivative $(\partial z/\partial x)_y$, in general, is different at different y values.

To obtain a relation for the total differential change in $z(x, y)$ for simultaneous changes in x and y , consider a small portion of the surface $z(x, y)$ shown in Fig. 12-4. When the independent variables x and y change by Δx and Δy , respectively, the dependent variable z changes by Δz , which can be expressed as

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

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 $\Delta x \rightarrow 0$ and $\Delta y \rightarrow 0$ and using the definitions of partial derivatives, we obtain

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

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.

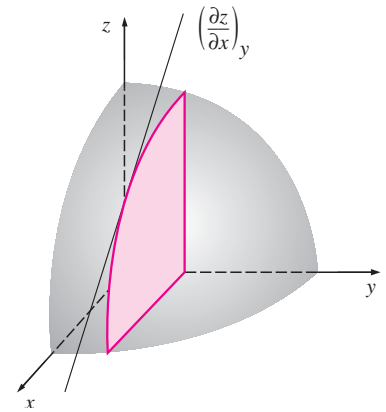


FIGURE 12-3
Geometric representation of partial derivative $(\partial z/\partial x)_y$.

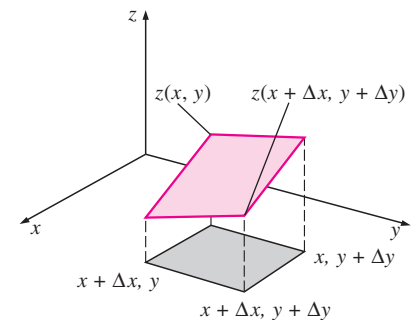


FIGURE 12-4
Geometric representation of total derivative dz for a function $z(x, y)$.

EXAMPLE 12-2 Total Differential versus Partial Differential

Consider air at 300 K and 0.86 m³/kg. The state of air changes to 302 K and 0.87 m³/kg as a result of some disturbance. Using Eq. 12-3, estimate the change in the pressure of air.

Solution The temperature and specific volume of air changes slightly during a process. The resulting change in pressure is to be determined.

Assumptions Air is an ideal gas.

Analysis Strictly speaking, Eq. 12-3 is valid for differential changes in variables. However, it can also be used with reasonable accuracy if these changes are small. The changes in T and ν , respectively, can be expressed as

$$dT \cong \Delta T = (302 - 300) \text{ K} = 2 \text{ K}$$

and

$$d\nu \cong \Delta \nu = (0.87 - 0.86) \text{ m}^3/\text{kg} = 0.01 \text{ m}^3/\text{kg}$$

An ideal gas obeys the relation $P\nu = RT$. Solving for P yields

$$P = \frac{RT}{\nu}$$

Note that R is a constant and $P = P(T, \nu)$. Applying Eq. 12-3 and using average values for T and ν ,

$$\begin{aligned} dP &= \left(\frac{\partial P}{\partial T}\right)_{\nu} dT + \left(\frac{\partial P}{\partial \nu}\right)_{T} d\nu = \frac{R dT}{\nu} - \frac{RT d\nu}{\nu^2} \\ &= (0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}) \left[\frac{2 \text{ K}}{0.865 \text{ m}^3/\text{kg}} - \frac{(301 \text{ K})(0.01 \text{ m}^3/\text{kg})}{(0.865 \text{ m}^3/\text{kg})^2} \right] \\ &= 0.664 \text{ kPa} - 1.155 \text{ kPa} \\ &= \mathbf{-0.491 \text{ kPa}} \end{aligned}$$

Therefore, the pressure will decrease by 0.491 kPa as a result of this disturbance. Notice that if the temperature had remained constant ($dT = 0$), the pressure would decrease by 1.155 kPa as a result of the 0.01 m³/kg increase in specific volume. However, if the specific volume had remained constant ($d\nu = 0$), the pressure would increase by 0.664 kPa as a result of the 2-K rise in temperature (Fig. 12-5). That is,

$$\left(\frac{\partial P}{\partial T}\right)_{\nu} dT = (\partial P)_{\nu} = 0.664 \text{ kPa}$$

$$\left(\frac{\partial P}{\partial \nu}\right)_{T} d\nu = (\partial P)_{T} = -1.155 \text{ kPa}$$

and

$$dP = (\partial P)_{\nu} + (\partial P)_{T} = 0.664 - 1.155 = -0.491 \text{ kPa}$$

Discussion Of course, we could have solved this problem easily (and exactly) by evaluating the pressure from the ideal-gas relation $P = RT/\nu$ at the final state (302 K and 0.87 m³/kg) and the initial state (300 K and 0.86 m³/kg) and taking their difference. This yields -0.491 kPa, which is exactly the value obtained above. Thus the small finite quantities (2 K, 0.01 m³/kg) can be approximated as differential quantities with reasonable accuracy.

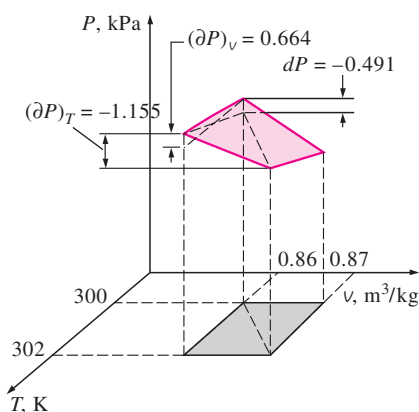


FIGURE 12-5

Geometric representation of the disturbance discussed in Example 12-2.

Partial Differential Relations

Now let us rewrite Eq. 12–3 as

$$dz = M dx + N dy \quad (12-4)$$

where

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

Taking the partial derivative of M with respect to y and of N with respect to x yields

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

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:

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

This is an important relation for partial derivatives, and it is used in calculus to test whether a differential dz is exact or inexact. In thermodynamics, this relation forms the basis for the development of the Maxwell relations discussed in the next section.

Finally, we develop two important relations for partial derivatives—the reciprocity and the cyclic relations. The function $z = z(x, y)$ can also be expressed as $x = x(y, z)$ if y and z are taken to be the independent variables. Then the total differential of x becomes, from Eq. 12–3,

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

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,

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

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 ($dz \neq 0$). 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

$$\left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z} \right)_y = \frac{1}{\left(\frac{\partial z}{\partial x} \right)_y} \quad (12-8)$$

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

○

○

Function: $z + 2xy - 3y^2z = 0$

1) $z = \frac{2xy}{3y^2 - 1} \rightarrow \left(\frac{\partial z}{\partial x}\right)_y = \frac{2y}{3y^2 - 1}$

○

2) $x = \frac{3y^2z - z}{2y} \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = \frac{3y^2 - 1}{2y}$

Thus, $\left(\frac{\partial z}{\partial x}\right)_y = \frac{1}{\left(\frac{\partial x}{\partial z}\right)_y}$

○

○

FIGURE 12-6

Demonstration of the reciprocity relation for the function $z + 2xy - 3y^2z = 0$.



FIGURE 12-7

Partial differentials are powerful tools that are supposed to make life easier, not harder.

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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).

EXAMPLE 12-3 Verification of Cyclic and Reciprocity Relations

Using the ideal-gas equation of state, verify (a) the cyclic relation and (b) the reciprocity relation at constant P .

Solution The cyclic and reciprocity relations are to be verified for an ideal gas. **Analysis** The ideal-gas equation of state $Pv = RT$ involves the three variables P , v , and T . Any two of these can be taken as the independent variables, with the remaining one being the dependent variable.

(a) Replacing x , y , and z in Eq. 12-9 by P , v , and T , respectively, we can express the cyclic relation for an ideal gas as

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

where

$$P = P(v, T) = \frac{RT}{v} \rightarrow \left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{v^2}$$

$$v = v(P, T) = \frac{RT}{P} \rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

$$T = T(P, v) = \frac{Pv}{R} \rightarrow \left(\frac{\partial T}{\partial P}\right)_v = \frac{v}{R}$$

Substituting yields

$$\left(-\frac{RT}{v^2}\right) \left(\frac{R}{P}\right) \left(\frac{v}{R}\right) = -\frac{RT}{Pv} = -1$$

which is the desired result.

(b) The reciprocity rule for an ideal gas at $P = \text{constant}$ can be expressed as

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{(\partial T / \partial v)_P}$$

Performing the differentiations and substituting, we have

$$\frac{R}{P} = \frac{1}{P/R} \rightarrow \frac{R}{P} = \frac{R}{P}$$

Thus the proof is complete.

12-2 ■ THE MAXWELL RELATIONS

The equations that relate the partial derivatives of properties P , v , T , and s of a simple compressible system to each other are called the *Maxwell relations*. They are obtained from the four Gibbs equations by exploiting the exactness of the differentials of thermodynamic properties.

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

$$du = T ds - P dv \quad (12-10)$$

$$dh = T ds + v dP \quad (12-11)$$

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

$$a = u - Ts \quad (12-12)$$

$$g = h - Ts \quad (12-13)$$

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:

$$da = -s dT - P dv \quad (12-14)$$

$$dg = -s dT + v dP \quad (12-15)$$

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

$$dz = M dx + N dy \quad (12-4)$$

with

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

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

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

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

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

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

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.

