Chapter 12

THERMODYNAMIC PROPERTY RELATIONS

Thermodynamics: An Engineering Approach
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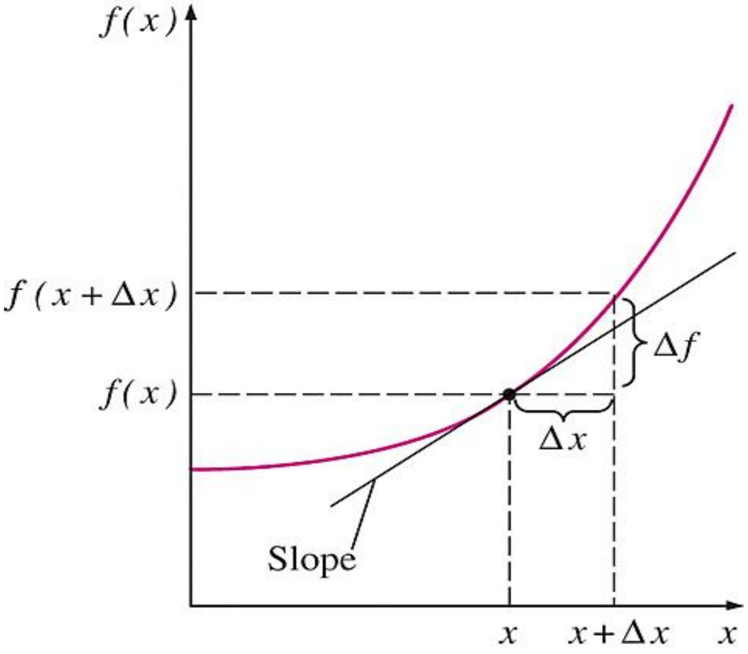
PARTIAL DERIVATIVES AND ASSOCIATED RELATIONS

SLOPE of the Function:

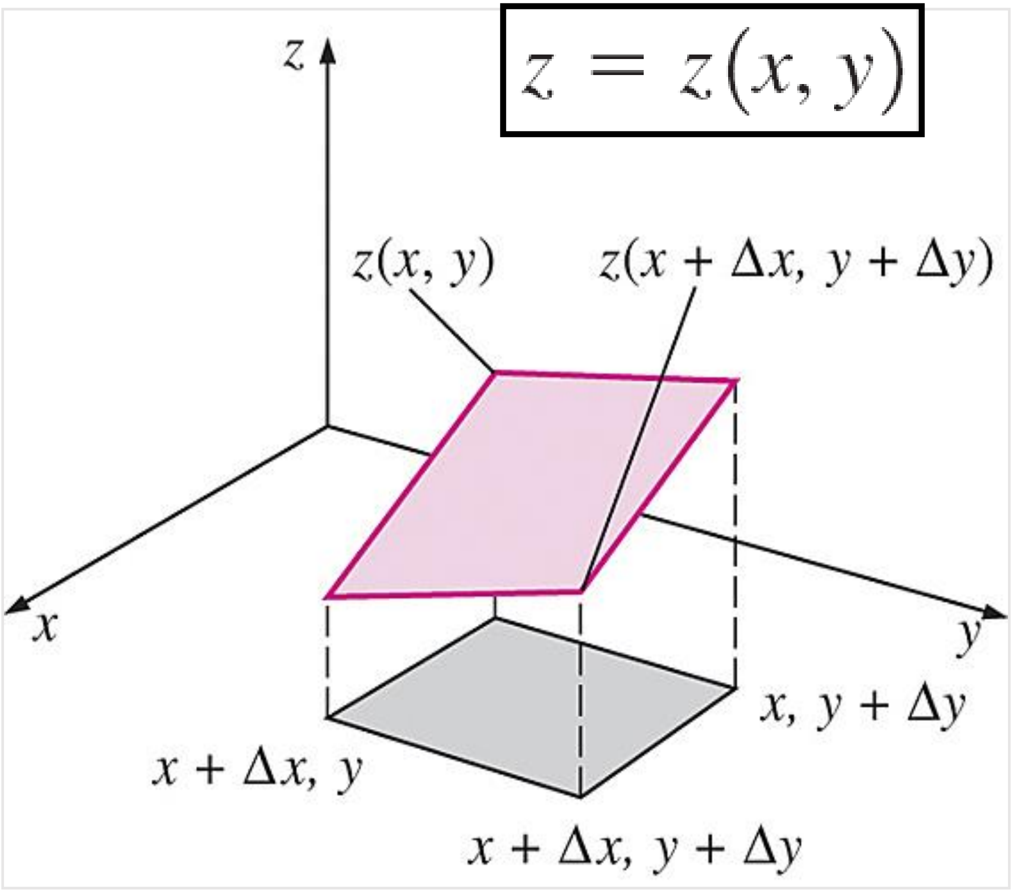
$$f = f(x)$$



Derivative of a function at a specified point represents the *slope of function at that point*.

Total Derivative:

$$\boxed{z = z(x, y)}$$



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

PARTIAL DERIVATIVES AND ASSOCIATED RELATIONS

- ☐ 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.

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

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

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

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

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

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.

