Thermodynamics: An Engineering Approach, 6th Edition
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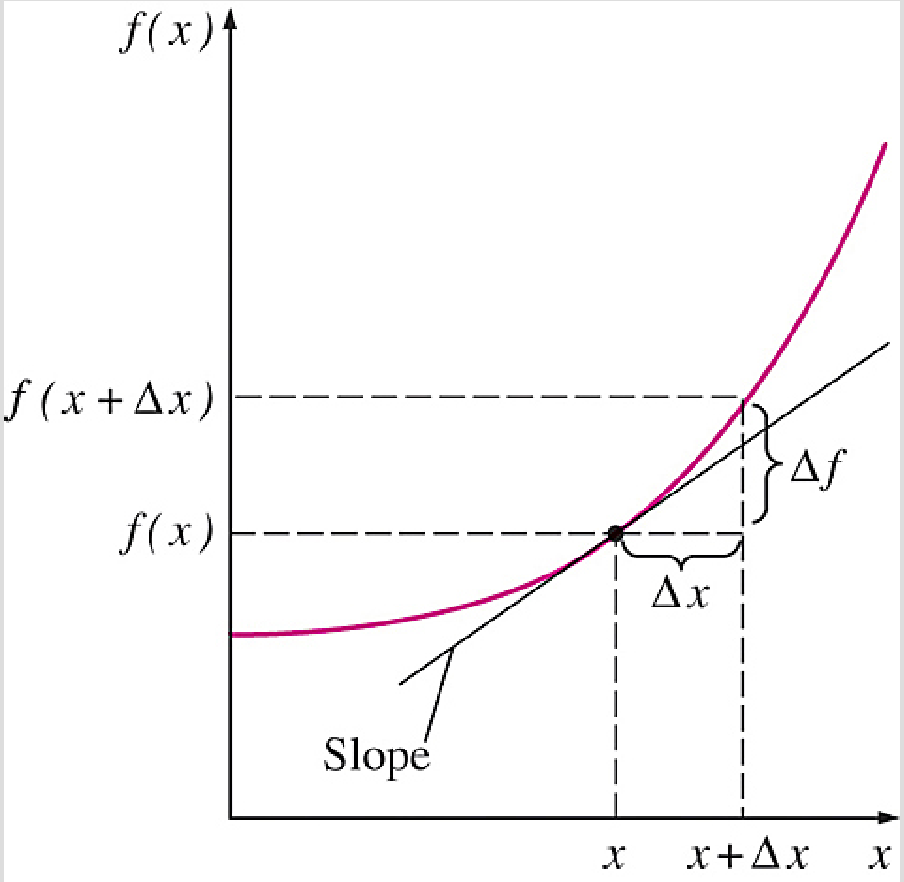
Chapter 12

THERMODYNAMIC PROPERTY RELATIONS

Objectives

- 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.

A LITTLE MATH—PARTIAL DERIVATIVES AND ASSOCIATED RELATIONS



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

The state postulate: 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.