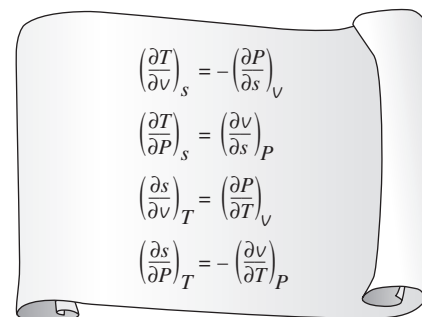


FIGURE 12-8

Maxwell relations are extremely valuable in thermodynamic analysis.

EXAMPLE 12-4 Verification of the Maxwell Relations

Verify the validity of the last Maxwell relation (Eq. 12-19) for steam at 250°C and 300 kPa.

Solution The validity of the last Maxwell relation is to be verified for steam at a specified state.

Analysis The last Maxwell relation states that for a simple compressible substance, the change in entropy with pressure at constant temperature is equal to the negative of the change in specific volume with temperature at constant pressure.

If we had explicit analytical relations for the entropy and specific volume of steam in terms of other properties, we could easily verify this by performing the indicated derivations. However, all we have for steam are tables of properties listed at certain intervals. Therefore, the only course we can take to solve this problem is to replace the differential quantities in Eq. 12-19 with corresponding finite quantities, using property values from the tables (Table A-6 in this case) at or about the specified state.

$$\begin{aligned} \left(\frac{\partial s}{\partial P}\right)_T &\stackrel{?}{=} -\left(\frac{\partial v}{\partial T}\right)_P \\ \left(\frac{\Delta s}{\Delta P}\right)_{T=250^\circ\text{C}} &\stackrel{?}{=} -\left(\frac{\partial v}{\partial T}\right)_{P=300\text{ kPa}} \\ \left[\frac{s_{400\text{ kPa}} - s_{200\text{ kPa}}}{(400 - 200)\text{ kPa}}\right]_{T=250^\circ\text{C}} &\stackrel{?}{=} -\left[\frac{v_{300^\circ\text{C}} - v_{200^\circ\text{C}}}{(300 - 200)^\circ\text{C}}\right]_{P=300\text{ kPa}} \\ \frac{(7.3804 - 7.7100)\text{ kJ/kg}\cdot\text{K}}{(400 - 200)\text{ kPa}} &\stackrel{?}{=} -\frac{(0.87535 - 0.71643)\text{ m}^3/\text{kg}}{(300 - 200)^\circ\text{C}} \\ -0.00165\text{ m}^3/\text{kg}\cdot\text{K} &\cong -0.00159\text{ m}^3/\text{kg}\cdot\text{K} \end{aligned}$$

since $\text{kJ} = \text{kPa}\cdot\text{m}^3$ and $\text{K} \equiv ^\circ\text{C}$ for temperature differences. The two values are within 4 percent of each other. This difference is due to replacing the differential quantities by relatively large finite quantities. Based on the close agreement between the two values, the steam seems to satisfy Eq. 12-19 at the specified state.

Discussion This example shows that the entropy change of a simple compressible system during an isothermal process can be determined from a knowledge of the easily measurable properties P , v , and T alone.

12-3 ■ THE CLAPEYRON EQUATION

The Maxwell relations have far-reaching implications in thermodynamics and are frequently used to derive useful thermodynamic relations. The Clapeyron equation is one such relation, and it enables us to determine the enthalpy change associated with a phase change (such as the enthalpy of vaporization h_{fg}) from a knowledge of P , v , and T data alone.

Consider the third Maxwell relation, Eq. 12-18:

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

During a phase-change process, the pressure is the saturation pressure, which depends on the temperature only and is independent of the specific

volume. That is, $P_{\text{sat}} = f(T_{\text{sat}})$. Therefore, the partial derivative $(\partial P/\partial T)_v$ can be expressed as a total derivative $(dP/dT)_{\text{sat}}$, which is the slope of the saturation curve on a P - T diagram at a specified saturation state (Fig. 12–9). This slope is independent of the specific volume, and thus it can be treated as a constant during the integration of Eq. 12–18 between two saturation states at the same temperature. For an isothermal liquid–vapor phase-change process, for example, the integration yields

$$s_g - s_f = \left(\frac{dP}{dT} \right)_{\text{sat}} (v_g - v_f) \quad (12-20)$$

or

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{s_{fg}}{v_{fg}} \quad (12-21)$$

During this process the pressure also remains constant. Therefore, from Eq. 12–11,

$$dh = T ds + v dP \xrightarrow{0} \int_f^g dh = \int_f^g T ds \rightarrow h_{fg} = T s_{fg}$$

Substituting this result into Eq. 12–21, we obtain

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{h_{fg}}{T v_{fg}} \quad (12-22)$$

which is called the **Clapeyron equation** after the French engineer and physicist E. Clapeyron (1799–1864). 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

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{h_{12}}{T v_{12}} \quad (12-23)$$

where the subscripts 1 and 2 indicate the two phases.

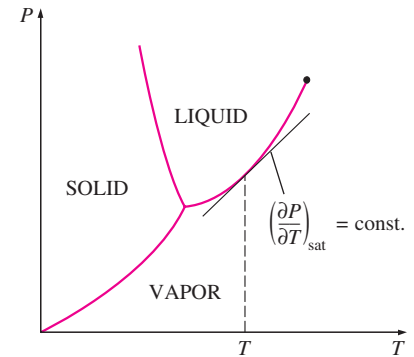


FIGURE 12–9

The slope of the saturation curve on a P - T diagram is constant at a constant T or P .

EXAMPLE 12–5 Evaluating the h_{fg} of a Substance from the P - v - T Data

Using the Clapeyron equation, estimate the value of the enthalpy of vaporization of refrigerant-134a at 20°C, and compare it with the tabulated value.

Solution The h_{fg} of refrigerant-134a is to be determined using the Clapeyron equation.

Analysis From Eq. 12–22,

$$h_{fg} = T v_{fg} \left(\frac{dP}{dT} \right)_{\text{sat}}$$

where, from Table A-11,

$$\begin{aligned} v_{fg} &= (v_g - v_f)_{@ 20^\circ\text{C}} = 0.035969 - 0.0008161 = 0.035153 \text{ m}^3/\text{kg} \\ \left(\frac{dP}{dT}\right)_{\text{sat}, 20^\circ\text{C}} &\cong \left(\frac{\Delta P}{\Delta T}\right)_{\text{sat}, 20^\circ\text{C}} = \frac{P_{\text{sat @ } 24^\circ\text{C}} - P_{\text{sat @ } 16^\circ\text{C}}}{24^\circ\text{C} - 16^\circ\text{C}} \\ &= \frac{646.18 - 504.58 \text{ kPa}}{8^\circ\text{C}} = 17.70 \text{ kPa/K} \end{aligned}$$

since $\Delta T(^{\circ}\text{C}) \equiv \Delta T(\text{K})$. Substituting, we get

$$\begin{aligned} h_{fg} &= (293.15 \text{ K})(0.035153 \text{ m}^3/\text{kg})(17.70 \text{ kPa/K}) \left(\frac{1 \text{ kJ}}{1 \text{ kPa} \cdot \text{m}^3}\right) \\ &= \mathbf{182.40 \text{ kJ/kg}} \end{aligned}$$

The tabulated value of h_{fg} at 20°C is 182.27 kJ/kg . The small difference between the two values is due to the approximation used in determining the slope of the saturation curve at 20°C .

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

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

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.

EXAMPLE 12–6 Extrapolating Tabular Data with the Clapeyron Equation

Estimate the saturation pressure of refrigerant-134a at -50°F , using the data available in the refrigerant tables.

Solution The saturation pressure of refrigerant-134a is to be determined using other tabulated data.

Analysis Table A-11E lists saturation data at temperatures -40°F and above. Therefore, we should either resort to other sources or use extrapolation

to obtain saturation data at lower temperatures. Equation 12–24 provides an intelligent way to extrapolate:

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

In our case $T_1 = -40^\circ\text{F}$ and $T_2 = -50^\circ\text{F}$. For refrigerant-134a, $R = 0.01946$ Btu/lbm \cdot R. Also from Table A-11E at -40°F , we read $h_{fg} = 97.100$ Btu/lbm and $P_1 = P_{\text{sat @ } -40^\circ\text{F}} = 7.432$ psia. Substituting these values into Eq. 12–24 gives

$$\ln\left(\frac{P_2}{7.432 \text{ psia}}\right) \cong \frac{97.100 \text{ Btu/lbm}}{0.01946 \text{ Btu/lbm} \cdot \text{R}}\left(\frac{1}{420 \text{ R}} - \frac{1}{410 \text{ R}}\right)$$

$$P_2 \cong \mathbf{5.56 \text{ psia}}$$

Therefore, according to Eq. 12–24, the saturation pressure of refrigerant-134a at -50°F is 5.56 psia. The actual value, obtained from another source, is 5.506 psia. Thus the value predicted by Eq. 12–24 is in error by about 1 percent, which is quite acceptable for most purposes. (If we had used linear extrapolation instead, we would have obtained 5.134 psia, which is in error by 7 percent.)