$$du = T\,ds - P\,dv \qquad a = u - Ts$$

Helmholtz function

$$dh = T\,ds + v\,dP \qquad g = h - Ts$$

Gibbs function

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

$$\longrightarrow$$

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

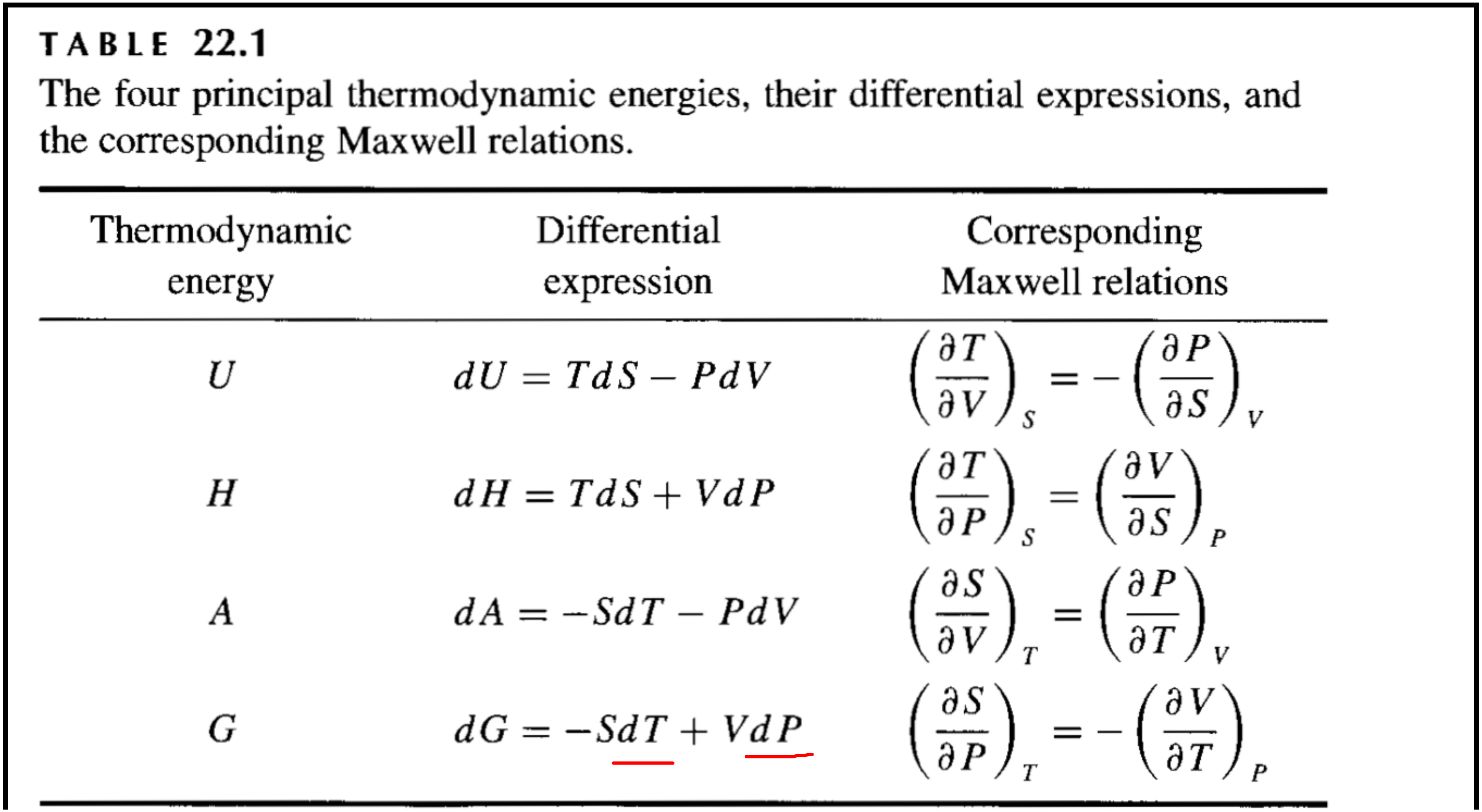


TABLE 22.1

The four principal thermodynamic energies, their differential expressions, and the corresponding Maxwell relations.

Thermodynamic energy	Differential expression	Corresponding Maxwell relations
U	$dU = TdS - PdV$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$
H	$dH = TdS + VdP$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$
A	$dA = -SdT - PdV$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$
G	$dG = -S\underline{dT} + V\underline{dP}$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

- *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 MAXWELL RELATIONS

$$dU = TdS - pdV$$

It clearly suggests a functional relation: $U = U(S,V)$

Therefore, one can write: $dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$

From the two differential forms it follows that: $\left(\frac{\partial U}{\partial S}\right)_V = T$ and $\left(\frac{\partial U}{\partial V}\right)_S = -p$

Now, we simply apply the Euler Criterion and we get a Maxwell relation: $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$

THE MAXWELL RELATIONS

$$G \equiv U - TS + pV$$

$$dG = dU - TdS - SdT + pdV + VdP$$

but $dU = TdS - pdV$, so

$$dG = TdS - TdS - pdV + pdV - SdT + Vdp$$

$dG = -SdT + Vdp;$ so: $G = G(T, p)$

$$\text{Then: } dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$$

By comparing the two *dG* forms

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

and

$$\boxed{\left(\frac{\partial G}{\partial p}\right)_T = V}$$

By applying the Euler Criterion to the *dG* form obtained, we get another useful Maxwell relation:

$$\boxed{-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p}$$

Two more important relations for partial derivatives

Reciprocity relation:

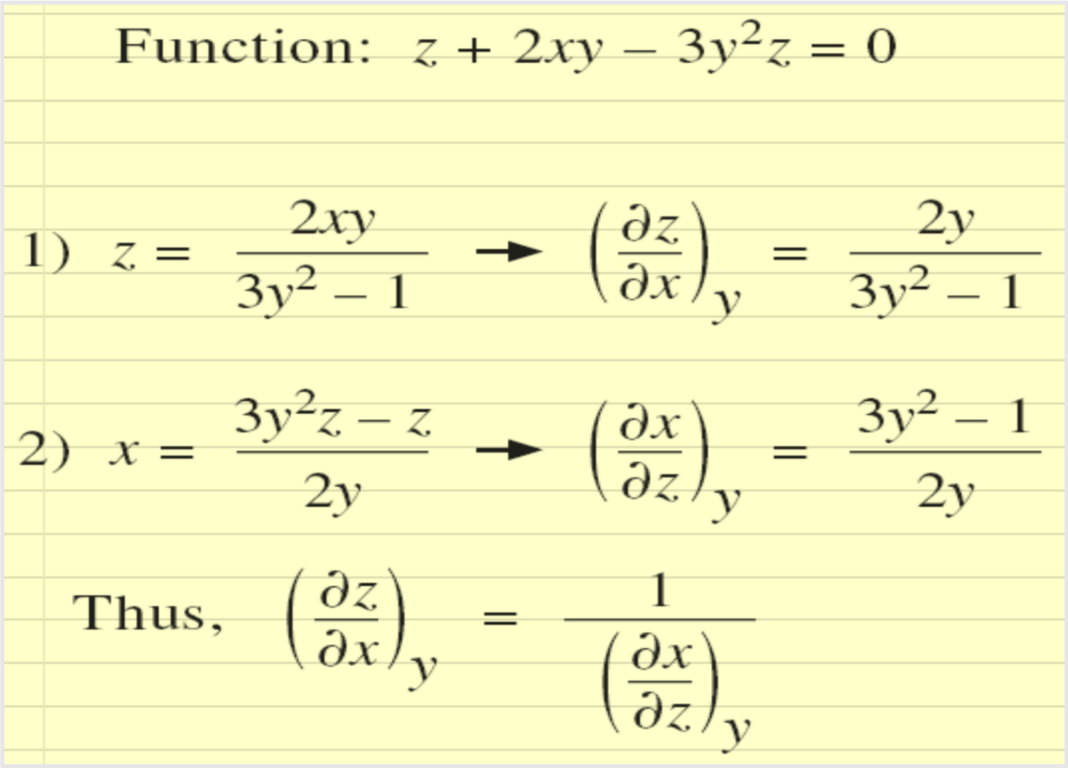
$$\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial x}\right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{(\partial z/\partial x)_y}$$