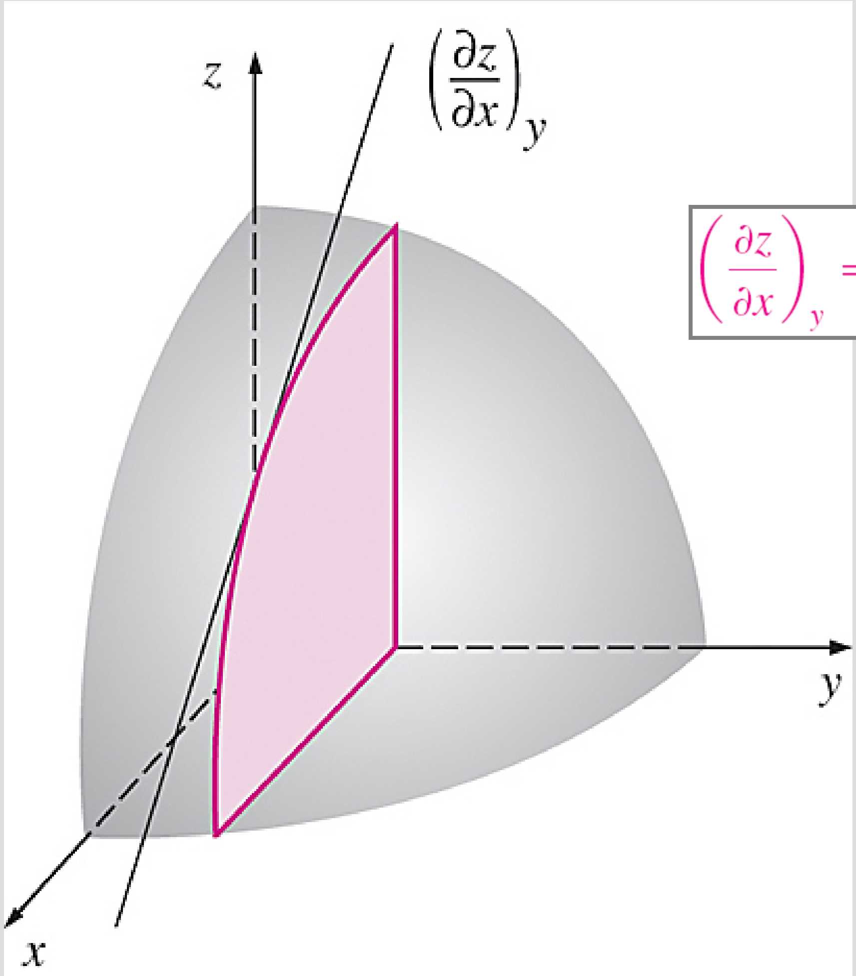
$$z = z(x, y)$$

$$f = f(x)$$

$$\frac{df}{dx} = \lim_{\Delta x \to 0} \frac{\Delta f}{\Delta x} = \lim_{\Delta x \to 0} \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

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

Partial Differentials



Geometric representation of partial derivative $(\partial z/\partial x)_y$.

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

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

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.

The changes indicated by d and ∂ are identical for independent variables, but not for dependent variables.

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

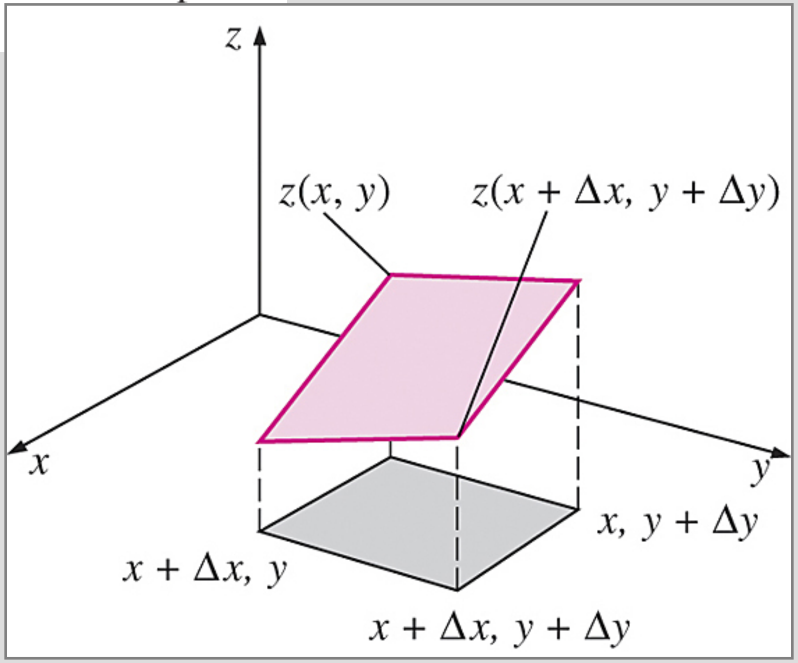
$$\Delta z = \frac{z(x + \Delta x, y + \Delta y) - z(x, y + \Delta y)}{\Delta x}\Delta x + \frac{z(x, y + \Delta y) - z(x, y)}{\Delta y}\Delta y$$

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

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

This is the fundamental relation for the **total differential** of a dependent variable in terms of its partial derivatives with respect to the independent variables.

Geometric representation of total derivative *dz* for a function *z*(*x*, *y*).



Partial Differential Relations

$$dz = M\,dx + N\,dy$$

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

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

The order of differentiation is immaterial for properties since they are continuous point functions and have exact differentials. Thus,

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

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

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

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

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

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

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

Reciprocity relation

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

Cyclic relation

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.

$$du = T\,ds - P\,dv$$

$$dh = T\,ds + v\,dP$$

$$a = u - Ts \quad \text{Helmholtz function}$$

$$g = h - Ts \quad \text{Gibbs function}$$

$$da = du - T\,ds - s\,dT \qquad dg = dh - T\,ds - s\,dT$$

$$\rightarrow \quad da = -s\,dT - P\,dv \qquad dg = -s\,dT + v\,dP$$

$$dz = M\,dx + N\,dy \quad \rightarrow \quad \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

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

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

Maxwell relations

Maxwell relations 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*.

These Maxwell relations are limited to simple compressible systems.

