

Thermodynamics: An Engineering Approach

8th Edition

Yunus A. Çengel, Michael A. Boles
McGraw-Hill, 2015

CHAPTER 12

THERMODYNAMIC PROPERTY RELATIONS

Vaibhav Arghode, Department of Aerospace Engineering
Indian Institute of Technology Kanpur

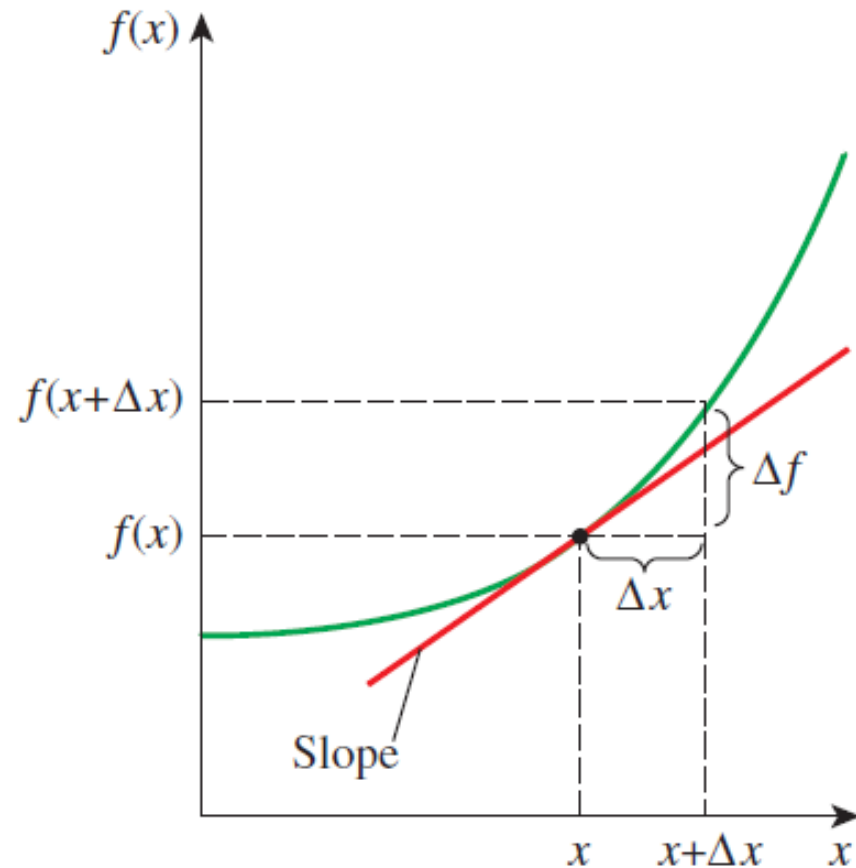
Adapted from the lecture slides by **Mehmet Kanoglu** Copyright © The McGraw-Hill Education.

Permission required for reproduction or display.

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 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

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

$$f = f(x)$$

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

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

FIGURE 12–1

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

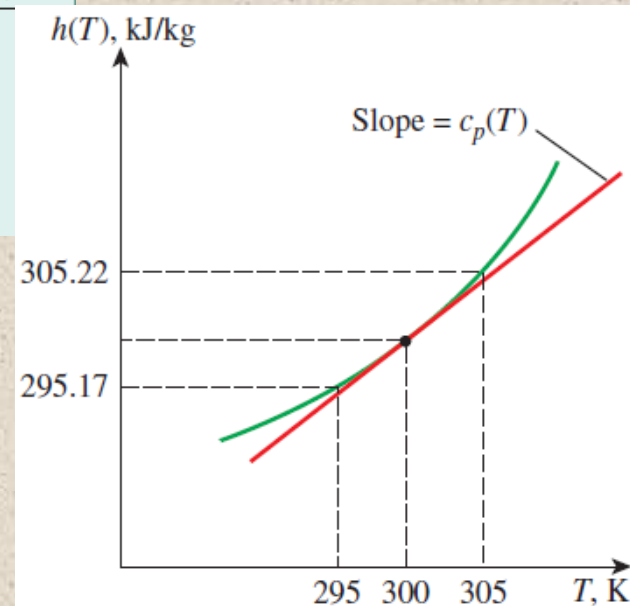
EXAMPLE 12–1 Approximating Differential Quantities by Differences

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):

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



Partial Differentials

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

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

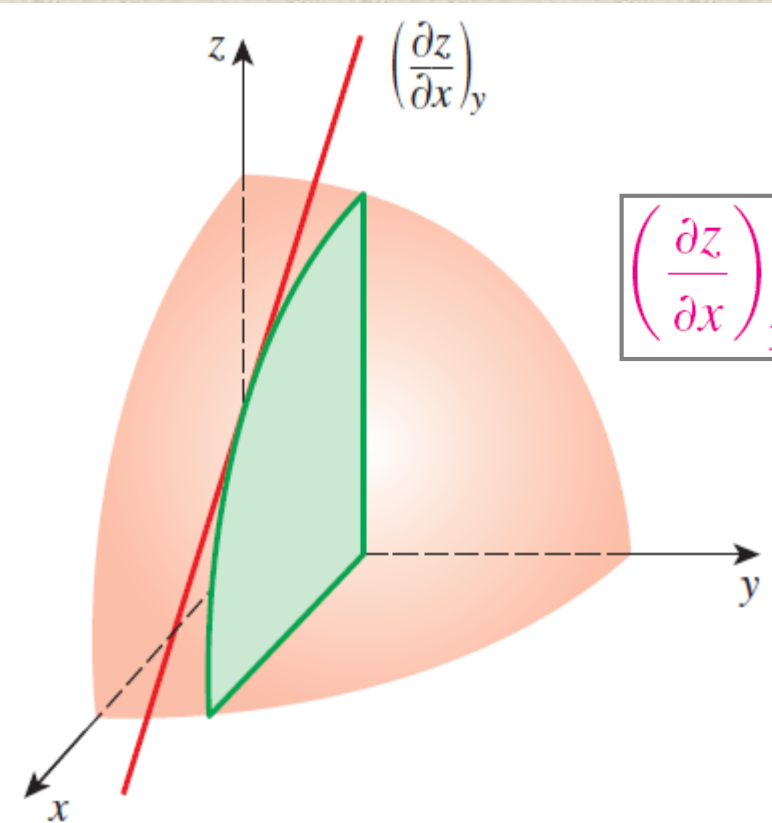


FIGURE 12-3

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

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

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

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

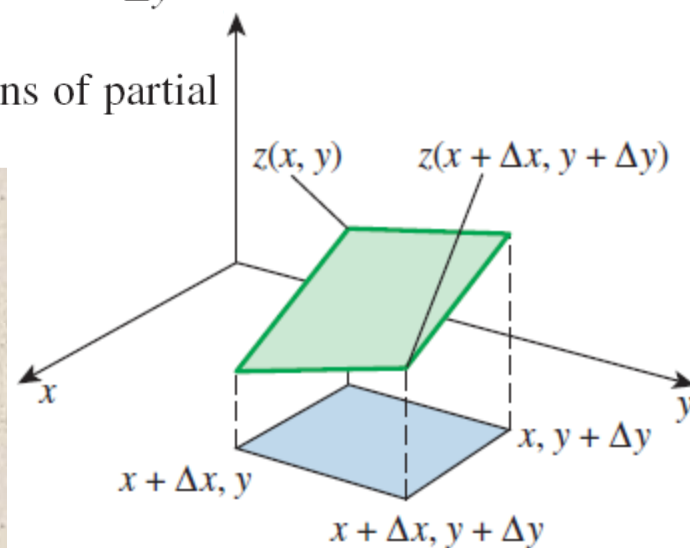


FIGURE 12–4

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

Example: 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 the expression for total differential, estimate the change in the pressure of air.