Cyclic relation:

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

Demonstration of the reciprocity relation for the function:

***z* + 2*xy* – 3*y*²*z* = 0.**



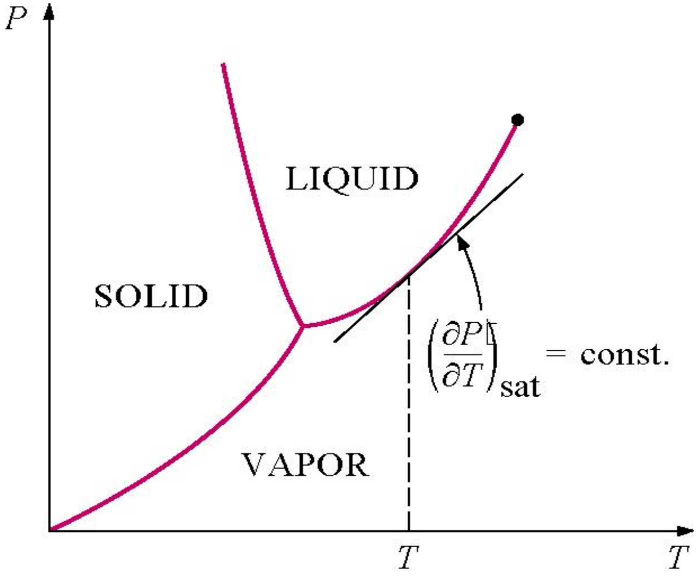
Function: $z + 2xy - 3y^2z = 0$

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

One Application:
CLAPEYRON EQUATION for Phase Change



- The ***Clapeyron equation*** enables us to determine the enthalpy change associated with a phase change, h_{fg}, from knowledge of ***P, v, T*** data alone.
- Consider the third **Maxwell relation:**

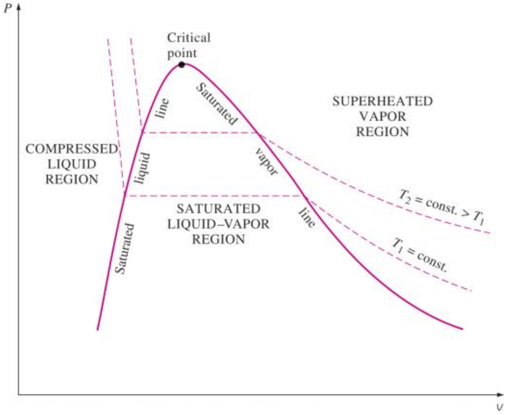
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

- During phase change, $P_{sat} = f(T_{sat})$ & *independent of specific volume.* Therefore, the partial derivative $(\partial P/\partial T)_v$ can be expressed as a total derivative $\mathbf{(dP/dT)_{sat}}$, which is the slope of the saturation curve on a P-T diagram at a specified state.
- Slope is *independent of the specific volume*, and thus it can be treated as a constant during the integration of the third Maxwell relation between two saturation states at the same temperature.

- ☐ For liquid-vapor phase-change process, the integration yields:

$$\int_f^g ds = \int_f^g \left(\frac{\partial P}{\partial T}\right)_v dv$$

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



- ☐ During the phase-change process, the pressure also remains constant. Therefore, from the following enthalpy relation, the *Clapeyron equation* is obtained:

$$dh = T\,ds + \cancelto{0}{v\,dP}$$

$$\int_f^g dh = \int_f^g T\,ds = T\int_f^g ds$$

$$h_g - h_f = h_{fg} = T s_{fg}$$

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

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

Clapeyron equation

❑ 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**

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

❑ 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} (***enthalpy of sublimation***) of the substance.

Clapeyron–Clausius equation

Example

Using only *P-v-T* data, estimate the **enthalpy of vaporization** of water at 45°C.

Solution:

Using *the P-v-T* data for water from **Table A-4**

$$v_{fg} = (v_g - v_f)_{@45^o C} = (15.251 - 0.001010)\frac{m^3}{kg}$$

$$= 15.250\frac{m^3}{kg}$$

$$\left(\frac{dP}{dT}\right)_{sat} \cong \left(\frac{\Delta P}{\Delta T}\right)_{sat,\,45^o C} = \frac{P_{sat@50^o C} - P_{sat@40^o C}}{50^o C - 40^o C}$$

$$= \frac{(12.35 - 7.385)kPa}{10^o K} = 0.4965\frac{kPa}{K}$$

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

$$= (40 + 273.15)K(15.250\frac{m^3}{kg})(0.4965\frac{kPa}{K})\frac{kJ}{m^3 kPa}$$

$$= 2371.1\frac{kJ}{kg}$$

The actual value of h_{fg} is 2394.0 kJ/kg. The **Clapeyron equation** approximation is low by about 1 percent due to the approximation of the slope of the saturation curve at 45°C.

Another Application: Ideal Gases

- Internal energy of ideal gas depends only on temperature.
- Show that internal energy of ideal gas does not depend on specific volume.
- Let us apply the following partial derivative for an ideal gas:

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

For ideal gases:

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

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

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

- This result helps to show that the internal energy of an ideal gas does not depend upon specific volume.
- To completely show that internal energy of an ideal gas is independent of specific volume, we need to show that the *specific heats of ideal gases are functions of temperature only.*
- We can derive the Relations (→ Right) for ***dh*** and ***ds*** where:
  ***h* = *h*(*T*,*P*)** and ***s* = *s*(*T*,*v*)** or ***s* = *s*(*T*,*P*)**

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

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

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

GENERAL RELATIONS FOR *du, dh, ds,* c_v, c_p for gases

1) The **state postulate** established that the state of a **simple compressible system** (**gases**) is completely specified by *two independent, intensive properties.*
2) 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.
3) The calculation of these properties from measurable ones depends on the availability of simple and accurate relations between the two groups.
4) 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*.
5) Property values at specified states can be determined after selecting a reference state.