THE CLAPEYRON EQUATION

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

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

or

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

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

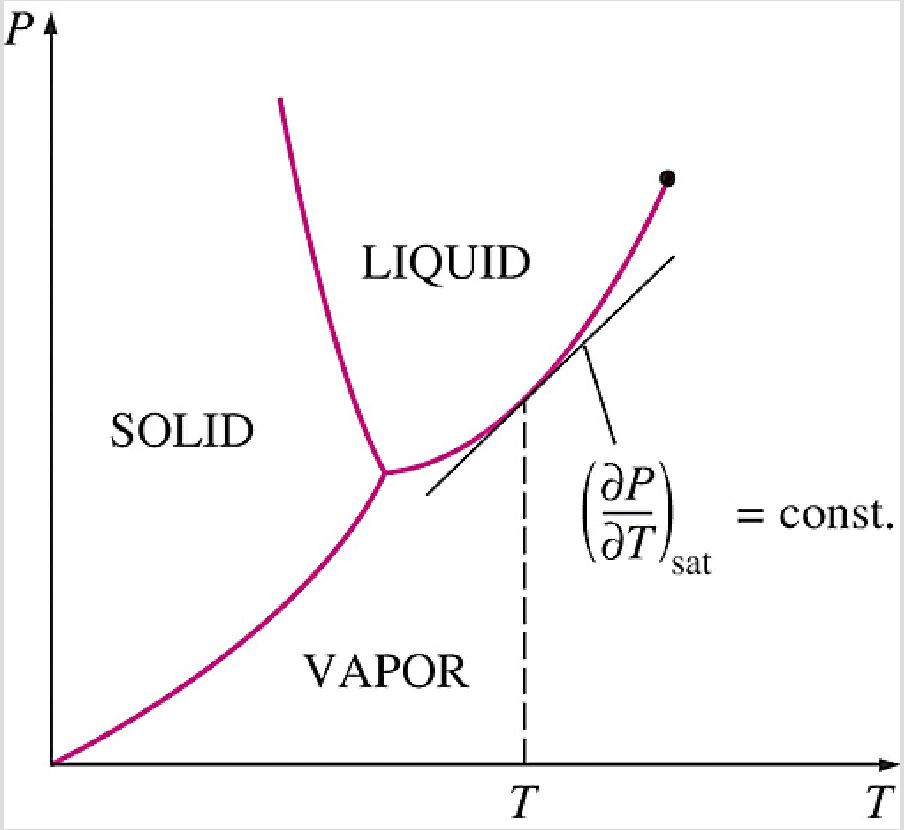
$$dh = T\,ds + v\,\overset{\nearrow 0}{dP} \rightarrow \int_f^g dh = \int_f^g T\,ds \rightarrow h_{fg} = Ts_{fg}$$

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

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

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

Clapeyron equation



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

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

General form of the Clapeyron equation when the subscripts 1 and 2 indicate the two phases.

The Clapeyron equation can be simplified for liquid–vapor and solid–vapor phase changes by utilizing some approximations.

At low pressures $v_g \gg v_f \rightarrow v_{fg} \cong v_g$

Treating vapor as an ideal gas $v_g = RT/P$

Substituting these equations into the Clapeyron equation

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

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

Integrating between two saturation states

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

Clapeyron–Clausius equation

The Clapeyron–Clausius equation 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.

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, we should be able to calculate all the properties of a system such as internal energy, enthalpy, and entropy at any state once two independent, intensive properties are available.
- 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

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

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

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

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

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

Equating the coefficients of dT and $d\mathrm{v}$ in Eqs. 12–25 and 12–27 gives

$$\left(\frac{\partial s}{\partial T}\right)_{\mathrm{v}} = \frac{c_{\mathrm{v}}}{T}$$

$$\left(\frac{\partial u}{\partial \mathrm{v}}\right)_{T} = T\left(\frac{\partial s}{\partial \mathrm{v}}\right)_{T} - P \tag{12–28}$$

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

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

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

$$du = c_{\mathrm{v}}\, dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{v}} - P\right] d\mathrm{v} \tag{12–29}$$

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:

$$u_2 - u_1 = \int_{T_1}^{T_2} c_{\mathrm{v}}\, dT + \int_{\mathrm{v}_1}^{\mathrm{v}_2} \left[T\left(\frac{\partial P}{\partial T}\right)_{\mathrm{v}} - P\right] d\mathrm{v}$$

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

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

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,

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

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

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

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

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{c_p}{T}$$

$$\left(\frac{\partial h}{\partial P}\right)_T = v + T\left(\frac{\partial s}{\partial P}\right)_T \tag{12–34}$$

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:

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

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:

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

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 $h = u + Pv$:

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

Entropy Changes

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

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

and

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

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

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

and

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

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

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

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

and

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

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:

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

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:

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

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

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

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)

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

and

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

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

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

Mayer relation

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

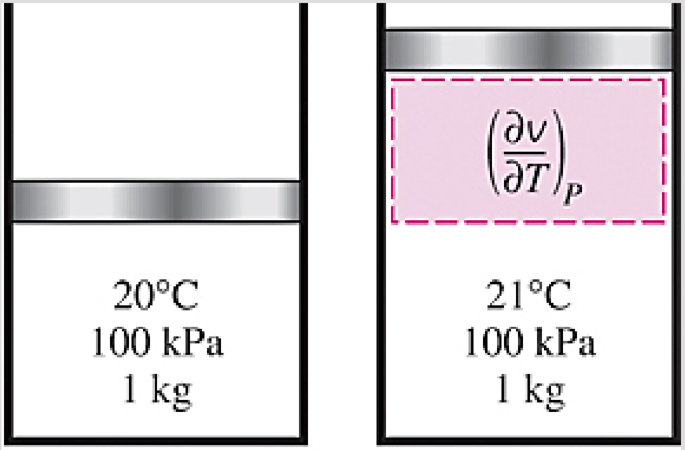
Conclusions from Mayer relation:

1. The right hand side of the equation is always greater than or equal to zero. Therefore, we conclude that

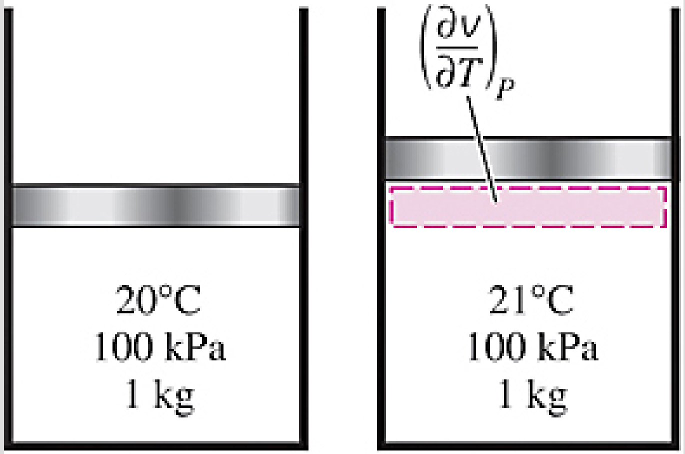
$$c_p \geq c_v$$

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

3. The two specific heats are identical for truly incompressible substances since v constant. The difference between the two specific heats is very small and is usually disregarded for substances that are *nearly* incompressible, such as liquids and solids.