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

$$dv \equiv \Delta v = (0.87 - 0.86) \text{ m}^3/\text{kg} = 0.01 \text{ m}^3/\text{kg}$$

$$P = \frac{RT}{v} \quad (\text{assume ideal gas})$$

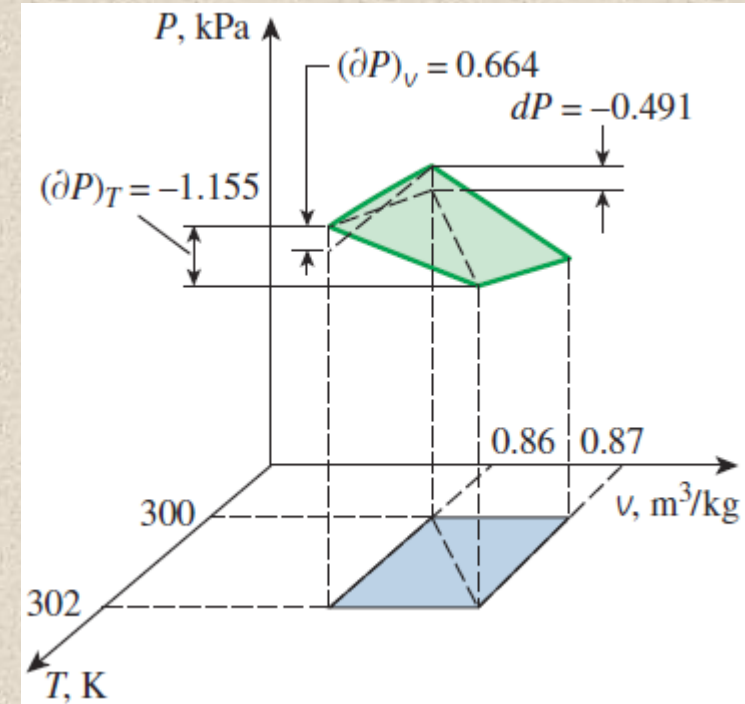
$$dP = \left(\frac{\partial P}{\partial T} \right)_v dT + \left(\frac{\partial P}{\partial v} \right)_T dv = \frac{R dT}{v} - \frac{RT dv}{v^2} = \mathbf{-0.491 \text{ kPa}}$$

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

(Constant temperature = 300 K, specific volume decreases from 0.86 to 0.87 m³/kg)

$$\left(\frac{\partial P}{\partial v} \right)_T dv = (\partial P)_T = -1.155 \text{ kPa}$$

(Constant specific volume = 0.86 m³/kg, temperature increases from 300 to 302 K)



Direct calculation: $\Delta P = P_2 - P_1 = R(T_2/v_2 - T_1/v_1) = -0.491 \text{ kPa}$

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

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

Partial Differential Relations

z dependent on x, y

x dependent on z, y

[the function $z = z(x, y)$ can also be expressed as $x = x(y, z)$]

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

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

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

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

Eliminating dx

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

Rearranging,

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

Partial Differential Relations

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

- y is independent of z and thus can be varied independently. e.g., 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 the times, the terms in the brackets must equal zero, regardless of the values of y and z

$$\left(\frac{\partial x}{\partial z} \right)_y \left(\frac{\partial z}{\partial x} \right)_y = 1 \rightarrow \left(\frac{\partial x}{\partial z} \right)_y = \frac{1}{\left(\frac{\partial z}{\partial x} \right)_y} \quad \text{Reciprocity relation}$$

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

Demonstration of Reciprocity Relations

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

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

$$\text{Function: } z + 2xy - 3y^2z = 0$$

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

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

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

Example: 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 .

$$Pv = RT \quad (\text{use: } x = P, y = v, z = T)$$

(a) 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.

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

$$du = T ds - P dv$$

$$dh = T ds + v dP$$

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

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



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

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



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

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

THE MAXWELL RELATIONS

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

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

$$dh = T ds + v dP \rightarrow \left(\frac{\partial T}{\partial P} \right)_s = \left(\frac{\partial v}{\partial s} \right)_P$$

$$da = -s dT - P dv \rightarrow \left(\frac{\partial s}{\partial v} \right)_T = \left(\frac{\partial P}{\partial T} \right)_v$$

$$dg = -s dT + v dP \rightarrow \left(\frac{\partial s}{\partial P} \right)_T = - \left(\frac{\partial v}{\partial T} \right)_P$$