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):

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

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Using the definition of c_v, we have

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

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

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

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

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

Equating the coefficients of dT and $d\nu$ in Eqs. 12–25 and 12–27 gives

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

$$\left(\frac{\partial u}{\partial \nu}\right)_{T} = T\left(\frac{\partial s}{\partial \nu}\right)_{T} - P \qquad \textbf{(12–28)}$$

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

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

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

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

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

The change in internal energy of a simple compressible system associated with a change of state from (T_1, ν_1) to (T_2, ν_2) is determined by integration:

$$u_2 - u_1 = \int_{T_1}^{T_2} c_{\nu}\, dT + \int_{\nu_1}^{\nu_2} \left[T\left(\frac{\partial P}{\partial T}\right)_{\nu} - P\right] d\nu$$

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,

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

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

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

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

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

(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:

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

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

(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:

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

(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 $h = u + Pv$:

$$h_2 - h_1 = u_2 - u_1 + (P_2 v_2 - P_1 v_1)$$

(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

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

and

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

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

$$\boxed{\begin{gathered} \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T \\ \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \end{gathered}}$$

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

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

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

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

and

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

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

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

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

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

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)

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

and

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

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

$$c_p - c_v = \frac{vT\beta^2}{\alpha} \tag{12–49}$$

THE JOULE-THOMSON COEFFICIENT

- For ideal gases, their internal energy depends only on temperature, but not on volume and pressure. If there are *interactions between the gas molecule*s, their behavior is described by non-ideal (real) gas equations od state.

- These *interactions* cause a change in temperature if they are expanded or compressed. This change in temperature is subject of the **Joule-Thomson experiment**. It describes the change in temperature of a gas as a result of a change in pressure.

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

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

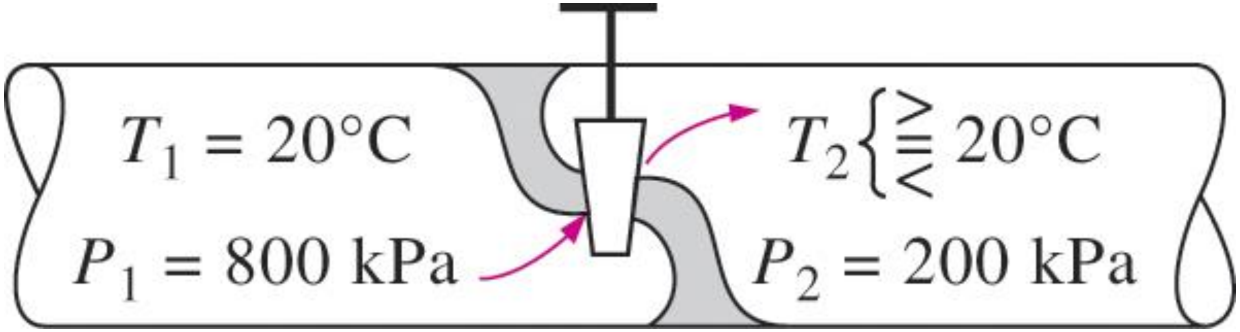
$$\mu_{\mathrm{JT}} \begin{cases} < 0 & \text{temperature increases} \\ = 0 & \text{temperature remains constant} \\ > 0 & \text{temperature decreases} \end{cases}$$

THE JOULE-THOMSON COEFFICIENT

1) If **attraction dominates** the interaction between the gas particles the gas cools down upon expansion, as energy is required to distribute the particles within the larger volume. *The Joule-Thomson coefficient is* ***positive*** *in this case.*

2) If **repulsion dominates** the interaction between the gas particles, the gas heats up upon expansion and the Joule-Thomson coefficient is negative.

3) For the ideal gas μ = 0, as the inner energy of the ideal gas only depends on temperature and not on pressure or volume.



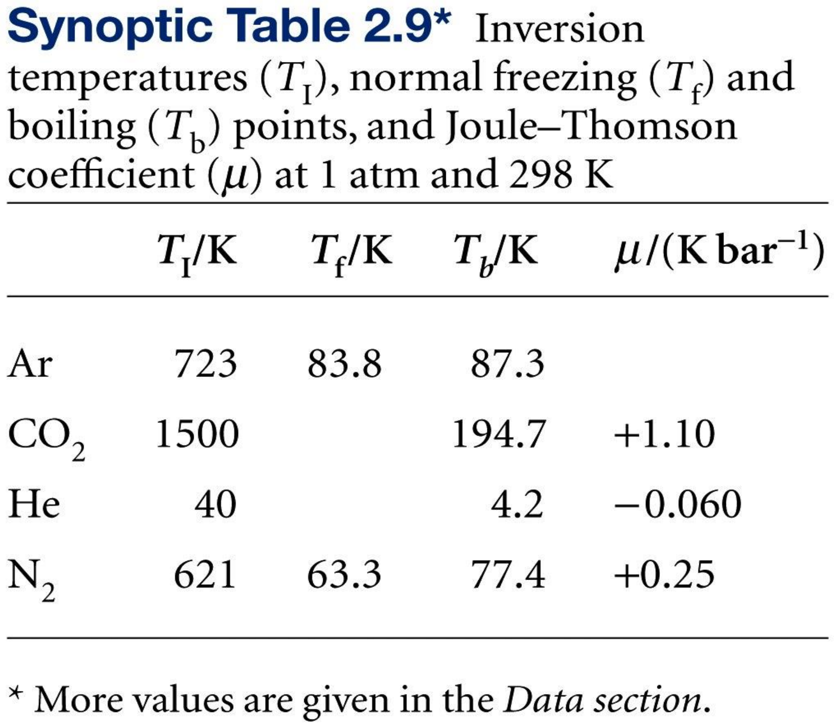
The Joule-Thomson Effect

- ☐ Isothermal J-T coefficient important in **liquification of gases.**
- ☐ If the process occurs within a temperature and pressure range that ensures that the effect is positive (the gas temperature decreases as its pressure is reduced), then throttling results in gas cooling and can be successfully used to liquefy gases.