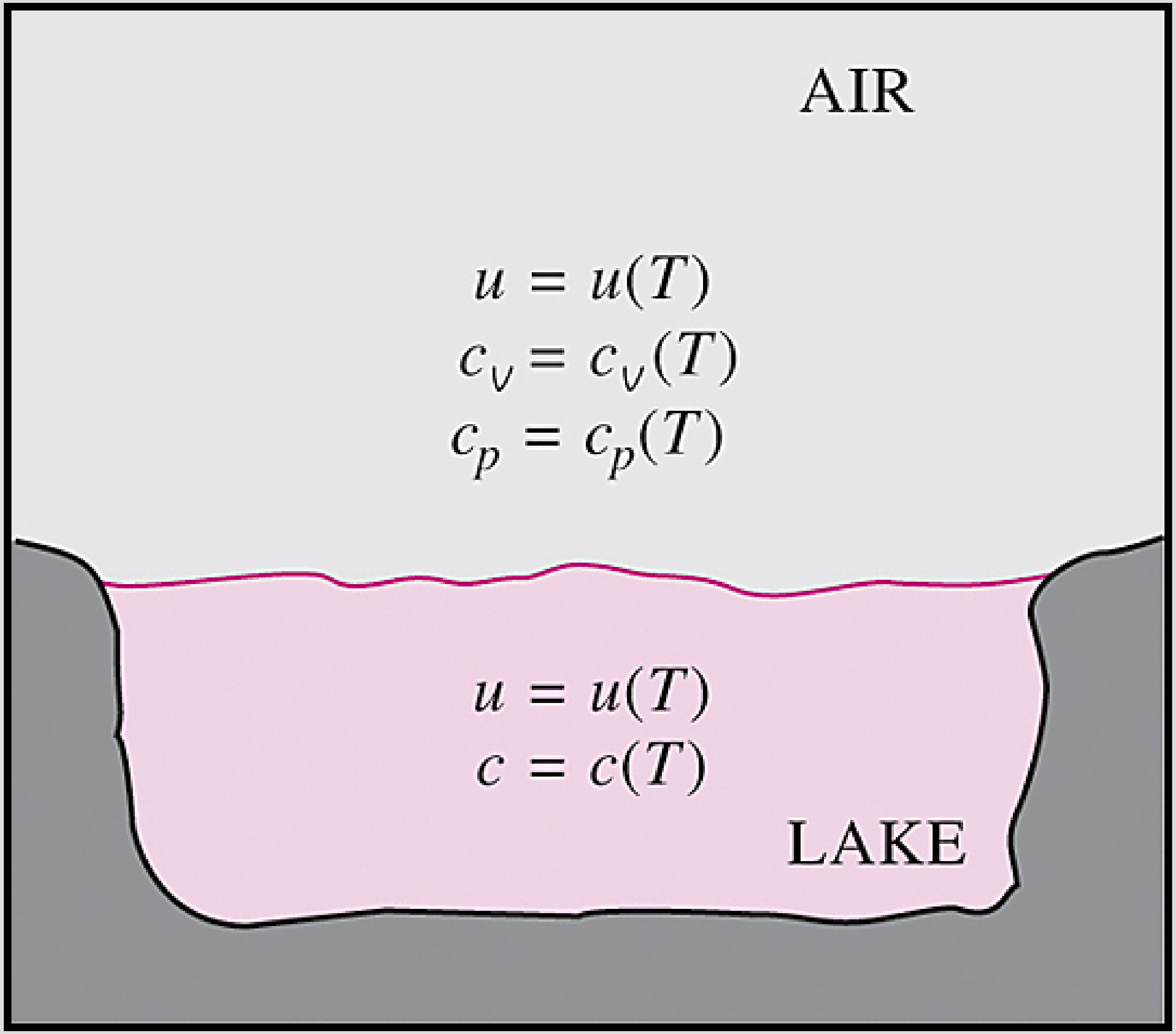


(*a*) A substance with a large β



(*b*) A substance with a small β

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



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:

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

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

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

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,

$$c_p - c_v = R$$

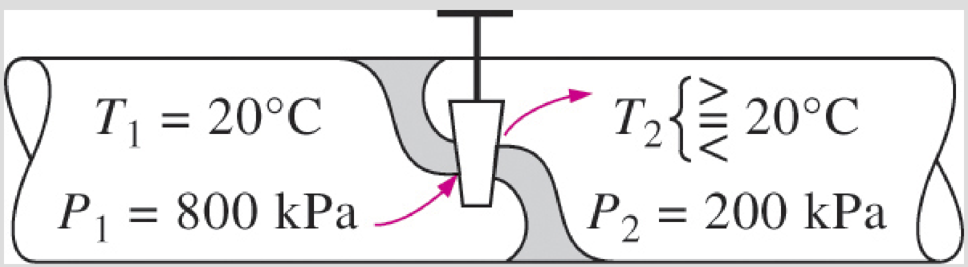
THE JOULE-THOMSON COEFFICIENT

The temperature behavior of a fluid during a throttling (*h* = constant) process is described by the Joule-Thomson coefficient

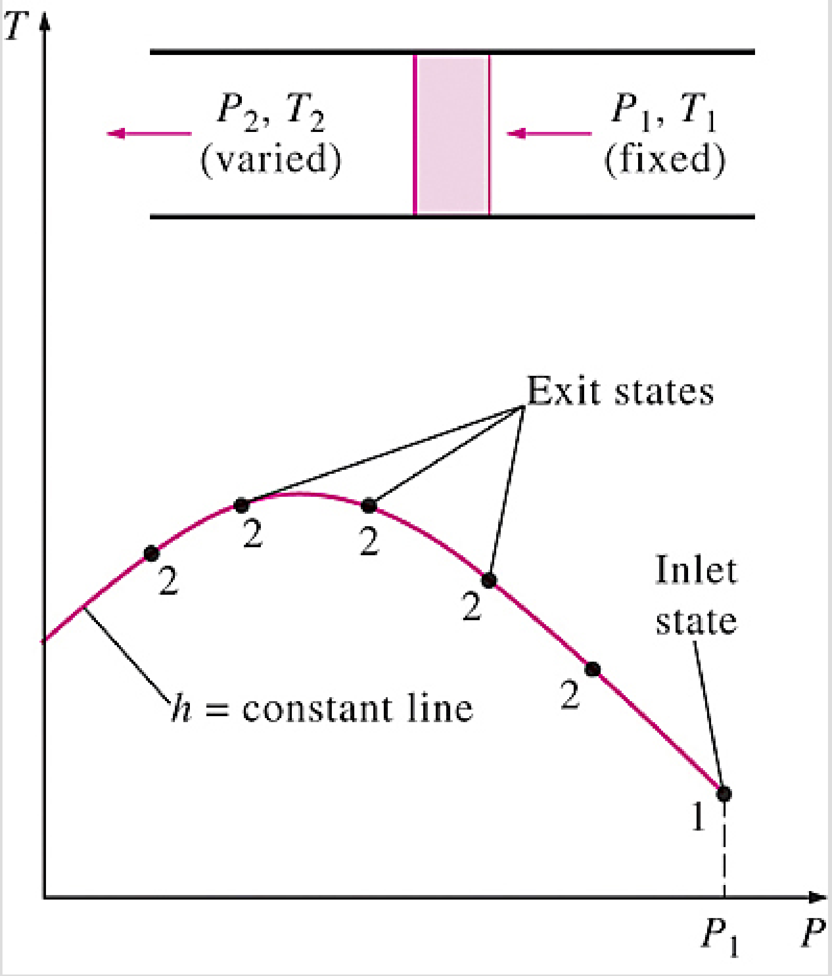
$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