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

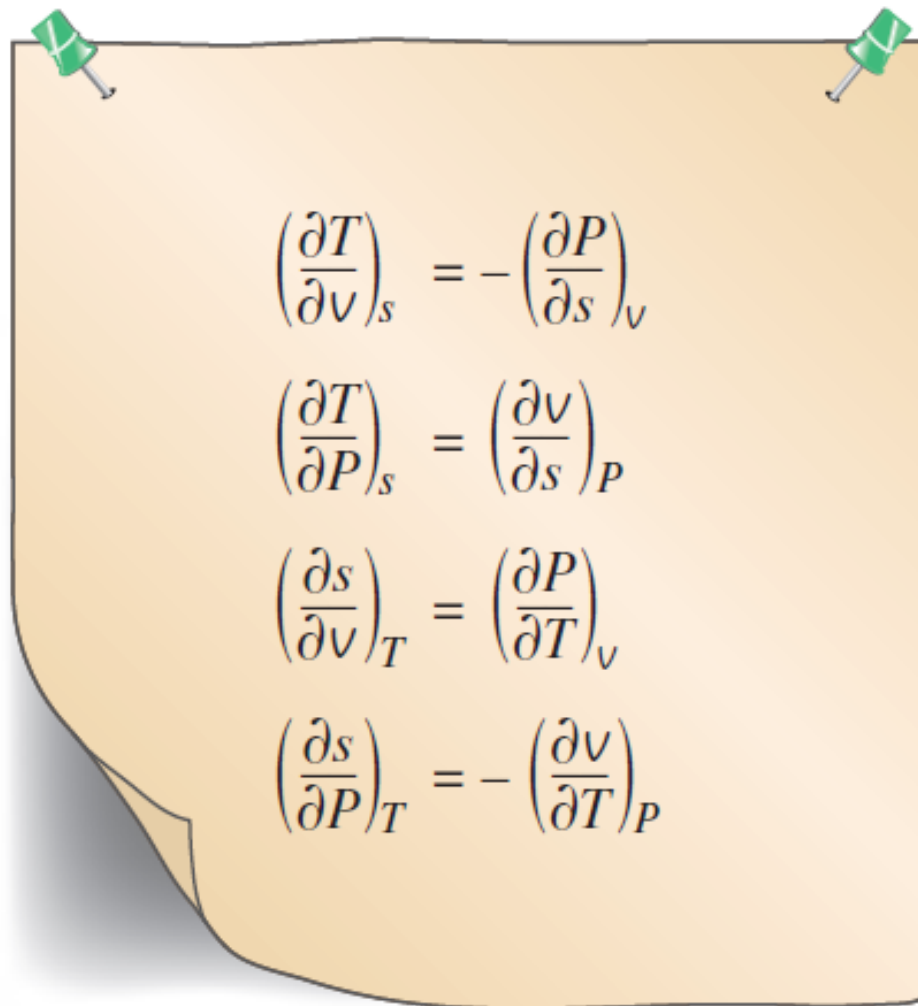

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v$$
$$\left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial v}{\partial s}\right)_P$$
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$
$$\left(\frac{\partial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

FIGURE 12–7

Maxwell relations are extremely valuable in thermodynamic analysis.

Example: Verification of the Maxwell Relations

Verify the validity of the last Maxwell relation 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.

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

Approximate
differentials with
differences:

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

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

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

$$-0.00165\text{ m}^3/\text{kg}\cdot\text{K} \equiv -0.00159\text{ m}^3/\text{kg}\cdot\text{K}$$

TABLE A-6

Superheated water

T °C	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K	v m ³ /kg	u kJ/kg	h kJ/kg	s kJ/kg·K
	$P = 0.20 \text{ MPa (120.21}^{\circ}\text{C)}$				$P = 0.30 \text{ MPa (133.52}^{\circ}\text{C)}$				$P = 0.40 \text{ MPa (143.61}^{\circ}\text{C)}$			
Sat.	0.88578	2529.1	2706.3	7.1270	0.60582	2543.2	2724.9	6.9917	0.46242	2553.1	2738.1	6.8955
150	0.95986	2577.1	2769.1	7.2810	0.63402	2571.0	2761.2	7.0792	0.47088	2564.4	2752.8	6.9306
200	1.08049	2654.6	2870.7	7.5081	0.71643	2651.0	2865.9	7.3132	0.53434	2647.2	2860.9	7.1723
250	1.19890	2731.4	2971.2	7.7100	0.79645	2728.9	2967.9	7.5180	0.59520	2726.4	2964.5	7.3804
300	1.31623	2808.8	3072.1	7.8941	0.87535	2807.0	3069.6	7.7037	0.65489	2805.1	3067.1	7.5677
400	1.54934	2967.2	3277.0	8.2236	1.03155	2966.0	3275.5	8.0347	0.77265	2964.9	3273.9	7.9003
500	1.78142	3131.4	3487.7	8.5153	1.18672	3130.6	3486.6	8.3271	0.88936	3129.8	3485.5	8.1933
600	2.01302	3302.2	3704.8	8.7793	1.34139	3301.6	3704.0	8.5915	1.00558	3301.0	3703.3	8.4580
700	2.24434	3479.9	3928.8	9.0221	1.49580	3479.5	3928.2	8.8345	1.12152	3479.0	3927.6	8.7012
800	2.47550	3664.7	4159.8	9.2479	1.65004	3664.3	4159.3	9.0605	1.23730	3663.9	4158.9	8.9274
900	2.70656	3856.3	4397.7	9.4598	1.80417	3856.0	4397.3	9.2725	1.35298	3855.7	4396.9	9.1394
1000	2.93755	4054.8	4642.3	9.6599	1.95824	4054.5	4642.0	9.4726	1.46859	4054.3	4641.7	9.3396
1100	3.16848	4259.6	4893.3	9.8497	2.11226	4259.4	4893.1	9.6624	1.58414	4259.2	4892.9	9.5295
1200	3.39938	4470.5	5150.4	10.0304	2.26624	4470.3	5150.2	9.8431	1.69966	4470.2	5150.0	9.7102
1300	3.63026	4687.1	5413.1	10.2029	2.42019	4686.9	5413.0	10.0157	1.81516	4686.7	5412.8	9.8828

Example: Verification of the Maxwell Relations

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

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 the relation at the specified state.

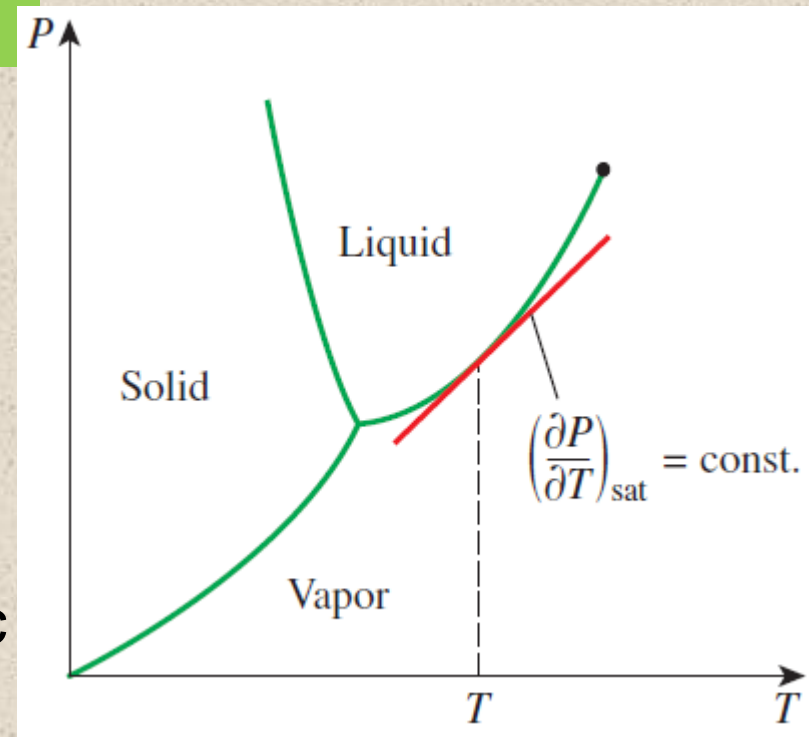
Discussion This example shows that the entropy change of a simple compressible system during an isothermal process can be determined from a knowledge of the easily measurable properties P , v , and T alone.

THE CLAPEYRON EQUATION

Consider the third Maxwell relation

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

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

For an **isothermal liquid–vapor phase-change process**, for example, the integration yields:

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

THE CLAPEYRON EQUATION

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

During this process the pressure also remains constant

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

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

This is called the **Clapeyron equation**

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

EXAMPLE: Evaluating the h_{fg} of a Substance

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.