- ☐ **For real gases: $\mu_T \neq 0$**
  1) If $\mu_T > 0$, then gas ***cools on expansion*** (desired effect).
  2) If $\mu_T < 0$, then gas heats on expansion at T > gas *inversion temperature* (critical temperature below which the gas expanding at constant enthalpy will experience a temperature decrease; and above which will experience a temperature increase).

THE JOULE-THOMSON COEFFICIENT

- Fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line.
- A cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature (Figure).

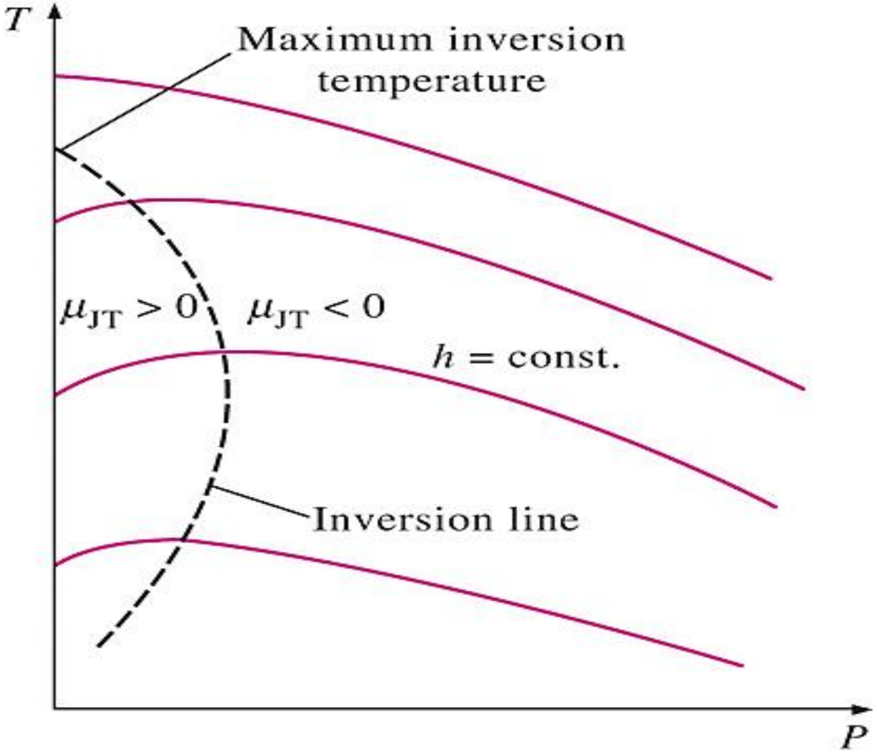


Synoptic Table 2.9* Inversion temperatures (T_I), normal freezing (T_f) and boiling (T_b) points, and Joule–Thomson coefficient (μ) at 1 atm and 298 K

	T_I/K	T_f/K	T_b/K	$\mu/(\mathrm{K\ bar^{-1}})$
Ar	723	83.8	87.3	
CO_2	1500		194.7	+1.10
He	40		4.2	−0.060
N_2	621	63.3	77.4	+0.25

* More values are given in the *Data section*.

Table 2-9
Atkins Physical Chemistry, Eighth Edition



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

THE JOULE-THOMSON COEFFICIENT

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.

THE Δ*h*, Δ*u*, AND Δ*s* OF REAL GASES

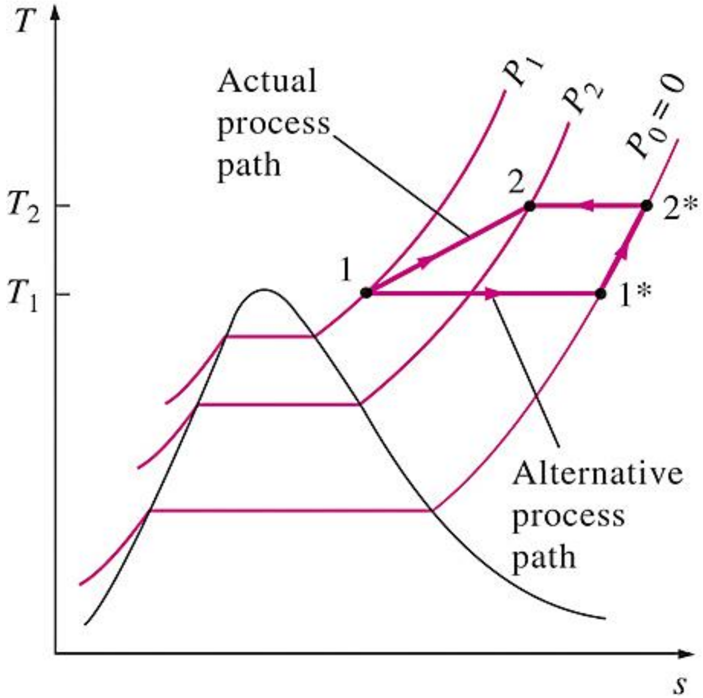
1) Gases at low pressures behave as ideal gases and obey the relation **$Pv = RT$**. The properties of ideal gases are relatively easy to evaluate since the properties u, h, c_v, and c_p depend on temperature only.
2) At high pressures, gases deviate considerably from ideal-gas behavior, and it becomes necessary to account for this deviation.
3) In **Chapter 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.
4) We extend the analysis to evaluate the *changes in the enthalpy, internal energy, and entropy* of non-ideal (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.