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

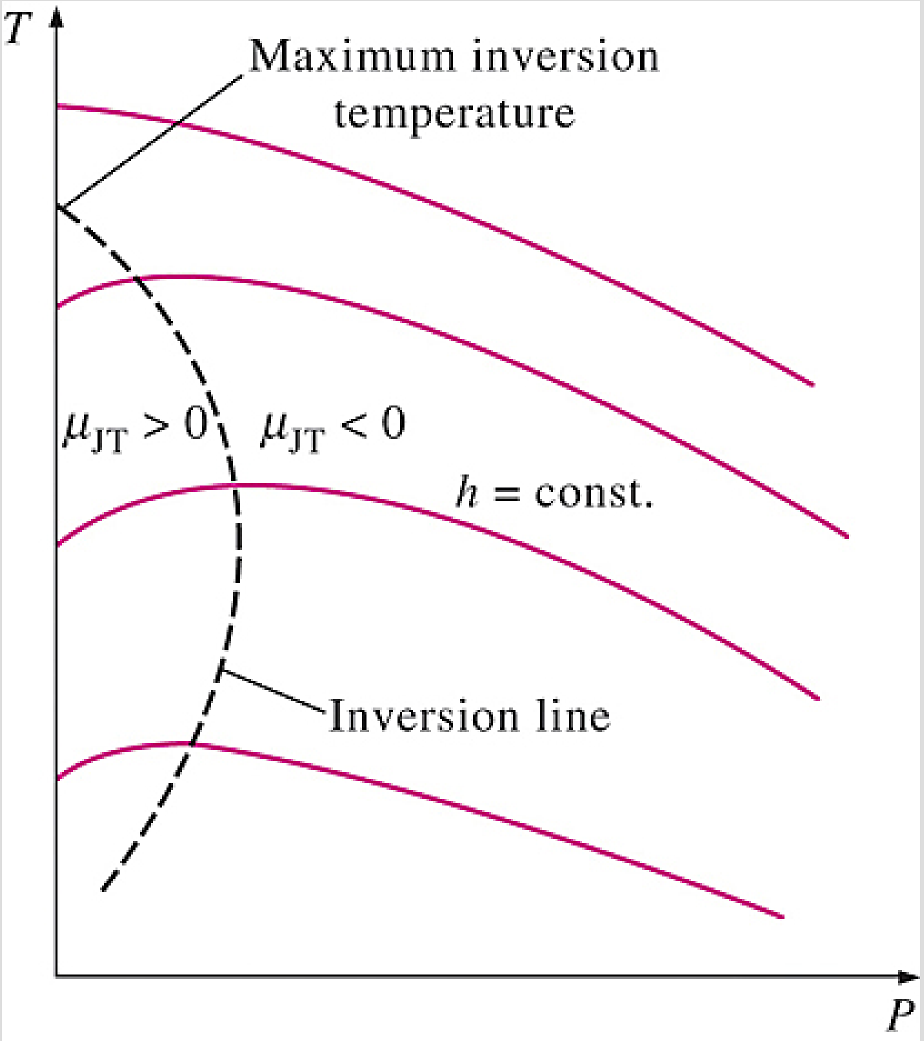
The Joule-Thomson coefficient represents the slope of *h* = constant lines on a *T-P* diagram.



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



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



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

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.

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

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

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.

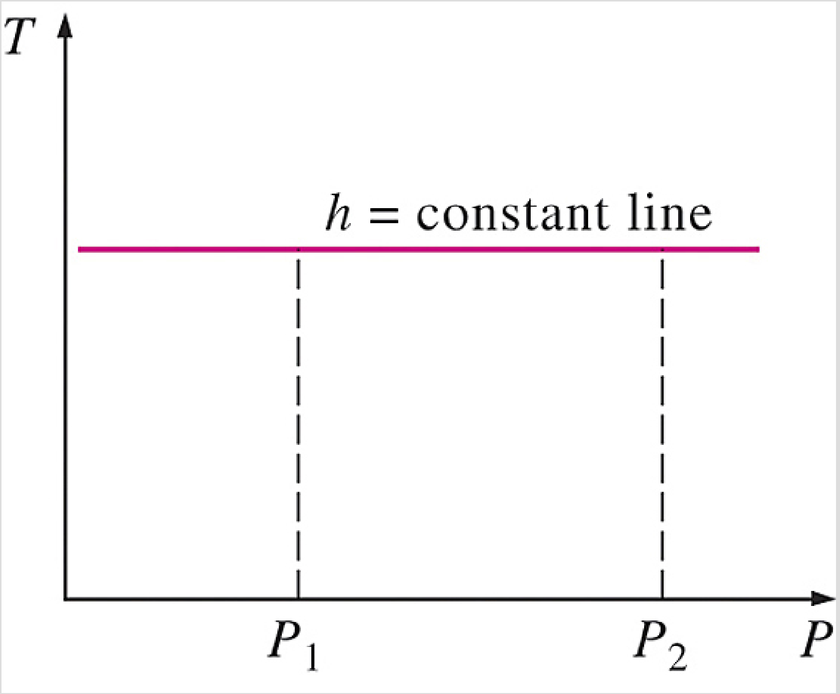
Solution It is to be shown that $\mu_{JT} = 0$ for an ideal gas.