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

The state postulate established that the state of a simple compressible system is completely specified by two independent, intensive properties. Therefore, at least theoretically, we should be able to calculate all the properties of a system at any state once two independent, intensive properties are available. This is certainly good news for properties that cannot be measured directly such as internal energy, enthalpy, and entropy. However, the calculation of these properties from measurable ones depends on the availability of simple and accurate relations between the two groups.

In this section we develop general relations for changes in internal energy, enthalpy, and entropy in terms of pressure, specific volume, temperature, and specific heats alone. We also develop some general relations involving specific heats. The relations developed will enable us to determine the *changes* in these properties. The property values at specified states can be determined only after the selection of a reference state, the choice of which is quite arbitrary.

Internal Energy Changes

We choose the internal energy to be a function of T and v ; that is, $u = u(T, v)$ and take its total differential (Eq. 12–3):

$$du = \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv$$

Using the definition of c_v , we have

$$du = c_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv \quad (12-25)$$

Now we choose the entropy to be a function of T and v ; that is, $s = s(T, v)$ and take its total differential,

$$ds = \left(\frac{\partial s}{\partial T} \right)_v dT + \left(\frac{\partial s}{\partial v} \right)_T dv \quad (12-26)$$

Substituting this into the $T ds$ relation $du = T ds - P dv$ yields

$$du = T \left(\frac{\partial s}{\partial T} \right)_v dT + \left[T \left(\frac{\partial s}{\partial v} \right)_T - P \right] dv \quad (12-27)$$

Equating the coefficients of dT and dv in Eqs. 12-25 and 12-27 gives

$$\begin{aligned} \left(\frac{\partial s}{\partial T} \right)_v &= \frac{c_v}{T} \\ \left(\frac{\partial u}{\partial v} \right)_T &= T \left(\frac{\partial s}{\partial v} \right)_T - P \end{aligned} \quad (12-28)$$

Using the third Maxwell relation (Eq. 12-18), we get

$$\left(\frac{\partial u}{\partial v} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_v - P$$

Substituting this into Eq. 12-25, we obtain the desired relation for du :

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

The change in internal energy of a simple compressible system associated with a change of state from (T_1, v_1) to (T_2, v_2) is determined by integration:

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

Enthalpy Changes

The general relation for dh is determined in exactly the same manner. This time we choose the enthalpy to be a function of T and P , that is, $h = h(T, P)$, and take its total differential,

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

Using the definition of c_p , we have

$$dh = c_p dT + \left(\frac{\partial h}{\partial P} \right)_T dP \quad (12-31)$$

Now we choose the entropy to be a function of T and P ; that is, we take $s = s(T, P)$ and take its total differential,

$$ds = \left(\frac{\partial s}{\partial T} \right)_P dT + \left(\frac{\partial s}{\partial P} \right)_T dP \quad (12-32)$$

Substituting this into the $T ds$ relation $dh = T ds + v dP$ gives

$$dh = T \left(\frac{\partial s}{\partial T} \right)_P dT + \left[v + T \left(\frac{\partial s}{\partial P} \right)_T \right] dP \quad (12-33)$$

Equating the coefficients of dT and dP in Eqs. 12–31 and 12–33, we obtain

$$\begin{aligned}\left(\frac{\partial s}{\partial T}\right)_P &= \frac{c_p}{T} \\ \left(\frac{\partial h}{\partial P}\right)_T &= v + T\left(\frac{\partial s}{\partial P}\right)_T\end{aligned}\quad (12-34)$$

Using the fourth Maxwell relation (Eq. 12–19), we have

$$\left(\frac{\partial h}{\partial P}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_P$$

Substituting this into Eq. 12–31, we obtain the desired relation for dh :

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

The change in enthalpy of a simple compressible system associated with a change of state from (T_1, P_1) to (T_2, P_2) is determined by integration:

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

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 $h = u + Pv$:

$$h_2 - h_1 = u_2 - u_1 + (P_2 v_2 - P_1 v_1) \quad (12-37)$$

Entropy Changes

Below we develop two general relations for the entropy change of a simple compressible system.

The first relation is obtained by replacing the first partial derivative in the total differential ds (Eq. 12–26) by Eq. 12–28 and the second partial derivative by the third Maxwell relation (Eq. 12–18), yielding

$$ds = \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dV \quad (12-38)$$

and

$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_v}{T} dT + \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_v dV \quad (12-39)$$

The second relation is obtained by replacing the first partial derivative in the total differential of ds (Eq. 12–32) by Eq. 12–34, and the second partial derivative by the fourth Maxwell relation (Eq. 12–19), yielding

$$ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP \quad (12-40)$$

and

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

Either relation can be used to determine the entropy change. The proper choice depends on the available data.

Specific Heats c_v and c_p

Recall that the specific heats of an ideal gas depend on temperature only. For a general pure substance, however, the specific heats depend on specific volume or pressure as well as the temperature. Below we develop some general relations to relate the specific heats of a substance to pressure, specific volume, and temperature.

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

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

and

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

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:

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

The integration on the right-hand side requires a knowledge of the P - v - T behavior of the substance alone. The notation indicates that v should be differentiated twice with respect to T while P is held constant. The resulting expression should be integrated with respect to P while T is held constant.

Another desirable general relation involving specific heats is one that relates the two specific heats c_p and c_v . The advantage of such a relation is obvious: We will need to determine only one specific heat (usually c_p) and calculate the other one using that relation and the P - v - T data of the substance. We start the development of such a relation by equating the two ds relations (Eqs. 12-38 and 12-40) and solving for dT :

$$dT = \frac{T(\partial P/\partial T)_v}{c_p - c_v} dv + \frac{T(\partial v/\partial T)_P}{c_p - c_v} dP$$

Choosing $T = T(v, P)$ and differentiating, we get

$$dT = \left(\frac{\partial T}{\partial v}\right)_P dv + \left(\frac{\partial T}{\partial P}\right)_v dP$$

Equating the coefficient of either dv or dP of the above two equations gives the desired result:

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

An alternative form of this relation is obtained by using the cyclic relation:

$$\left(\frac{\partial P}{\partial T}\right)_v \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial v}{\partial P}\right)_T = -1 \rightarrow \left(\frac{\partial P}{\partial T}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial P}{\partial v}\right)_T$$

Substituting the result into Eq. 12–45 gives

$$c_p - c_v = -T \left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial P}{\partial v}\right)_T \quad (12-46)$$

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

$$\beta = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p \quad (12-47)$$

and

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

Substituting these two relations into Eq. 12–46, we obtain a third general relation for $c_p - c_v$:

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

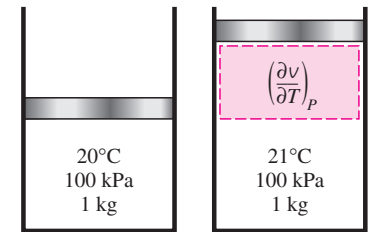
It is called the **Mayer relation** in honor of the German physician and physicist J. R. Mayer (1814–1878). We can draw several conclusions from this equation:

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*:

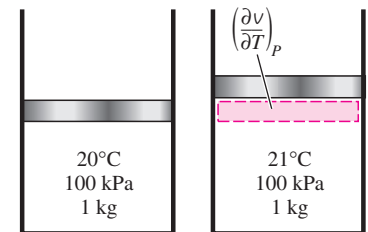
$$c_p \geq c_v \quad (12-50)$$

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 $v = \text{constant}$. 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.



(a) A substance with a large β



(b) A substance with a small β

FIGURE 12-10

The volume expansivity (also called the *coefficient of volumetric expansion*) is a measure of the change in volume with temperature at constant pressure.

EXAMPLE 12-7 Internal Energy Change of a van der Waals Gas

Derive a relation for the internal energy change as a gas that obeys the van der Waals equation of state. Assume that in the range of interest c_v varies according to the relation $c_v = c_1 + c_2 T$, where c_1 and c_2 are constants.

Solution A relation is to be obtained for the internal energy change of a van der Waals gas.

Analysis The change in internal energy of any simple compressible system in any phase during any process can be determined from Eq. 12–30:

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

The van der Waals equation of state is

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

Then

$$\left(\frac{\partial P}{\partial T} \right)_v = \frac{R}{v - b}$$

Thus,

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

Substituting gives

$$u_2 - u_1 = \int_{T_1}^{T_2} (c_1 + c_2 T) dT + \int_{v_1}^{v_2} \frac{a}{v^2} dv$$

Integrating yields

$$u_2 - u_1 = c_1(T_2 - T_1) + \frac{c_2}{2}(T_2^2 - T_1^2) + a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$$

which is the desired relation.

EXAMPLE 12–8 Internal Energy as a Function of Temperature Alone

Show that the internal energy of (a) an ideal gas and (b) an incompressible substance is a function of temperature only, $u = u(T)$.

Solution It is to be shown that $u = u(T)$ for ideal gases and incompressible substances.