Questions on Applying to Different CASES:

- Non-isothermal ideal, Δh =
- Isothermal Ideal, Δh =
- Isothermal non-ideal, Δh =
- Isobaric non-ideal, Δh =

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:

$$h_2 - h_1 = \underbrace{(h_2 - h_2^*)}_{\textit{enthalpy departure}} + (h_2^* - h_1^*) + \underbrace{(h_1^* - h_1)}_{\textit{enthalpy departure}}$$

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

Constant T

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

Ideal gas

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

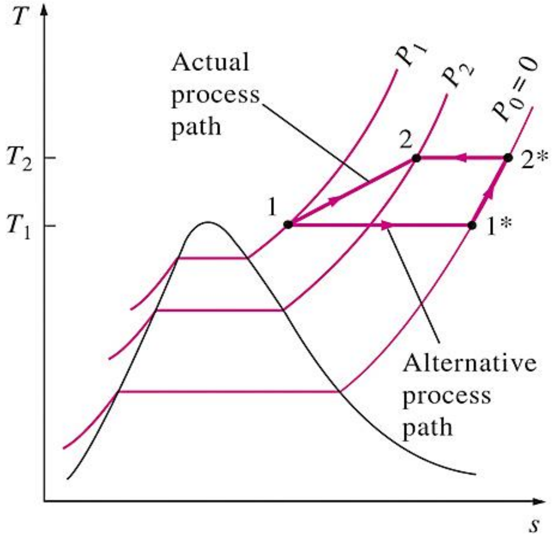
Constant T

- 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,

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

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

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



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.***

For a real gas during a process 1-2:

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

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

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

Note:
Properties per mole

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*

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

Using the approach in the figure

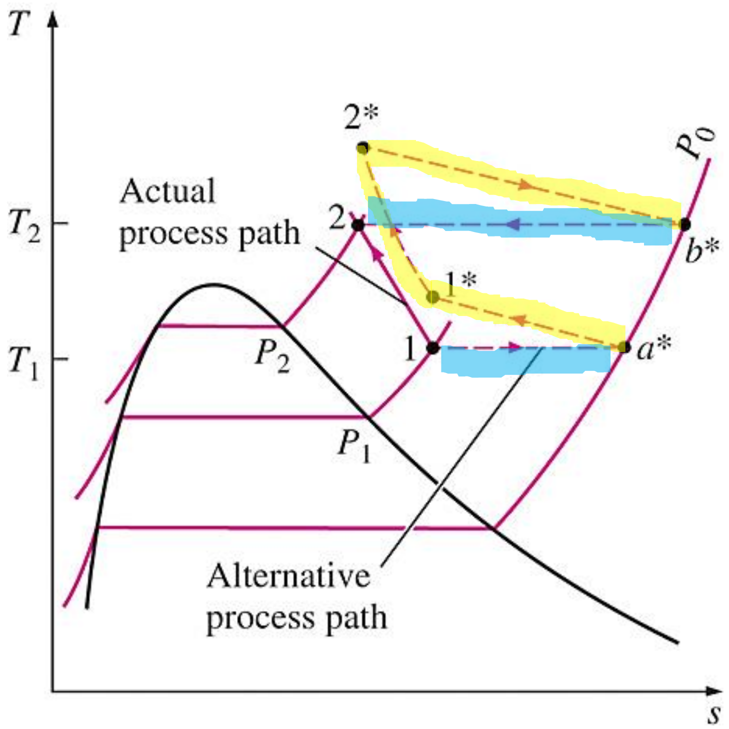
$$s_2 - s_1 = (s_2 - s_b^*) + (s_b^* - s_2^*) + (s_2^* - s_1^*) + (s_1^* - s_a^*) + (s_a^* - s_1)$$

During isothermal process

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

$\mathrm{v} = ZRT/P$ $\mathrm{v}^* = \mathrm{v}_{\text{ideal}} = RT/P$

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



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

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

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

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.*

For a real gas during a process 1-2:

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

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

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

EXAMPLE 12–1 Approximating Differential Quantities by Differences

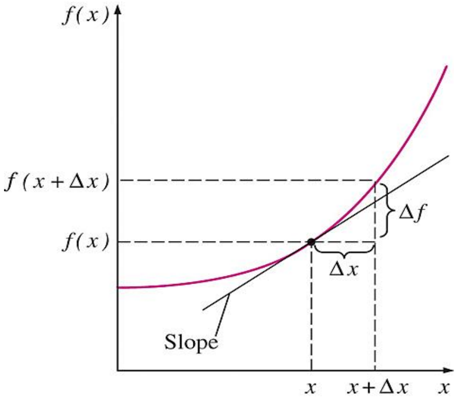
The c_p of ideal gases depends on temperature only, and it is expressed as $c_p(T) = dh(T)/dT$. Determine the c_p of air at 300 K, using the enthalpy data from Table A–17, and compare it to the value listed in Table A–2*b*.

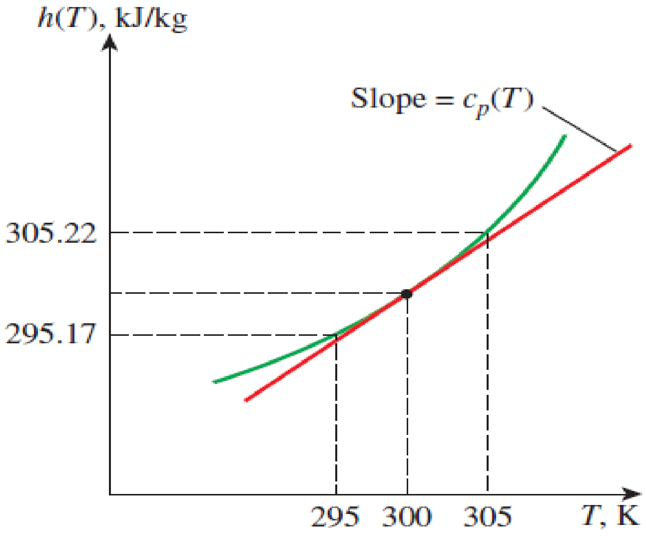
SOLUTION The c_p value of air at a specified temperature is to be determined using enthalpy data.