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

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

Approximate
differentials with
differences:

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

$$\begin{aligned} h_{fg} &= (293.15 \text{ K})(0.035196 \text{ m}^3/\text{kg})(17.70 \text{ kPa/K}) \left(\frac{1 \text{ kJ}}{1 \text{ kPa} \cdot \text{m}^3} \right) \\ &= \mathbf{182.62 \text{ kJ/kg}} \end{aligned}$$

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.

TABLE A-11

Saturated refrigerant-134a—Temperature

Temp., T °C	Sat. press., P_{sat} kPa	<i>Specific volume, m^3/kg</i>	
		Sat. liquid, ν_f	Sat. vapor, ν_g
10	414.89	0.0007929	0.049466
12	443.31	0.0007973	0.046354
14	473.19	0.0008018	0.043471
16	504.58	0.0008064	0.040798
18	537.52	0.0008112	0.038317
20	572.07	0.0008160	0.036012
22	608.27	0.0008209	0.033867
24	646.18	0.0008260	0.031869
26	685.84	0.0008312	0.030008
28	727.31	0.0008366	0.028271
30	770.64	0.0008421	0.02671

Try this: approximate differentials with differences with the closest available data in the table (18°C and 22°C)

$$h_{\text{fg}} = 182.52 \text{ kJ/kg}$$

Note that this value is closer to the tabulated value

$$\begin{aligned} \left(\frac{dP}{dT} \right)_{\text{sat}, 20^\circ\text{C}} &\cong \left(\frac{\Delta P}{\Delta T} \right)_{\text{sat}, 20^\circ\text{C}} = \frac{P_{\text{sat @ } 22^\circ\text{C}} - P_{\text{sat @ } 18^\circ\text{C}}}{22^\circ\text{C} - 18^\circ\text{C}} \\ &= \frac{608.27 - 537.52 \text{ kPa}}{4^\circ\text{C}} = 17.69 \text{ kPa/K} \end{aligned}$$

THE CLAPEYRON-CLAUSIUS EQUATION

The Clapeyron equation can be simplified for liquid–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:

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

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

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

THE CLAPEYRON-CLAUSIUS EQUATION

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

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:

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

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

EXAMPLE: Extrapolating Tabular Data with the Clapeyron Equation

Estimate the saturation pressure of refrigerant-134a at -45°C , using the data available in the refrigerant tables

Table A–11 lists saturation data at temperatures -40°C and above. Therefore, we should either resort to other sources or use extrapolation to obtain saturation data at lower temperatures.

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

In our case $T_1 = -40^{\circ}\text{C}$ and $T_2 = -45^{\circ}\text{C}$. For refrigerant-134a, $R = 0.08149 \text{ kJ/kg}\cdot\text{K}$. Also from Table A–11 at -40°C , we read $h_{fg} = 225.86 \text{ kJ/kg}$ and $P_1 = P_{\text{sat}@-40^{\circ}\text{C}} = 51.25 \text{ kPa}$.

$$\ln\left(\frac{P_2}{51.25 \text{ kPa}}\right) \cong \frac{225.86 \text{ kJ/kg}}{0.08149 \text{ kJ/kg}\cdot\text{K}}\left(\frac{1}{233 \text{ K}} - \frac{1}{228 \text{ K}}\right)$$
$$P_2 \cong 39.48 \text{ kPa}$$

TABLE A-11

Saturated refrigerant-134a—Temperature table

Temp., $T^{\circ}\text{C}$	Sat. press., P_{sat} kPa	Specific volume, m^3/kg		Internal energy, kJ/kg			Enthalpy, kJ/kg		
		Sat. liquid, v_f	Sat. vapor, v_g	Sat. liquid, u_f	Evap., u_{fg}	Sat. vapor, u_g	Sat. liquid, h_f	Evap., h_{fg}	Sat. vapor, h_g
-40	51.25	0.0007053	0.36064	-0.036	207.42	207.38	0.00	225.86	225.86
-38	56.86	0.0007082	0.32718	2.472	206.06	208.53	2.512	224.62	227.13
-36	62.95	0.0007111	0.29740	4.987	204.69	209.68	5.032	223.37	228.40
-34	69.56	0.0007141	0.27082	7.509	203.32	210.83	7.559	222.10	229.66
-32	76.71	0.0007171	0.24706	10.04	201.94	211.97	10.09	220.83	230.93
-30	84.43	0.0007201	0.22577	12.58	200.55	213.12	12.64	219.55	232.19

the saturation pressure of refrigerant-134a at -45°C is 39.48 kPa. The actual value, obtained from another source, is 39.15 kPa. Thus the value predicted 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 37.23 kPa, which is in error by 7 percent.)

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
- This is very helpful for obtaining properties that cannot be measured directly such as internal energy, enthalpy and entropy
- Here we develop general relations for changes in internal energy, enthalpy, and entropy in terms of pressure, specific volume, temperature, and specific heats alone

GENERAL RELATIONS FOR du , dh , ds , c_v , AND c_p

- 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 :

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

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 $d\upsilon$ in Eqs. 12–25 and 12–27 gives

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

Using the third Maxwell relation

$$\left(\frac{\partial u}{\partial \upsilon}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_{\upsilon} - P \qquad \left(\frac{\partial s}{\partial \upsilon}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\upsilon}$$

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

$$du = c_{\upsilon} dT + \left[T\left(\frac{\partial P}{\partial T}\right)_{\upsilon} - P \right] d\upsilon \quad (12-29)$$

The change in internal energy of a simple compressible system associated with a change of state from (T_1, υ_1) to (T_2, υ_2) is determined by integration:

$$u_2 - u_1 = \int_{T_1}^{T_2} c_{\upsilon} dT + \int_{\upsilon_1}^{\upsilon_2} \left[T\left(\frac{\partial P}{\partial T}\right)_{\upsilon} - P \right] d\upsilon \quad (12-30)$$

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

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

Using the fourth Maxwell relation

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

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

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

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:

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

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 $h = u + Pv$:

$$h_2 - h_1 = u_2 - u_1 + (P_2v_2 - P_1v_1) \quad (12-37)$$

Entropy Changes (first relation)

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

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

$$\left(\frac{\partial s}{\partial T} \right)_v = \frac{c_v}{T}$$

See the section “Internal Energy Changes”
eqn. 12-28

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

Third Maxwell relation

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

and

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

Entropy Changes (second relation)

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,

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

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

See the section “Enthalpy Changes”
eqn. 12-34

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

Fourth Maxwell relation

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

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.

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.

Specific Heats c_v and c_p

$$dz = M dx + N dy$$

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

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

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

See the section “Entropy Changes” eqn. 12-38

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

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

See the section “Entropy Changes” eqn. 12-40

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:

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

The integration on the right-hand side requires a knowledge of the P - υ - T behavior of the substance alone.

Specific Heats ($c_p - c_v$)

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.