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

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



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

THE Δh, Δu, AND Δs OF REAL GASES

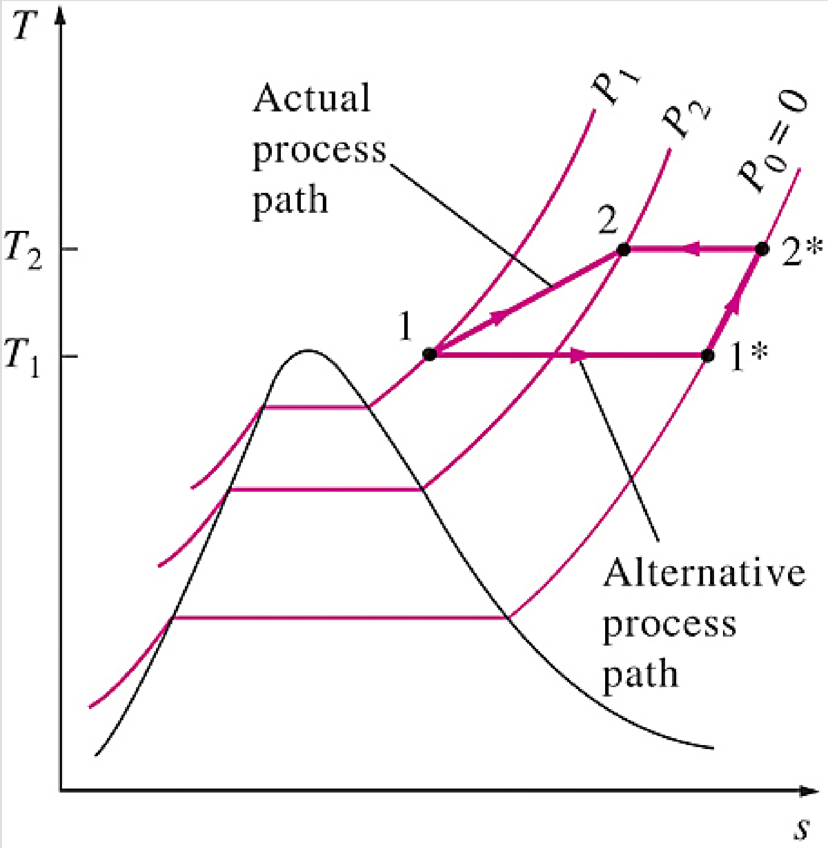
- Gases at low pressures behave as ideal gases and obey the relation $Pv = RT$. The properties of ideal gases are relatively easy to evaluate since the properties u, h, c_v, and c_p depend on temperature only.
- At high pressures, however, gases deviate considerably from ideal-gas behavior, and it becomes 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*

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

For an isothermal process $dT = 0$, and the first term vanishes. For a constant-pressure process, $dP = 0$, and the second term vanishes.



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

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

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

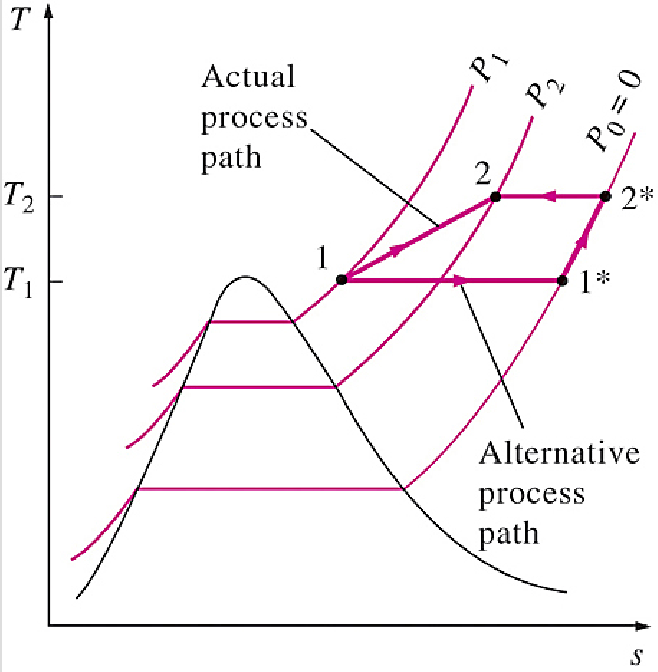
$$h_2 - h_2^* = 0 + \int_{P_2^*}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_2} dP = \int_{P_0}^{P_2} \left[v - T\left(\frac{\partial v}{\partial T}\right)_P \right]_{T=T_2} dP$$

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

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

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,

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



$$T = T_{cr}T_R \text{ and } P = P_{cr}P_R$$

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

Enthalpy departure factor

The values of Z_h are presented in graphical form as a function of P_R (reduced pressure) and T_R (reduced temperature) in the **generalized enthalpy departure chart**.