Analysis The differential change in the internal energy of a general simple compressible system is given by Eq. 12–29 as

$$du = c_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

(a) For an ideal gas $Pv = RT$. Then

$$T \left(\frac{\partial P}{\partial T} \right)_v - P = T \left(\frac{R}{v} \right) - P = P - P = 0$$

Thus,

$$du = c_v dT$$

To complete the proof, we need to show that c_v is not a function of v either. This is done with the help of Eq. 12–42:

$$\left(\frac{\partial c_v}{\partial v} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_v$$

For an ideal gas $P = RT/v$. Then

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v} \quad \text{and} \quad \left(\frac{\partial^2 P}{\partial T^2}\right)_v = \left[\frac{\partial(R/v)}{\partial T}\right]_v = 0$$

Thus,

$$\left(\frac{\partial c_v}{\partial v}\right)_T = 0$$

which states that c_v does not change with specific volume. That is, c_v is not a function of specific volume either. Therefore we conclude that the internal energy of an ideal gas is a function of temperature only (Fig. 12–11).

(b) For an incompressible substance, $v = \text{constant}$ and thus $dv = 0$. Also from Eq. 12–49, $c_p = c_v = c$ since $\alpha = \beta = 0$ for incompressible substances. Then Eq. 12–29 reduces to

$$du = c \, dT$$

Again we need to show that the specific heat c depends on temperature only and not on pressure or specific volume. This is done with the help of Eq. 12–43:

$$\left(\frac{\partial c_p}{\partial P}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_P = 0$$

since $v = \text{constant}$. Therefore, we conclude that the internal energy of a truly incompressible substance depends on temperature only.

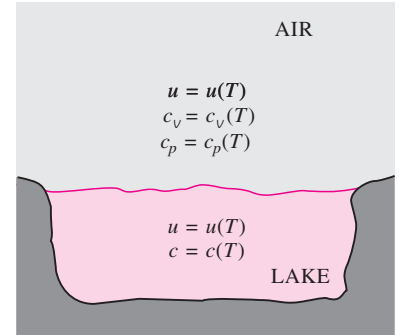


FIGURE 12–11

The internal energies and specific heats of ideal gases and incompressible substances depend on temperature only.

EXAMPLE 12–9 The Specific Heat Difference of an Ideal Gas

Show that $c_p - c_v = R$ for an ideal gas.

Solution It is to be shown that the specific heat difference for an ideal gas is equal to its gas constant.

Analysis This relation is easily proved by showing that the right-hand side of Eq. 12–46 is equivalent to the gas constant R of the ideal gas:

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

$$P = \frac{RT}{v} \rightarrow \left(\frac{\partial P}{\partial v}\right)_T = -\frac{RT}{v^2} = -\frac{P}{v}$$

$$v = \frac{RT}{P} \rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \left(\frac{R}{P}\right)^2$$

Substituting,

$$-T\left(\frac{\partial v}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial v}\right)_T = -T\left(\frac{R}{P}\right)^2 \left(-\frac{P}{v}\right) = R$$

Therefore,

$$c_p - c_v = R$$

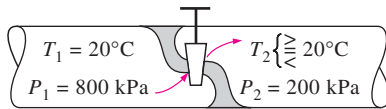


FIGURE 12-12

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

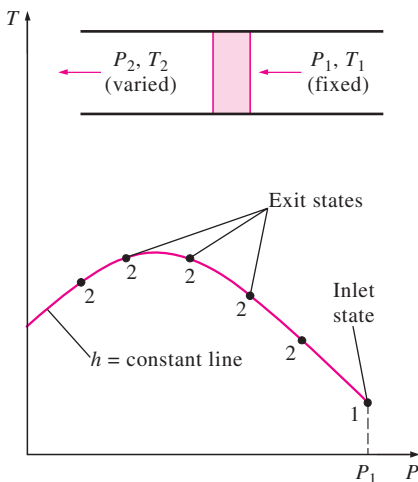


FIGURE 12-13

The development of an $h = \text{constant}$ line on a P - T diagram.

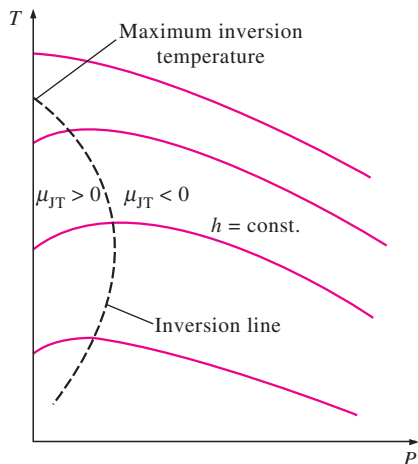


FIGURE 12-14

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

12-5 ■ THE JOULE-THOMSON COEFFICIENT

When a fluid passes through a restriction such as a porous plug, a capillary tube, or an ordinary valve, its pressure decreases. As we have shown in Chap. 5, the enthalpy of the fluid remains approximately constant during such a throttling process. You will remember that a fluid may experience a large drop in its temperature as a result of throttling, which forms the basis of operation for refrigerators and air conditioners. This is not always the case, however. 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 ($h = \text{constant}$) process is described by the **Joule-Thomson coefficient**, defined as

$$\mu = \left(\frac{\partial T}{\partial P} \right)_h \quad (12-51)$$

Thus the Joule-Thomson coefficient is a measure of the change in temperature with pressure during a constant-enthalpy process. Notice that if

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

during a throttling process.

A careful look at its defining equation reveals that the Joule-Thomson coefficient represents the slope of $h = \text{constant}$ lines on a T - P diagram. Such diagrams can be easily constructed from temperature and pressure measurements alone during throttling processes. A fluid at a fixed temperature and pressure T_1 and P_1 (thus fixed enthalpy) is forced to flow through a porous plug, and its temperature and pressure downstream (T_2 and P_2) are measured. The experiment is repeated for different sizes of porous plugs, each giving a different set of T_2 and P_2 . Plotting the temperatures against the pressures gives us an $h = \text{constant}$ line on a T - P diagram, as shown in Fig. 12-13. Repeating the experiment for different sets of inlet pressure and temperature and plotting the results, we can construct a T - P diagram for a substance with several $h = \text{constant}$ lines, as shown in Fig. 12-14.

Some constant-enthalpy lines on the T - P diagram pass through a point of zero slope or zero Joule-Thomson coefficient. The line that passes through these points is called the **inversion line**, and the temperature at a point where a constant-enthalpy line intersects the inversion line is called the **inversion temperature**. The temperature at the intersection of the $P = 0$ line (ordinate) and the upper part of the inversion line is called the **maximum inversion temperature**. Notice that the slopes of the $h = \text{constant}$ lines are negative ($\mu_{JT} < 0$) at states to the right of the inversion line and positive ($\mu_{JT} > 0$) to the left of the inversion line.

A throttling process proceeds along a constant-enthalpy line in the direction of decreasing pressure, that is, from right to left. Therefore, the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line. However, the fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line. 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.

Next we would like to develop a general relation for the Joule-Thomson coefficient in terms of the specific heats, pressure, specific volume, and temperature. This is easily accomplished by modifying the generalized relation for enthalpy change (Eq. 12–35)

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

For an $h = \text{constant}$ process we have $dh = 0$. Then this equation can be rearranged to give

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

which is the desired relation. Thus, the Joule-Thomson coefficient can be determined from a knowledge of the constant-pressure specific heat and the P - v - T behavior of the substance. Of course, it is also possible to predict the constant-pressure specific heat of a substance by using the Joule-Thomson coefficient, which is relatively easy to determine, together with the P - v - T data for the substance.

EXAMPLE 12–10 Joule-Thomson Coefficient of an Ideal Gas

Show that the Joule-Thomson coefficient of an ideal gas is zero.

Solution It is to be shown that $\mu_{JT} = 0$ for an ideal gas.

Analysis For an ideal gas $v = RT/P$, and thus

$$\left(\frac{\partial v}{\partial T} \right)_p = \frac{R}{P}$$

Substituting this into Eq. 12–52 yields

$$\mu_{JT} = \frac{-1}{c_p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right] = \frac{-1}{c_p} \left[v - T \frac{R}{P} \right] = -\frac{1}{c_p} (v - v) = 0$$

Discussion This result is not surprising since the enthalpy of an ideal gas is a function of temperature only, $h = h(T)$, which requires that the temperature remain constant when the enthalpy remains constant. Therefore, a throttling process cannot be used to lower the temperature of an ideal gas (Fig. 12–15).

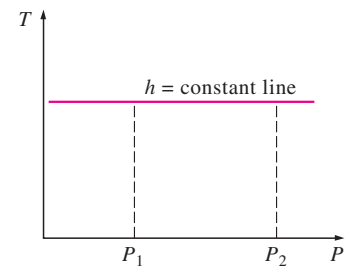


FIGURE 12–15

The temperature of an ideal gas remains constant during a throttling process since $h = \text{constant}$ and $T = \text{constant}$ lines on a T - P diagram coincide.

12–6 ■ THE Δh , Δu , AND Δs OF REAL GASES

We have mentioned many times that gases at low pressures behave as ideal gases and obey the relation $Pv = RT$. The properties of ideal gases are relatively easy to evaluate since the properties u , h , c_v , and c_p depend on temperature only. At high pressures, however, gases deviate considerably from ideal-gas behavior, and it becomes necessary to account for this deviation.

In Chap. 3 we accounted for the deviation in properties P , v , and T by either using more complex equations of state or evaluating the compressibility factor Z from the compressibility charts. Now we extend the analysis to evaluate the changes in the enthalpy, internal energy, and entropy of nonideal (real) gases, using the general relations for du , dh , and ds developed earlier.