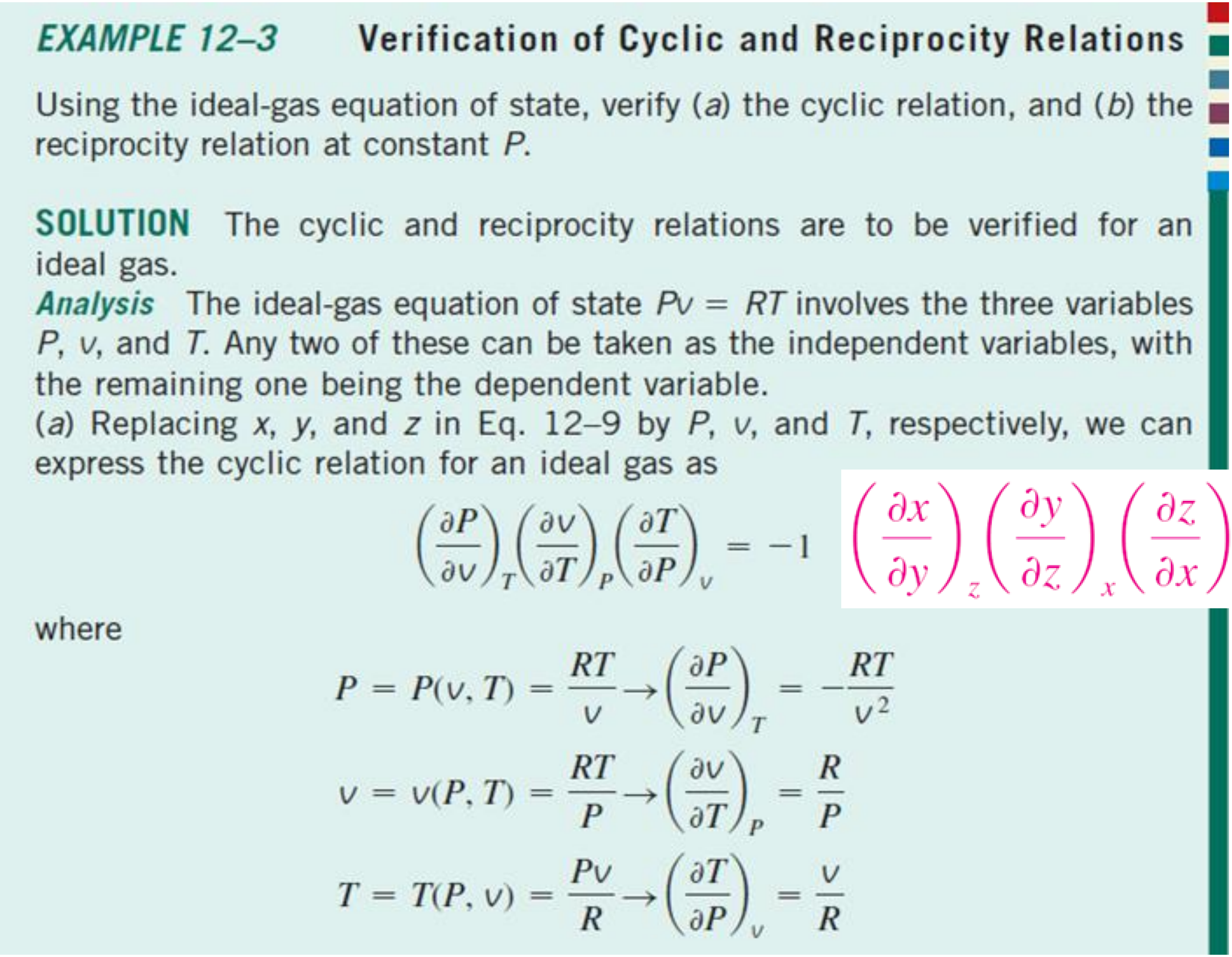
Analysis The c_p value of air at 300 K is listed in Table A–2*b* to be 1.005 kJ/kg·K. This value could also be determined by differentiating the function $h(T)$ with respect to T and evaluating the result at $T = 300$ K. However, the function $h(T)$ is not available. But, we can still determine the c_p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

$$c_p(300\text{ K}) = \left[\frac{dh(T)}{dT}\right]_{T=300\text{ K}} \cong \left[\frac{\Delta h(T)}{\Delta T}\right]_{T\cong 300\text{ K}} = \frac{h(305\text{ K}) - h(295\text{ K})}{(305 - 295)\text{ K}}$$

$$= \frac{(305.22 - 295.17)\text{ kJ/kg}}{(305 - 295)\text{ K}} = \mathbf{1.005\ kJ/kg\cdot K}$$







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

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

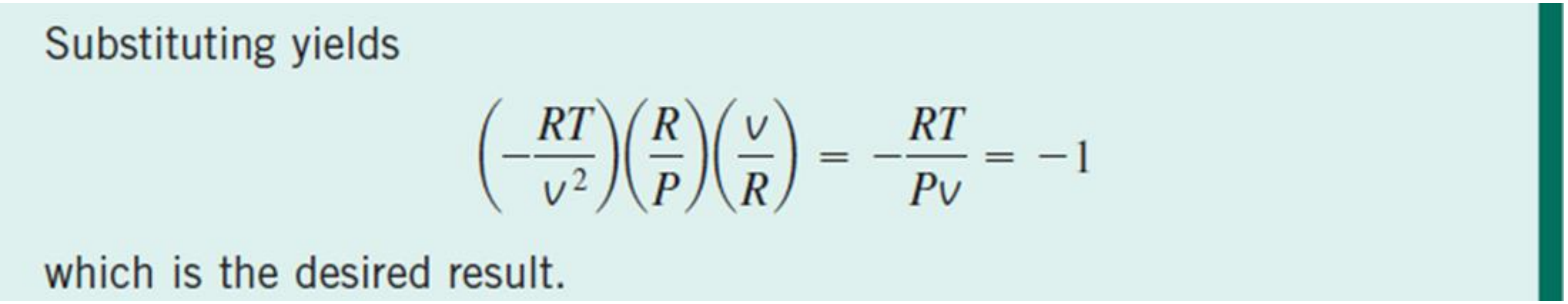
$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