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

**Equate and
solve for dT**

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

See the section “Entropy Changes”
eqn. 12-38

See the section “Entropy Changes”
eqn. 12-40

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

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

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

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

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

Specific Heats ($c_p - c_v$)

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

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

$$c_p - c_v = T \left(\frac{\partial v}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_v \quad \text{See the section “Specific Heats ($c_p - c_v$)” eqn. 12-45}$$

We get:

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

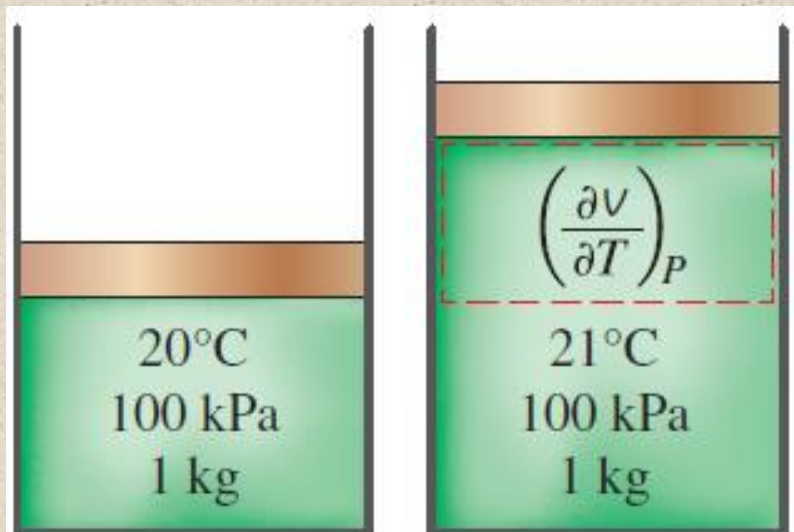
This relation can be expressed in terms of two other thermodynamic properties called the **volume expansivity** β and the **isothermal compressibility** α , which are defined as

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

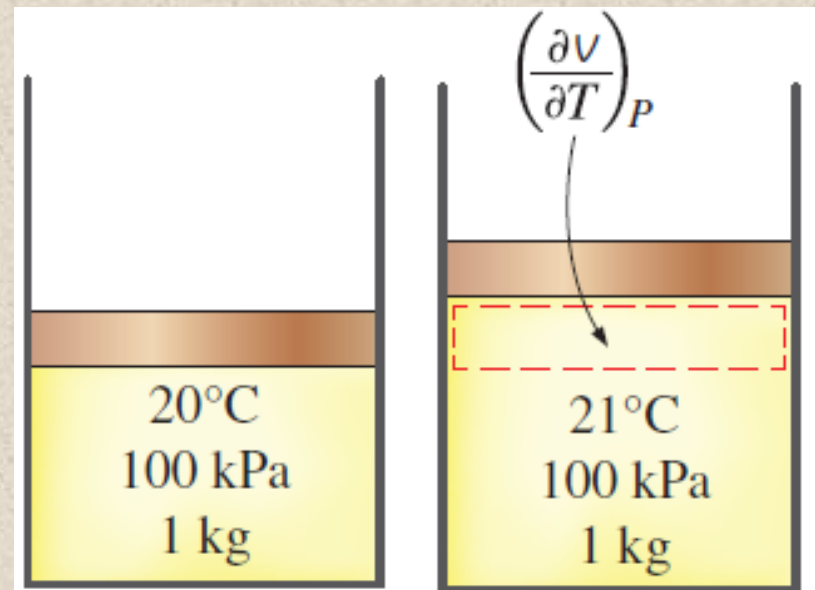
Volume expansivity (β) is a measure of increase in volume of a substance with increase in temperature at constant pressure (12-47)

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

Isothermal compressibility (α) is a measure of decrease in volume of a substance with increase in pressure at constant temperature (12-48)



(a) A substance with a large β



(b) A substance with a small β

Isothermal compressibility (α)

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

Volume expansivity (β)

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

Substituting the expressions for α and β into:

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

See the section “Specific Heats ($c_p - c_v$)”
eqn. 12-46

We get:

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

Mayer relation

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

Mayer relation

Conclusions from Mayer relation:

1. The isothermal compressibility (α) is a positive quantity for all substances in all phases. The volume expansivity (β) 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: $c_p \geq c_v$

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 $v = \text{constant}$. 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

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

Derive a relation for the internal energy change for 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

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

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

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

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, $u = u(T)$.

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

See the section “Internal Energy Changes”
eqn. 12-29

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

$$T \left(\frac{\partial P}{\partial T} \right)_v - P = T \left(\frac{R}{v} \right) - P = P - P = 0 \quad \Rightarrow \quad du = c_v dT$$

To complete the proof, we need to show that c_v is not a function of v either.

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

See the section “Specific Heats c_v and c_p ”
eqn. 12-42

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

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

(b) For an incompressible substance, $v = \text{constant}$ and thus $dv = 0$.

$$\alpha = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T \quad \beta = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_P \quad c_p - c_v = \frac{vT\beta^2}{\alpha}$$

$c_p = c_v = c$ since $\alpha = \beta = 0$ for incompressible substances.

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

See the section “Internal Energy Changes”
eqn. 12-29

$$du = c dT$$

Again we need to show that the specific heat c depends on temperature only and not on pressure or specific volume.