Enthalpy Changes of Real Gases

The enthalpy of a real gas, in general, depends on the pressure as well as on the temperature. Thus the enthalpy change of a real gas during a process can be evaluated from the general relation for dh (Eq. 12-36)

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

where P_1 , T_1 and P_2 , T_2 are the pressures and temperatures of the gas at the initial and the final states, respectively. For an isothermal process $dT = 0$, and the first term vanishes. For a constant-pressure process, $dP = 0$, and the second term vanishes.

Properties are point functions, and thus the change in a property between two specified states is the same no matter which process path is followed. This fact can be exploited to greatly simplify the integration of Eq. 12-36. Consider, for example, the process shown on a T - s diagram in Fig. 12-16. The enthalpy change during this process $h_2 - h_1$ can be determined by performing the integrations in Eq. 12-36 along a path that consists of two isothermal ($T_1 = \text{constant}$ and $T_2 = \text{constant}$) lines and one isobaric ($P_0 = \text{constant}$) line instead of the actual process path, as shown in Fig. 12-16.

Although this approach increases the number of integrations, it also simplifies them since one property remains constant now during each part of the process. The pressure P_0 can be chosen to be very low or zero, so that the gas can be treated as an ideal gas during the $P_0 = \text{constant}$ process. Using a superscript asterisk (*) to denote an ideal-gas state, we can express the enthalpy change of a real gas during process 1-2 as

$$h_2 - h_1 = (h_2 - h_2^*) + (h_2^* - h_1^*) + (h_1^* - h_1) \quad (12-53)$$

where, from Eq. 12-36,

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

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

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

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. The calculation of enthalpy departure requires a knowledge of the P - v - T behavior of the gas. In the absence of such data, we can use the relation $Pv = ZRT$, where Z is the compressibility factor. Substituting

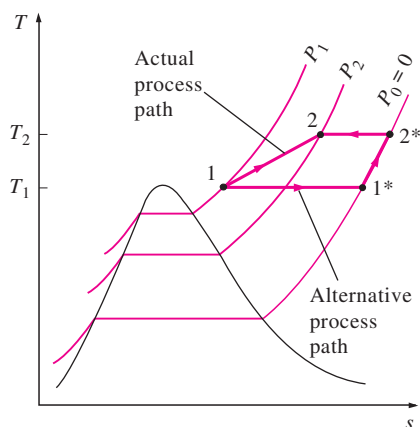


FIGURE 12-16

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

$v = ZRT/P$ and simplifying Eq. 12–56, we can write the enthalpy departure at any temperature T and pressure P as

$$(h^* - h)_T = -RT^2 \int_0^P \left(\frac{\partial Z}{\partial T} \right)_P \frac{dP}{P}$$

The above equation can be generalized by expressing it in terms of the reduced coordinates, using $T = T_{cr}T_R$ and $P = P_{cr}P_R$. After some manipulations, the enthalpy departure can be expressed in a nondimensionalized form as

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

where Z_h is called the **enthalpy departure factor**. The integral in the above equation can be performed graphically or numerically by employing data from the compressibility charts for various values of P_R and T_R . The values of Z_h are presented in graphical form as a function of P_R and T_R in Fig. A–29. This graph is called the **generalized enthalpy departure chart**, and it is used to determine the deviation of the enthalpy of a gas at a given P and T from the enthalpy of an ideal gas at the same T . By replacing h^* by h_{ideal} for clarity, Eq. 12–53 for the enthalpy change of a gas during a process 1–2 can be rewritten as

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

or

$$h_2 - h_1 = (h_2 - h_1)_{ideal} - RT_{cr} (Z_{h_2} - Z_{h_1}) \quad (12-59)$$

where the values of Z_{h_i} are determined from the generalized enthalpy departure chart and $(\bar{h}_2 - \bar{h}_1)_{ideal}$ is determined from the ideal-gas tables. Notice that the last terms on the right-hand side are zero for an ideal gas.

Internal Energy Changes of Real Gases

The internal energy change of a real gas is determined by relating it to the enthalpy change through the definition $\bar{h} = \bar{u} + P\bar{v} = \bar{u} + ZR_u T$:

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

Entropy Changes of Real Gases

The entropy change of a real gas is determined by following an approach similar to that used above for the enthalpy change. There is some difference in derivation, however, owing to the dependence of the ideal-gas entropy on pressure as well as the temperature.

The general relation for ds was expressed as (Eq. 12–41)

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

where P_1 , T_1 and P_2 , T_2 are the pressures and temperatures of the gas at the initial and the final states, respectively. The thought that comes to mind at this point is to perform the integrations in the previous equation first along a $T_1 = \text{constant}$ line to zero pressure, then along the $P = 0$ line to T_2 , and

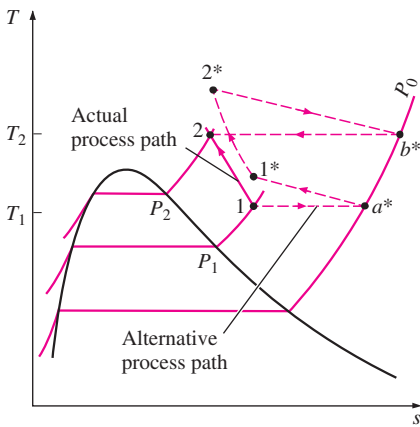


FIGURE 12-17

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

finally along the $T_2 = \text{constant}$ line to P_2 , as we did for the enthalpy. This approach is not suitable for entropy-change calculations, however, since it involves the value of entropy at zero pressure, which is infinity. We can avoid this difficulty by choosing a different (but more complex) path between the two states, as shown in Fig. 12-17. Then the entropy change can be expressed as

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

States 1 and 1* are identical ($T_1 = T_1^*$ and $P_1 = P_1^*$) 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.

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

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

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

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

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

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

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. The values of Z_s are presented in graphical form as a function of P_R and T_R in Fig. A-30. This graph is called the **generalized entropy departure chart**, and it is used to determine the deviation of the entropy of a gas at a given P and T from the entropy of an ideal gas at the same P and T . Replacing s^* by s_{ideal} for clarity, we can rewrite Eq. 12-61 for the entropy change of a gas during a process 1-2 as

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

or

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

where the values of Z_s are determined from the generalized entropy departure chart and the entropy change $(s_2 - s_1)_{\text{ideal}}$ is determined from the ideal-gas relations for entropy change. Notice that the last terms on the right-hand side are zero for an ideal gas.

EXAMPLE 12-11 The Δh and Δs of Oxygen at High Pressures

Determine the enthalpy change and the entropy change of oxygen per unit mole as it undergoes a change of state from 220 K and 5 MPa to 300 K and 10 MPa (a) by assuming ideal-gas behavior and (b) by accounting for the deviation from ideal-gas behavior.

Solution Oxygen undergoes a process between two specified states. The enthalpy and entropy changes are to be determined by assuming ideal-gas behavior and by accounting for the deviation from ideal-gas behavior.

Analysis The critical temperature and pressure of oxygen are $T_{\text{cr}} = 154.8$ K and $P_{\text{cr}} = 5.08$ MPa (Table A-1), respectively. The oxygen remains above its critical temperature; therefore, it is in the gas phase, but its pressure is quite high. Therefore, the oxygen will deviate from ideal-gas behavior and should be treated as a real gas.

(a) If the O_2 is assumed to behave as an ideal gas, its enthalpy will depend on temperature only, and the enthalpy values at the initial and the final temperatures can be determined from the ideal-gas table of O_2 (Table A-19) at the specified temperatures:

$$\begin{aligned} (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} &= \bar{h}_{2,\text{ideal}} - \bar{h}_{1,\text{ideal}} \\ &= (8736 - 6404) \text{ kJ/kmol} \\ &= \mathbf{2332 \text{ kJ/kmol}} \end{aligned}$$

The entropy depends on both temperature and pressure even for ideal gases. Under the ideal-gas assumption, the entropy change of oxygen is determined from

$$\begin{aligned} (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} &= \bar{s}_2^\circ - \bar{s}_1^\circ - R_u \ln \frac{P_2}{P_1} \\ &= (205.213 - 196.171) \text{ kJ/kmol} \cdot \text{K} - (8.314 \text{ kJ/kmol} \cdot \text{K}) \ln \frac{10 \text{ MPa}}{5 \text{ MPa}} \\ &= \mathbf{3.28 \text{ kJ/kmol} \cdot \text{K}} \end{aligned}$$

(b) The deviation from the ideal-gas behavior can be accounted for by determining the enthalpy and entropy departures from the generalized charts at each state:

$$\left. \begin{aligned} T_{R_1} &= \frac{T_1}{T_{\text{cr}}} = \frac{220 \text{ K}}{154.8 \text{ K}} = 1.42 \\ P_{R_1} &= \frac{P_1}{P_{\text{cr}}} = \frac{5 \text{ MPa}}{5.08 \text{ MPa}} = 0.98 \end{aligned} \right\} Z_{h_1} = 0.53, Z_{s_1} = 0.25$$

and

$$\left. \begin{aligned} T_{R_2} &= \frac{T_2}{T_{\text{cr}}} = \frac{300 \text{ K}}{154.8 \text{ K}} = 1.94 \\ P_{R_2} &= \frac{P_2}{P_{\text{cr}}} = \frac{10 \text{ MPa}}{5.08 \text{ MPa}} = 1.97 \end{aligned} \right\} Z_{h_2} = 0.48, Z_{s_2} = 0.20$$