where

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

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

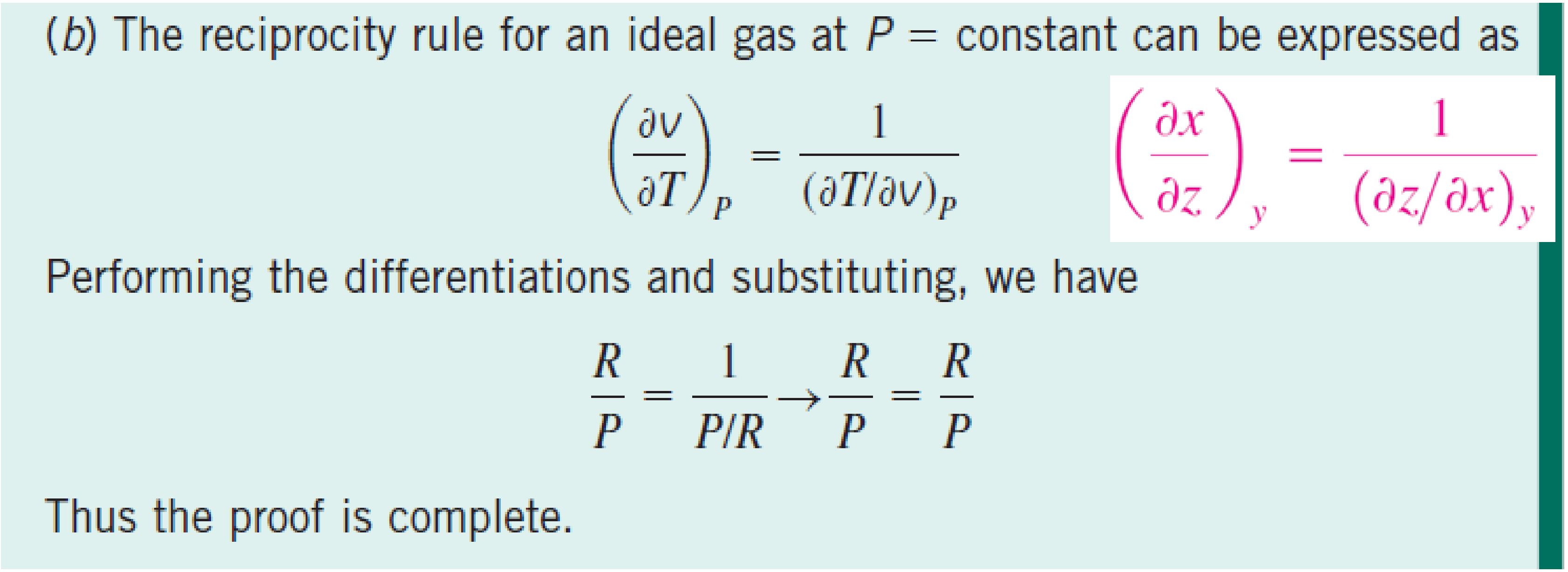
$$T = T(P, v) = \frac{Pv}{R} \rightarrow \left(\frac{\partial T}{\partial P}\right)_v = \frac{v}{R}$$



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 $P =$ constant can be expressed as

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

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

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.

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.

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.

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

$$\left(\frac{\Delta s}{\Delta P}\right)_{T=250^\circ\mathrm{C}} \overset{?}{\cong} -\left(\frac{\Delta v}{\Delta T}\right)_{P=300\ \mathrm{kPa}}$$

$$\left[\frac{s_{400\ \mathrm{kPa}} - s_{200\ \mathrm{kPa}}}{(400-200)\ \mathrm{kPa}}\right]_{T=250^\circ\mathrm{C}} \overset{?}{\cong} -\left[\frac{v_{300^\circ\mathrm{C}} - v_{200^\circ\mathrm{C}}}{(300-200)^\circ\mathrm{C}}\right]_{P=300\ \mathrm{kPa}}$$

$$\frac{(7.3804 - 7.7100)\ \mathrm{kJ/kg\cdot K}}{(400-200)\ \mathrm{kPa}} \overset{?}{\cong} -\frac{(0.87535 - 0.71643)\ \mathrm{m^3/kg}}{(300-200)^\circ\mathrm{C}}$$

$$-0.00165\ \mathrm{m^3/kg\cdot K} \cong -0.00159\ \mathrm{m^3/kg\cdot K}$$

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,

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

where, from Table A–11,

$$v_{fg} = (v_g - v_f)_{@\,20^\circ\text{C}} = 0.036012 - 0.0008160 = 0.035196\ \text{m}^3/\text{kg}$$

$$\left(\frac{dP}{dT}\right)_{\text{sat},20^\circ\text{C}} \cong \left(\frac{\Delta P}{\Delta T}\right)_{\text{sat},20^\circ\text{C}} = \frac{P_{\text{sat @ }24^\circ\text{C}} - P_{\text{sat @ }16^\circ\text{C}}}{24^\circ\text{C} - 16^\circ\text{C}}$$

$$= \frac{646.18 - 504.58\ \text{kPa}}{8^\circ\text{C}} = 17.70\ \text{kPa/K}$$

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

$$h_{fg} = (293.15\ \text{K})(0.035196\ \text{m}^3/\text{kg})(17.70\ \text{kPa/K})\left(\frac{1\ \text{kJ}}{1\ \text{kPa}\cdot\text{m}^3}\right)$$

$$= 182.62\ \text{kJ/kg}$$

The tabulated value of h_{fg} at 20°C is 182.33 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.

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.

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 12–9 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,

$$c_p - c_v = R$$

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. 12–14).

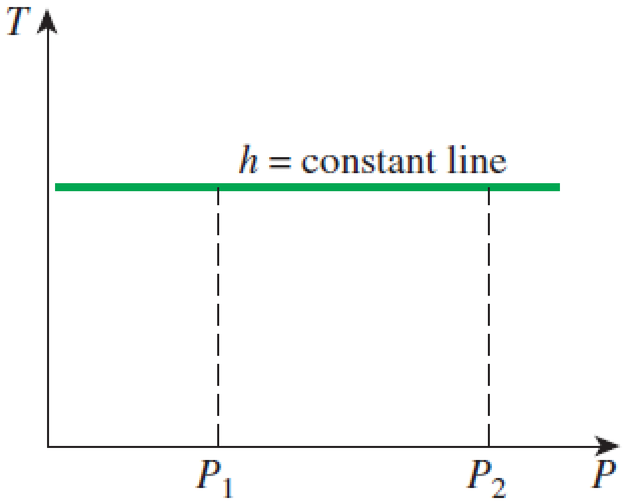


FIGURE 12–14
The temperature of an ideal gas remains constant during a throttling process since h = constant and T = constant lines on a T-P diagram coincide.

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 $T_{cr} = 154.8$ K and $P_{cr} = 5.08$ 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:

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

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

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = \bar{s}_2^\circ - \bar{s}_1^\circ - R_u \ln \frac{P_2}{P_1}$$

$$= (205.213 - 196.171)\ \text{kJ/kmol} \cdot \text{K} - (8.314\ \text{kJ/kmol} \cdot \text{K})\ln \frac{10\ \text{MPa}}{5\ \text{MPa}}$$

$$= \mathbf{3.28\ kJ/kmol \cdot K}$$

(*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,

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

and

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

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.