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

See the section “Specific Heats c_v and c_p ”
eqn. 12-43

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

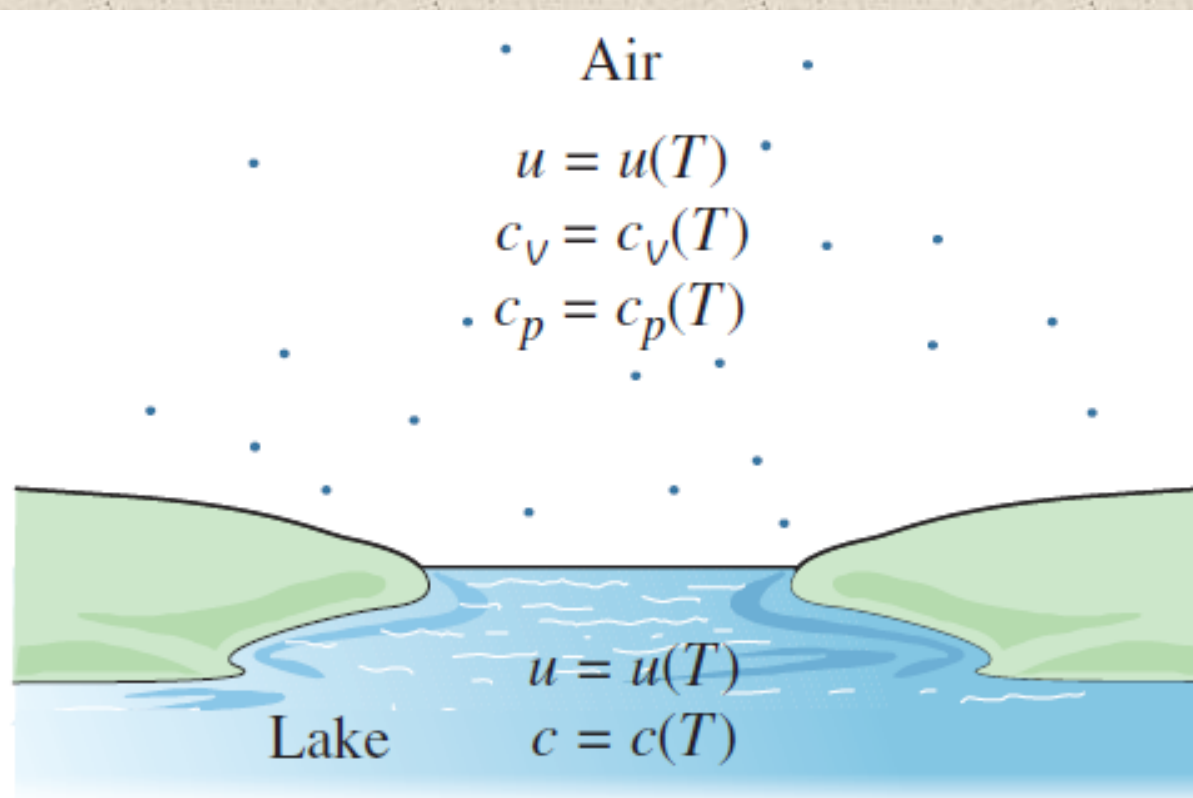


FIGURE 12–10

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.

See the section “Specific Heats ($c_p - c_v$)” eqn. 12-46

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

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

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

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,

$$c_p - c_v = R$$

THE JOULE-THOMSON COEFFICIENT

- A fluid may experience a large drop in temperature a result of throttling, which forms the basis of operation for refrigerators and air conditioners
- However, this is not the case always. The temperature of the fluid may remain unchanged, or it may even increase during a throttling process
- The temperature behavior of a fluid during a throttling ($h = \text{constant}$) process is described by the Joule-Thomson coefficient

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

The Joule-Thomson coefficient is a measure of the change in temperature with pressure during a constant-enthalpy process