Then the enthalpy and entropy changes of oxygen during this process are determined by substituting the values above into Eqs. 12–58 and 12–63,

$$\begin{aligned} \bar{h}_2 - \bar{h}_1 &= (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} - R_u T_{\text{cr}} (Z_{h_2} - Z_{h_1}) \\ &= 2332 \text{ kJ/kmol} - (8.314 \text{ kJ/kmol} \cdot \text{K}) [154.8 \text{ K} (0.48 - 0.53)] \\ &= \mathbf{2396 \text{ kJ/kmol}} \end{aligned}$$

and

$$\begin{aligned} \bar{s}_2 - \bar{s}_1 &= (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} - R_u (Z_{s_2} - Z_{s_1}) \\ &= 3.28 \text{ kJ/kmol} \cdot \text{K} - (8.314 \text{ kJ/kmol} \cdot \text{K}) (0.20 - 0.25) \\ &= \mathbf{3.70 \text{ kJ/kmol} \cdot \text{K}} \end{aligned}$$

Discussion Note that the ideal-gas assumption would underestimate the enthalpy change of the oxygen by 2.7 percent and the entropy change by 11.4 percent.

SUMMARY

Some thermodynamic properties can be measured directly, but many others cannot. Therefore, it is necessary to develop some relations between these two groups so that the properties that cannot be measured directly can be evaluated. The derivations are based on the fact that properties are point functions, and the state of a simple, compressible system is completely specified by any two independent, intensive properties.

The equations that relate the partial derivatives of properties P , v , T , and s of a simple compressible substance to each other are called the *Maxwell relations*. They are obtained from the *four Gibbs equations*, expressed as

$$du = T ds - P dv$$

$$dh = T ds + v dP$$

$$da = -s dT - P dv$$

$$dg = -s dT + v dP$$

The *Maxwell relations* are

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

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

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

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

The *Clapeyron equation* enables us to determine the enthalpy change associated with a phase change from a knowledge of P , v , and T data alone. It is expressed as

$$\left(\frac{dP}{dT} \right)_{\text{sat}} = \frac{h_{fg}}{T v_{fg}}$$

For liquid–vapor and solid–vapor phase-change processes at low pressures, it can be approximated as

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \cong \frac{h_{fg}}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)_{\text{sat}}$$

The changes in internal energy, enthalpy, and entropy of a simple compressible substance can be expressed in terms of pressure, specific volume, temperature, and specific heats alone as

$$du = c_v dT + \left[T \left(\frac{\partial P}{\partial T} \right)_v - P \right] dv$$

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

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

or

$$ds = \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T} \right)_p dP$$

For specific heats, we have the following general relations:

$$\left(\frac{\partial c_v}{\partial v} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_v$$

$$\left(\frac{\partial c_p}{\partial P} \right)_T = -T \left(\frac{\partial^2 v}{\partial T^2} \right)_p$$

$$c_{p,T} - c_{p0,T} = -T \int_0^P \left(\frac{\partial^2 v}{\partial T^2} \right)_p dP$$

$$c_p - c_v = -T \left(\frac{\partial v}{\partial T} \right)_p^2 \left(\frac{\partial P}{\partial v} \right)_T$$

$$c_p - c_v = \frac{vT\beta^2}{\alpha}$$

where β is the *volume expansivity* and α is the *isothermal compressibility*, defined as

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

The difference $c_p - c_v$ is equal to R for ideal gases and to zero for incompressible substances.

The temperature behavior of a fluid during a throttling ($h = \text{constant}$) process is described by the *Joule-Thomson coefficient*, defined as

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

The Joule-Thomson coefficient is a measure of the change in temperature of a substance with pressure during a constant-enthalpy process, and it can also be expressed as

$$\mu_{JT} = -\frac{1}{c_p} \left[v - T \left(\frac{\partial v}{\partial T} \right)_p \right]$$

The enthalpy, internal energy, and entropy changes of real gases can be determined accurately by utilizing *generalized enthalpy* or *entropy departure charts* to account for the deviation from the ideal-gas behavior by using the following relations:

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

$$\bar{u}_2 - \bar{u}_1 = (\bar{h}_2 - \bar{h}_1) - R_u (Z_2 T_2 - Z_1 T_1)$$

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

where the values of Z_h and Z_s are determined from the generalized charts.

REFERENCES AND SUGGESTED READINGS



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2. K. Wark and D. E. Richards. *Thermodynamics*. 6th ed. New York: McGraw-Hill, 1999.

PROBLEMS*

Partial Derivatives and Associated Relations

12-1C Consider the function $z(x, y)$. Plot a differential surface on x - y - z coordinates and indicate ∂x , dx , ∂y , dy , $(\partial z)_x$, $(\partial z)_y$, and dz .

12-2C What is the difference between partial differentials and ordinary differentials?

*Problems designated by a “C” are concept questions, and students are encouraged to answer them all. Problems designated by an “E” are in English units, and the SI users can ignore them. Problems with a CD-EES icon  are solved using EES, and complete solutions together with parametric studies are included on the enclosed DVD. Problems with a computer-EES icon  are comprehensive in nature, and are intended to be solved with a computer, preferably using the EES software that accompanies this text.

12-3C Consider the function $z(x, y)$, its partial derivatives $(\partial z/\partial x)_y$ and $(\partial z/\partial y)_x$, and the total derivative dz/dx .

(a) How do the magnitudes $(\partial x)_y$ and dx compare?

(b) How do the magnitudes $(\partial z)_y$ and dz compare?

(c) Is there any relation among dz , $(\partial z)_x$, and $(\partial z)_y$?

12-4C Consider a function $z(x, y)$ and its partial derivative $(\partial z/\partial y)_x$. Under what conditions is this partial derivative equal to the total derivative dz/dy ?

12-5C Consider a function $z(x, y)$ and its partial derivative $(\partial z/\partial y)_x$. If this partial derivative is equal to zero for all values of x , what does it indicate?

12-6C Consider a function $z(x, y)$ and its partial derivative $(\partial z/\partial y)_x$. Can this partial derivative still be a function of x ?

12-7C Consider a function $f(x)$ and its derivative df/dx . Can this derivative be determined by evaluating dx/df and taking its inverse?

12-8 Consider air at 400 K and 0.90 m³/kg. Using Eq. 12-3, determine the change in pressure corresponding to an increase of (a) 1 percent in temperature at constant specific volume, (b) 1 percent in specific volume at constant temperature, and (c) 1 percent in both the temperature and specific volume.

12-9 Repeat Problem 12-8 for helium.

12-10 Prove for an ideal gas that (a) the $P = \text{constant}$ lines on a T - v diagram are straight lines and (b) the high-pressure lines are steeper than the low-pressure lines.

12-11 Derive a relation for the slope of the $v = \text{constant}$ lines on a T - P diagram for a gas that obeys the van der Waals equation of state. *Answer: $(v - b)/R$*

12-12 Nitrogen gas at 400 K and 300 kPa behaves as an ideal gas. Estimate the c_p and c_v of the nitrogen at this state, using enthalpy and internal energy data from Table A-18, and compare them to the values listed in Table A-2b.


12-13E Nitrogen gas at 600 R and 30 psia behaves as an ideal gas. Estimate the c_p and c_v of the nitrogen at this state, using enthalpy and internal energy data from Table A-18E, and compare them to the values listed in Table A-2Eb. *Answers: 0.249 Btu/lbm · R, 0.178 Btu/lbm · R*

12-14 Consider an ideal gas at 400 K and 100 kPa. As a result of some disturbance, the conditions of the gas change to 404 K and 96 kPa. Estimate the change in the specific volume of the gas using (a) Eq. 12-3 and (b) the ideal-gas relation at each state.

12-15 Using the equation of state $P(v - a) = RT$, verify (a) the cyclic relation and (b) the reciprocity relation at constant v .

The Maxwell Relations

12-16 Verify the validity of the last Maxwell relation (Eq. 12-19) for refrigerant-134a at 80°C and 1.2 MPa.

12-17  Reconsider Prob. 12-16. Using EES (or other) software, verify the validity of the last Maxwell relation for refrigerant-134a at the specified state.

12-18E Verify the validity of the last Maxwell relation (Eq. 12-19) for steam at 800°F and 400 psia.

12-19 Using the Maxwell relations, determine a relation for $(\partial s/\partial P)_T$ for a gas whose equation of state is $P(v - b) = RT$. *Answer: $-R/P$*

12-20 Using the Maxwell relations, determine a relation for $(\partial s/\partial v)_T$ for a gas whose equation of state is $(P - a/v^2)(v - b) = RT$.

12-21 Using the Maxwell relations and the ideal-gas equation of state, determine a relation for $(\partial s/\partial v)_T$ for an ideal gas. *Answer: R/v*


The Clapeyron Equation

12-22C What is the value of the Clapeyron equation in thermodynamics?

12-23C Does the Clapeyron equation involve any approximations, or is it exact?