Z_h 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.

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

$$h_2 - h_1 = (h_2 - h_1)_{\text{ideal}} - RT_{cr}(Z_{h_2} - Z_{h_1})$$

For a real gas during a process 1-2

$(\bar{h}_2 - \bar{h}_1)_{\text{ideal}}$ from ideal gas tables

Internal Energy Changes of Real Gases

Using the definition $\bar{h} = \bar{u} + P\bar{v} = \bar{u} + ZR_uT$:

$$\bar{u}_2 - \bar{u}_1 = (\bar{h}_2 - \bar{h}_1) - R_u(Z_2T_2 - Z_1T_1)$$

Entropy Changes of Real Gases

General relation for *ds*

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

Using the approach in the figure

$$s_2 - s_1 = (s_2 - s_b^*) + (s_b^* - s_2^*) + (s_2^* - s_1^*) + (s_1^* - s_a^*) + (s_a^* - s_1)$$

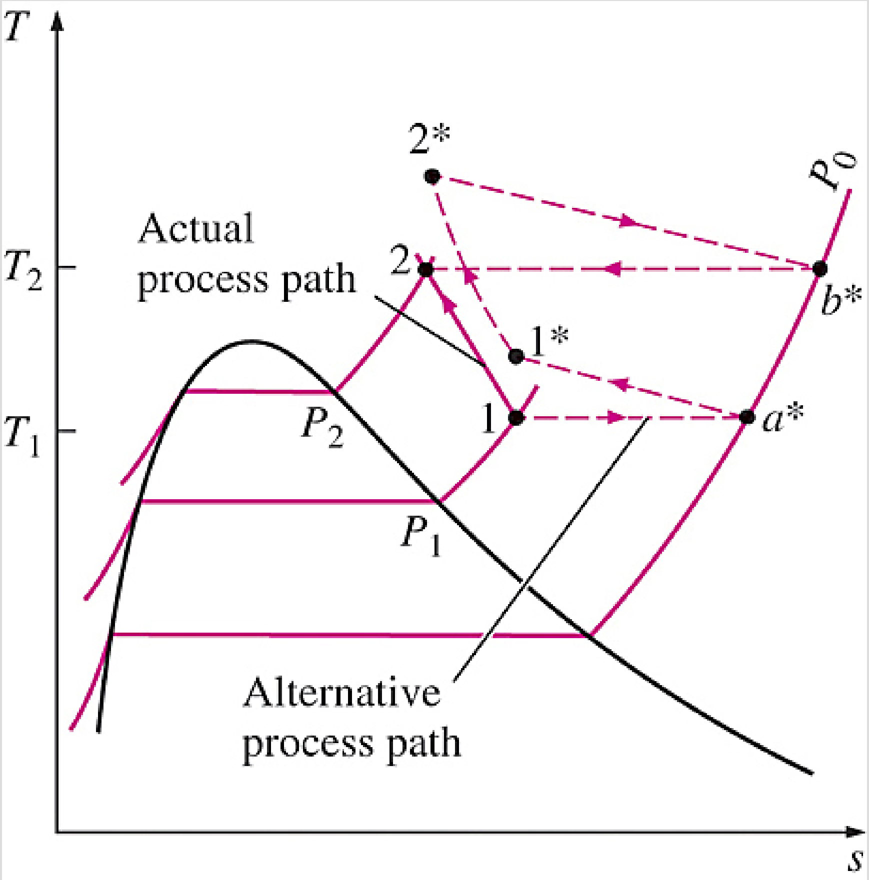
During isothermal process

$$(s_P - s_P^*)_T = (s_P - s_0^*)_T + (s_0^* - s_P^*)_T$$

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

$v = ZRT/P$ $\quad$ $v^* = v_{\text{ideal}} = RT/P$

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



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

$$T = T_{cr}T_R \text{ and } P = P_{cr}P_R$$

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

Entropy departure factor

$(\bar{s}^* - \bar{s})_{T,P}$ Entropy departure

The values of Z_s are presented in graphical form as a function of P_R (reduced pressure) and T_R (reduced temperature) in the **generalized entropy departure chart**.

Z_s 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.

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

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

For a real gas during a process 1-2

$(s_2 - s_1)_{\text{ideal}}$ from the ideal gas relations

Summary

- A little math—Partial derivatives and associated relations
  - ✓ Partial differentials
  - ✓ Partial differential relations
- The Maxwell relations
- The Clapeyron equation
- General relations for *du*, *dh*, *ds*, c_v, and c_p
  - ✓ Internal energy changes
  - ✓ Enthalpy changes
  - ✓ Entropy changes
  - ✓ Specific heats c_v and c_p
- The Joule-Thomson coefficient
- The Δh, Δu, and Δs of real gases
  - ✓ Enthalpy changes of real gases
  - ✓ Internal energy changes of real gases
  - ✓ Entropy changes of real gases