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

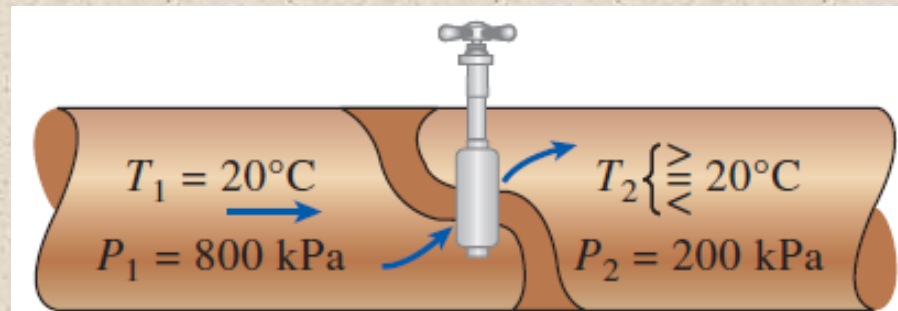


FIGURE 12–11

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

- 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

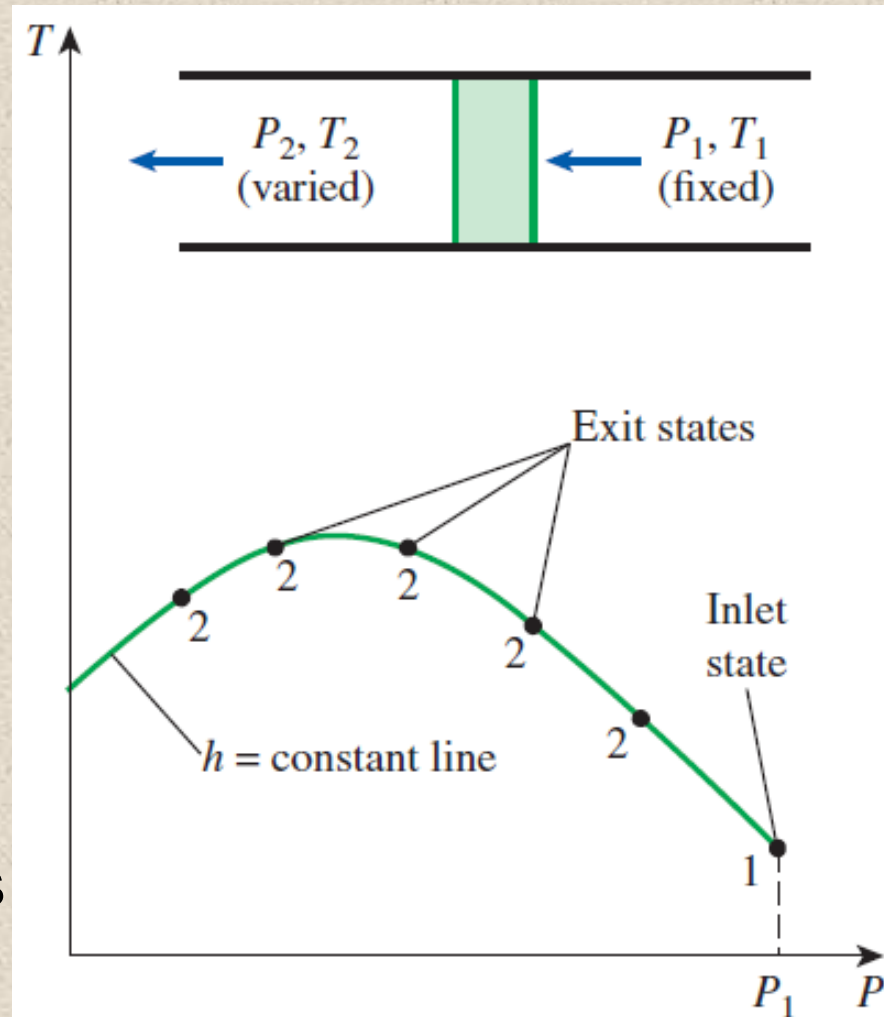


FIGURE 12-12

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

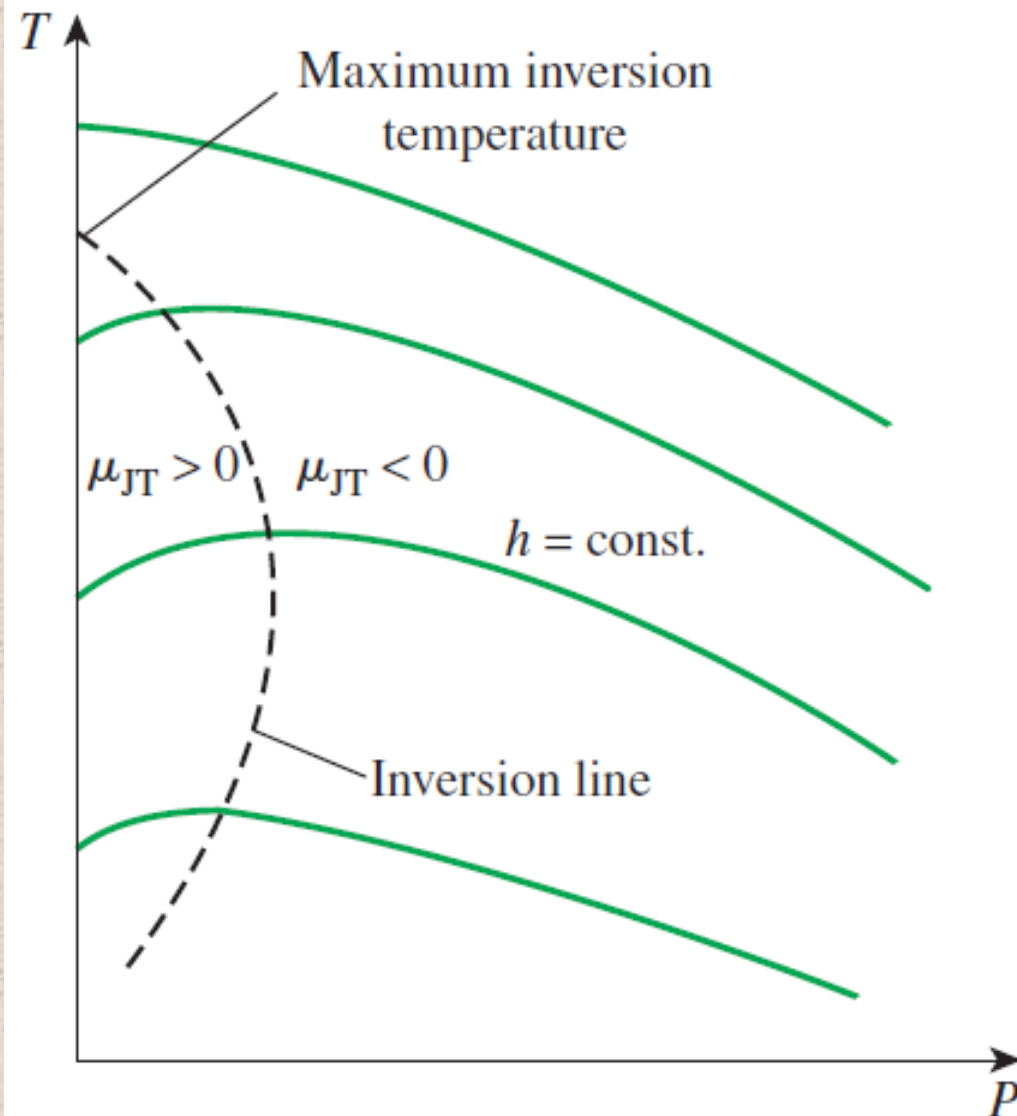


FIGURE 12-13

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**
- The fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line
- However, the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line

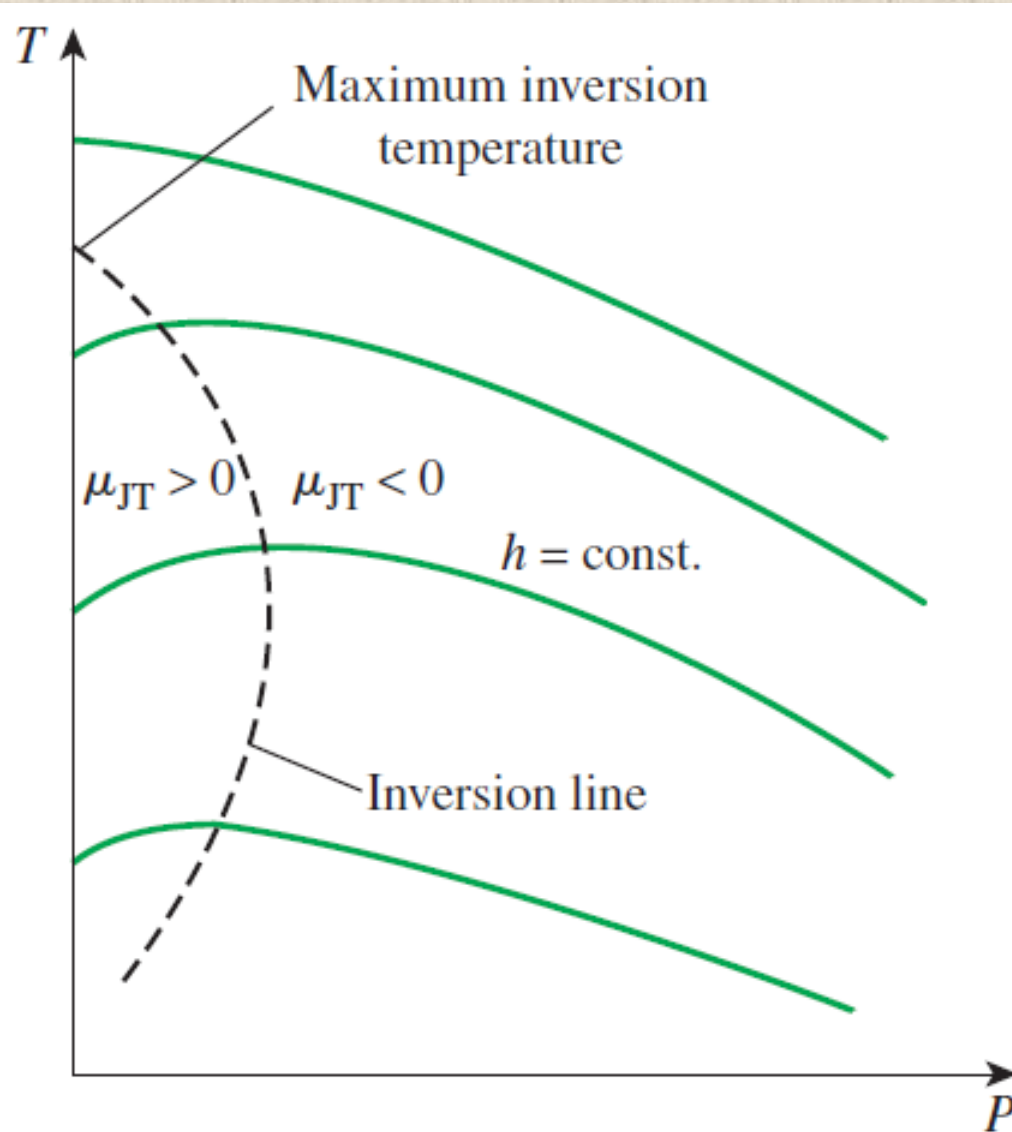


FIGURE 12–13

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

- It is clear from this diagram that a cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature
- e.g. for H_2 the maximum inversion temperature is -68°C
- Thus, at room temperature if hydrogen is throttled (pressure decreased in an isenthalpic process) its temperature will increase (safety hazard!)

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.