12-24C What approximations are involved in the Clapeyron-Clausius equation?


12-25 Using the Clapeyron equation, estimate the enthalpy of vaporization of refrigerant-134a at 40°C, and compare it to the tabulated value.

12-26  Reconsider Prob. 12-25. Using EES (or other) software, plot the enthalpy of vaporization of refrigerant-134a as a function of temperature over the temperature range -20 to 80°C by using the Clapeyron equation and the refrigerant-134a data in EES. Discuss your results.

12-27 Using the Clapeyron equation, estimate the enthalpy of vaporization of steam at 300 kPa, and compare it to the tabulated value.

12-28 Calculate the h_{fg} and s_{fg} of steam at 120°C from the Clapeyron equation, and compare them to the tabulated values.

12-29E  Determine the h_{fg} of refrigerant-134a at 50°F on the basis of (a) the Clapeyron equation and (b) the Clapeyron-Clausius equation. Compare your results to the tabulated h_{fg} value.

12-30  Plot the enthalpy of vaporization of steam as a function of temperature over the temperature range 10 to 200°C by using the Clapeyron equation and steam data in EES.

12-31 Using the Clapeyron-Clausius equation and the triple-point data of water, estimate the sublimation pressure of water at -30°C and compare to the value in Table A-8.

General Relations for du , dh , ds , c_v , and c_p

12-32C Can the variation of specific heat c_p with pressure at a given temperature be determined from a knowledge of P - v - T data alone?

12-33 Show that the enthalpy of an ideal gas is a function of temperature only and that for an incompressible substance it also depends on pressure.

12-34 Derive expressions for (a) Δu , (b) Δh , and (c) Δs for a gas that obeys the van der Waals equation of state for an isothermal process.

12-35 Derive expressions for (a) Δu , (b) Δh , and (c) Δs for a gas whose equation of state is $P(v - a) = RT$ for an isothermal process. *Answers: (a) 0, (b) $a(P_2 - P_1)$, (c) $-R \ln(P_2/P_1)$*

12-36 Derive expressions for $(\partial u/\partial P)_T$ and $(\partial h/\partial v)_T$ in terms of P , v , and T only.

12-37 Derive an expression for the specific-heat difference $c_p - c_v$ for (a) an ideal gas, (b) a van der Waals gas, and (c) an incompressible substance.

12-38 Estimate the specific-heat difference $c_p - c_v$ for liquid water at 15 MPa and 80°C. *Answer: 0.32 kJ/kg · K*

12-39E Estimate the specific-heat difference $c_p - c_v$ for liquid water at 1000 psia and 150°F. *Answer: 0.057 Btu/lbm · R*

12-40 Derive a relation for the volume expansivity β and the isothermal compressibility α (a) for an ideal gas and (b) for a gas whose equation of state is $P(v - a) = RT$.

12-41 Estimate the volume expansivity β and the isothermal compressibility α of refrigerant-134a at 200 kPa and 30°C.

The Joule-Thomson Coefficient

12-42C What does the Joule-Thomson coefficient represent?

12-43C Describe the inversion line and the maximum inversion temperature.

12-44C The pressure of a fluid always decreases during an adiabatic throttling process. Is this also the case for the temperature?


12-45C Does the Joule-Thomson coefficient of a substance change with temperature at a fixed pressure?


12-46C Will the temperature of helium change if it is throttled adiabatically from 300 K and 600 kPa to 150 kPa?

12-47 Consider a gas whose equation of state is $P(v - a) = RT$, where a is a positive constant. Is it possible to cool this gas by throttling?

12-48 Derive a relation for the Joule-Thomson coefficient and the inversion temperature for a gas whose equation of state is $(P + a/v^2)v = RT$.

12-49 Estimate the Joule-Thomson coefficient of steam at (a) 3 MPa and 300°C and (b) 6 MPa and 500°C.

12-50E  Estimate the Joule-Thomson coefficient of nitrogen at (a) 200 psia and 500 R and (b) 2000 psia and 400 R. Use nitrogen properties from EES or other source.

12-51E  Reconsider Prob. 12-50E. Using EES (or other) software, plot the Joule-Thomson coefficient for nitrogen over the pressure range 100 to 1500 psia at the enthalpy values 100, 175, and 225 Btu/lbm. Discuss the results.

12-52 Estimate the Joule-Thomson coefficient of refrigerant-134a at 0.7 MPa and 50°C.

12-53 Steam is throttled slightly from 1 MPa and 300°C. Will the temperature of the steam increase, decrease, or remain the same during this process?

The dh , du , and ds of Real Gases

12-54C What is the enthalpy departure?

12-55C On the generalized enthalpy departure chart, the normalized enthalpy departure values seem to approach zero as the reduced pressure P_R approaches zero. How do you explain this behavior?

12-56C Why is the generalized enthalpy departure chart prepared by using P_R and T_R as the parameters instead of P and T ?

12-57 Determine the enthalpy of nitrogen, in kJ/kg, at 175 K and 8 MPa using (a) data from the ideal-gas nitrogen table and (b) the generalized enthalpy departure chart. Compare your results to the actual value of 125.5 kJ/kg. *Answers: (a) 181.5 kJ/kg, (b) 121.6 kJ/kg*

12-58E Determine the enthalpy of nitrogen, in Btu/lbm, at 400 R and 2000 psia using (a) data from the ideal-gas nitrogen table and (b) the generalized enthalpy chart. Compare your results to the actual value of 177.8 Btu/lbm.

12-59 What is the error involved in the (a) enthalpy and (b) internal energy of CO_2 at 350 K and 10 MPa if it is assumed to be an ideal gas? *Answers: (a) 50%, (b) 49%*

12-60 Determine the enthalpy change and the entropy change of nitrogen per unit mole as it undergoes a change of state from 225 K and 6 MPa to 320 K and 12 MPa, (a) by assuming ideal-gas behavior and (b) by accounting for the deviation from ideal-gas behavior through the use of generalized charts.

12-61 Determine the enthalpy change and the entropy change of CO_2 per unit mass as it undergoes a change of state from 250 K and 7 MPa to 280 K and 12 MPa, (a) by assuming ideal-gas behavior and (b) by accounting for the deviation from ideal-gas behavior.

12-62 Methane is compressed adiabatically by a steady-flow compressor from 2 MPa and -10°C to 10 MPa and 110°C at a rate of 0.55 kg/s. Using the generalized charts, determine the required power input to the compressor. *Answer: 133 kW*

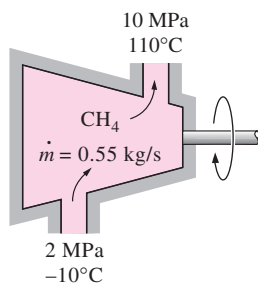




FIGURE P12-62

12-63  Propane is compressed isothermally by a piston-cylinder device from 100°C and 1 MPa to 4 MPa. Using the generalized charts, determine the work done and the heat transfer per unit mass of propane.


12-64  Reconsider Prob. 12-63. Using EES (or other) software, extend the problem to compare the solutions based on the ideal-gas assumption, generalized chart data, and real fluid data. Also extend the solution to methane.

12-65E Propane is compressed isothermally by a piston-cylinder device from 200°F and 200 psia to 800 psia. Using the generalized charts, determine the work done and the heat transfer per unit mass of the propane.

Answers: 45.3 Btu/lbm, 141 Btu/lbm

12-66 Determine the exergy destruction associated with the process described in Prob. 12-63. Assume $T_0 = 30^\circ\text{C}$.

12-67 Carbon dioxide enters an adiabatic nozzle at 8 MPa and 450 K with a low velocity and leaves at 2 MPa and 350 K. Using the generalized enthalpy departure chart, determine the exit velocity of the carbon dioxide. *Answer:* 384 m/s

12-68  Reconsider Prob. 12-67. Using EES (or other) software, compare the exit velocity to the nozzle assuming ideal-gas behavior, the generalized chart data, and EES data for carbon dioxide.

12-69 A 0.08-m³ well-insulated rigid tank contains oxygen at 220 K and 10 MPa. A paddle wheel placed in the tank is turned on, and the temperature of the oxygen rises to 250 K. Using the generalized charts, determine (a) the final pressure in the tank and (b) the paddle-wheel work done during this process. *Answers:* (a) 12,190 kPa, (b) 393 kJ

12-70 Carbon dioxide is contained in a constant-volume tank and is heated from 100°C and 1 MPa to 8 MPa. Determine the heat transfer and entropy change per unit mass of the carbon dioxide using (a) the ideal-gas assumption, (b) the generalized charts, and (c) real fluid data from EES or other sources.

Review Problems

12-71 For $\beta \geq 0$, prove that at every point of a single-phase region of an h - s diagram, the slope of a constant-pressure ($P = \text{constant}$) line is greater than the slope of a

constant-temperature ($T = \text{constant}$) line, but less than the slope of a constant-volume ($v = \text{constant}$) line.

12-72 Using the cyclic relation and the first Maxwell relation, derive the other three Maxwell relations.

12-73 Starting with the relation $dh = T ds + v dP$, show that the slope of a constant-pressure line on an h - s diagram (a) is constant in the saturation region and (b) increases with temperature in the superheated region.

12-74 Derive relations for (a) Δu , (b) Δh , and (c) Δs of a gas that obeys the equation of state $(P + a/v^2)v = RT$ for an isothermal process.

12-75 Show that

$$c_v = -T \left(\frac{\partial v}{\partial T} \right)_s \left(\frac{\partial P}{\partial T} \right)_v \quad \text{and} \quad c_p = T \left(\frac{\partial P}{\partial T} \right)_s \left(\frac{\partial v}{\partial T} \right)_p$$

12-76 Estimate the c_p of nitrogen at 300 kPa and 400 K, using (a) the relation in the above problem and (b) its definition. Compare your results to the value listed in Table A-2b.

12-77 Steam is throttled from 4.5 MPa and 300°C to 2.5 MPa. Estimate the temperature change of the steam during this process and the average Joule-Thomson coefficient.

Answers: -26.3°C, 13.1°C/MPa

12-78 A rigid tank contains 1.2 m³ of argon at -100°C and 1 MPa. Heat is now transferred to argon until the temperature in the tank rises to 0°C. Using the generalized charts, determine (a) the mass of the argon in the tank, (b) the final pressure, and (c) the heat transfer.

Answers: (a) 35.1 kg, (b) 1531 kPa, (c) 1251 kJ

12-79 Argon gas enters a turbine at 7 MPa and 600 K with a velocity of 100 m/s and leaves at 1 MPa and 280 K with a velocity of 150 m/s at a rate of 5 kg/s. Heat is being lost to the surroundings at 25°C at a rate of 60 kW. Using the generalized charts, determine (a) the power output of the turbine and (b) the exergy destruction associated with the process.

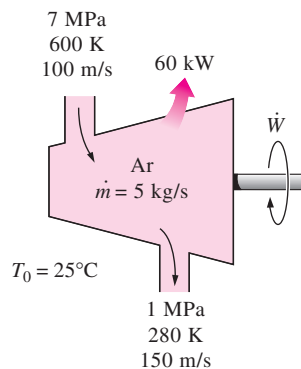



FIGURE P12-79

12-80  Reconsider Prob. 12-79. Using EES (or other) software, solve the problem assuming steam is the working fluid by using the generalized chart method and EES data for steam. Plot the power output and the exergy destruction rate for these two calculation methods against the turbine exit pressure as it varies over the range 0.1 to 1 MPa when the turbine exit temperature is 455 K.

12-81E Argon gas enters a turbine at 1000 psia and 1000 R with a velocity of 300 ft/s and leaves at 150 psia and 500 R with a velocity of 450 ft/s at a rate of 12 lbm/s. Heat is being lost to the surroundings at 75°F at a rate of 80 Btu/s. Using the generalized charts, determine (a) the power output of the turbine and (b) the exergy destruction associated with the process. *Answers: (a) 922 hp, (b) 121.5 Btu/s*

12-82 An adiabatic 0.2-m³ storage tank that is initially evacuated is connected to a supply line that carries nitrogen at 225 K and 10 MPa. A valve is opened, and nitrogen flows into the tank from the supply line. The valve is closed when the pressure in the tank reaches 10 MPa. Determine the final temperature in the tank (a) treating nitrogen as an ideal gas and (b) using generalized charts. Compare your results to the actual value of 293 K.

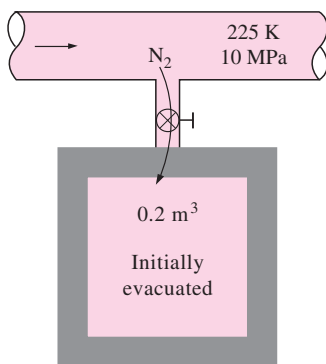


FIGURE P12-82

12-83 For a homogeneous (single-phase) simple pure substance, the pressure and temperature are independent properties, and any property can be expressed as a function of these two properties. Taking $v = v(P, T)$, show that the change in specific volume can be expressed in terms of the volume expansivity β and isothermal compressibility α as

$$\frac{dv}{v} = \beta dT - \alpha dP$$

Also, assuming constant average values for β and α , obtain a relation for the ratio of the specific volumes v_2/v_1 as a homogeneous system undergoes a process from state 1 to state 2.

12-84 Repeat Prob. 12-83 for an isobaric process.

12-85 The volume expansivity of water at 20°C is $\beta = 0.207 \times 10^{-6} \text{ K}^{-1}$. Treating this value as a constant, determine the change in volume of 1 m³ of water as it is heated from 10°C to 30°C at constant pressure.


12-86 The volume expansivity β values of copper at 300 K and 500 K are $49.2 \times 10^{-6} \text{ K}^{-1}$ and $54.2 \times 10^{-6} \text{ K}^{-1}$, respectively, and β varies almost linearly in this temperature range. Determine the percent change in the volume of a copper block as it is heated from 300 K to 500 K at atmospheric pressure.

12-87 Starting with $\mu_{JT} = (1/c_p) [T(\partial v/\partial T)_p - v]$ and noting that $Pv = ZRT$, where $Z = Z(P, T)$ is the compressibility factor, show that the position of the Joule-Thomson coefficient inversion curve on the T - P plane is given by the equation $(\partial Z/\partial T)_p = 0$.

12-88 Consider an infinitesimal reversible adiabatic compression or expansion process. By taking $s = s(P, v)$ and using the Maxwell relations, show that for this process $Pv^k = \text{constant}$, where k is the *isentropic expansion exponent* defined as

$$k = \frac{v}{P} \left(\frac{\partial P}{\partial v} \right)_s$$

Also, show that the isentropic expansion exponent k reduces to the specific heat ratio c_p/c_v for an ideal gas.

12-89  Refrigerant-134a undergoes an isothermal process at 60°C from 3 to 0.1 MPa in a closed system. Determine the work done by the refrigerant-134a by using the tabular (EES) data and the generalized charts, in kJ/kg.

12-90 Methane is contained in a piston-cylinder device and is heated at constant pressure of 4 MPa from 100 to 350°C. Determine the heat transfer, work and entropy change per unit mass of the methane using (a) the ideal-gas assumption, (b) the generalized charts, and (c) real fluid data from EES or other sources.

Fundamentals of Engineering (FE) Exam Problems

12-91 A substance whose Joule-Thomson coefficient is negative is throttled to a lower pressure. During this process, (select the correct statement)

- the temperature of the substance will increase.
- the temperature of the substance will decrease.
- the entropy of the substance will remain constant.
- the entropy of the substance will decrease.
- the enthalpy of the substance will decrease.

12-92 Consider the liquid-vapor saturation curve of a pure substance on the P - T diagram. The magnitude of the slope of the tangent line to this curve at a temperature T (in Kelvin) is

- (a) proportional to the enthalpy of vaporization h_{fg} at that temperature.
 (b) proportional to the temperature T .
 (c) proportional to the square of the temperature T .
 (d) proportional to the volume change v_{fg} at that temperature.
 (e) inversely proportional to the entropy change s_{fg} at that temperature.

12-93 Based on the generalized charts, the error involved in the enthalpy of CO_2 at 350 K and 8 MPa if it is assumed to be an ideal gas is

- (a) 0 (b) 20% (c) 35% (d) 26% (e) 65%

12-94 Based on data from the refrigerant-134a tables, the Joule-Thompson coefficient of refrigerant-134a at 0.8 MPa and 100°C is approximately

- (a) 0 (b) $-5^\circ\text{C}/\text{MPa}$ (c) $11^\circ\text{C}/\text{MPa}$
 (d) $8^\circ\text{C}/\text{MPa}$ (e) $26^\circ\text{C}/\text{MPa}$

12-95 For a gas whose equation of state is $P(v - b) = RT$, the specified heat difference $c_p - c_v$ is equal to

- (a) R (b) $R - b$ (c) $R + b$ (d) 0 (e) $R(1 + v/b)$

Design and Essay Problems

12-96 Consider the function $z = z(x, y)$. Write an essay on the physical interpretation of the ordinary derivative dz/dx and the partial derivative $(\partial z/\partial x)_y$. Explain how these two derivatives are related to each other and when they become equivalent.

12-97 There have been several attempts to represent the thermodynamic relations geometrically, the best known of these

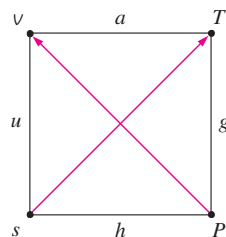


FIGURE P12-97

being Koenig's thermodynamic square shown in the figure. There is a systematic way of obtaining the four Maxwell relations as well as the four relations for du , dh , dg , and da from this figure. By comparing these relations to Koenig's diagram, come up with the rules to obtain these eight thermodynamic relations from this diagram.

12-98 Several attempts have been made to express the partial derivatives of the most common thermodynamic properties in a compact and systematic manner in terms of measurable properties. The work of P. W. Bridgman is perhaps the most fruitful of all, and it resulted in the well-known Bridgman's table. The 28 entries in that table are sufficient to express the partial derivatives of the eight common properties P , T , v , s , u , h , f , and g in terms of the six properties P , v , T , c_p , β , and α , which can be measured directly or indirectly with relative ease. Obtain a copy of Bridgman's table and explain, with examples, how it is used.