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

See the section “Enthalpy Changes”
eqn. 12-35

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.

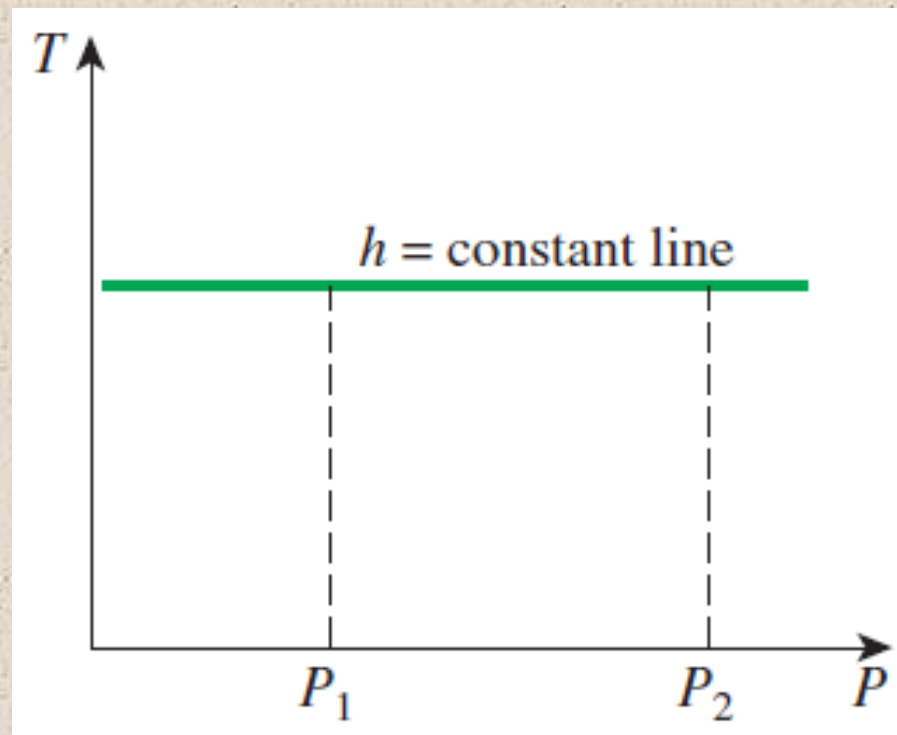


FIGURE 12-14

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.

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
- Earlier 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 chart
- Now 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
- 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

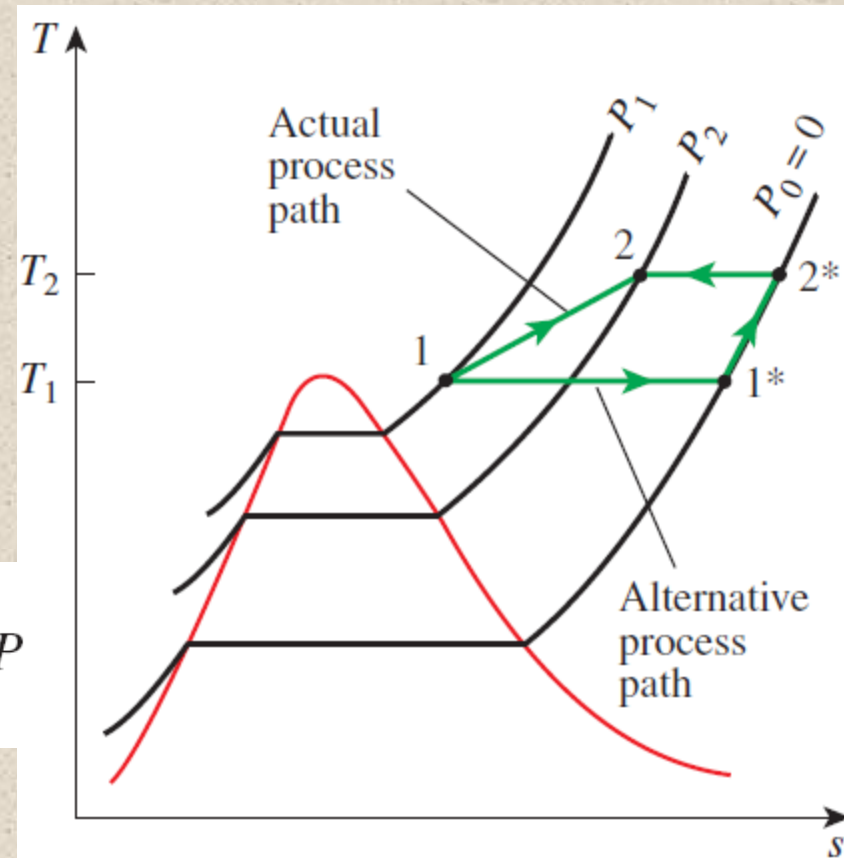


FIGURE 12-15

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

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

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

(Isothermal:

2*-2, dT = 0)

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

(Isobaric:

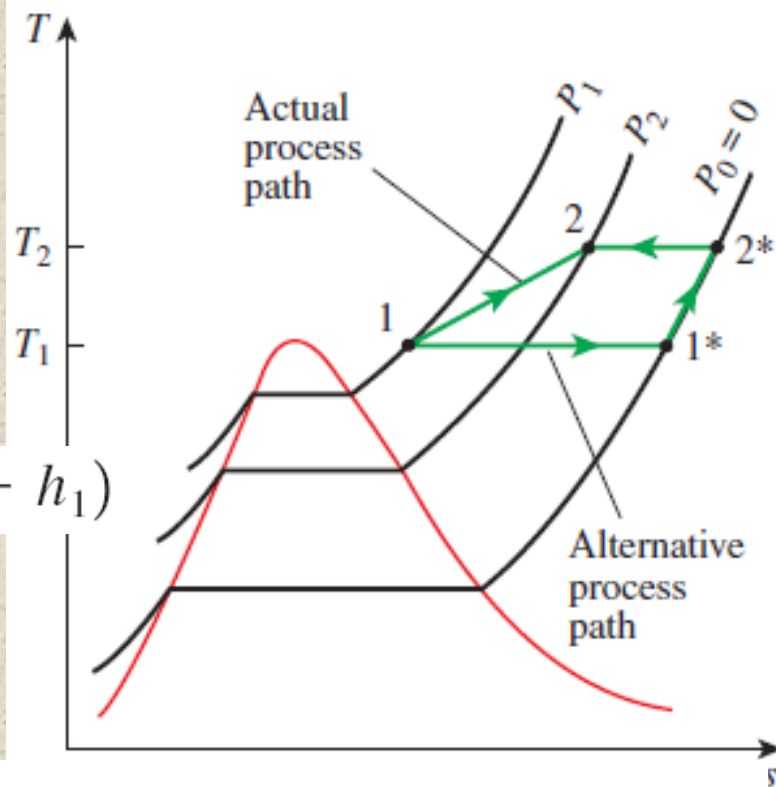
1*-2*, dP = 0)

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

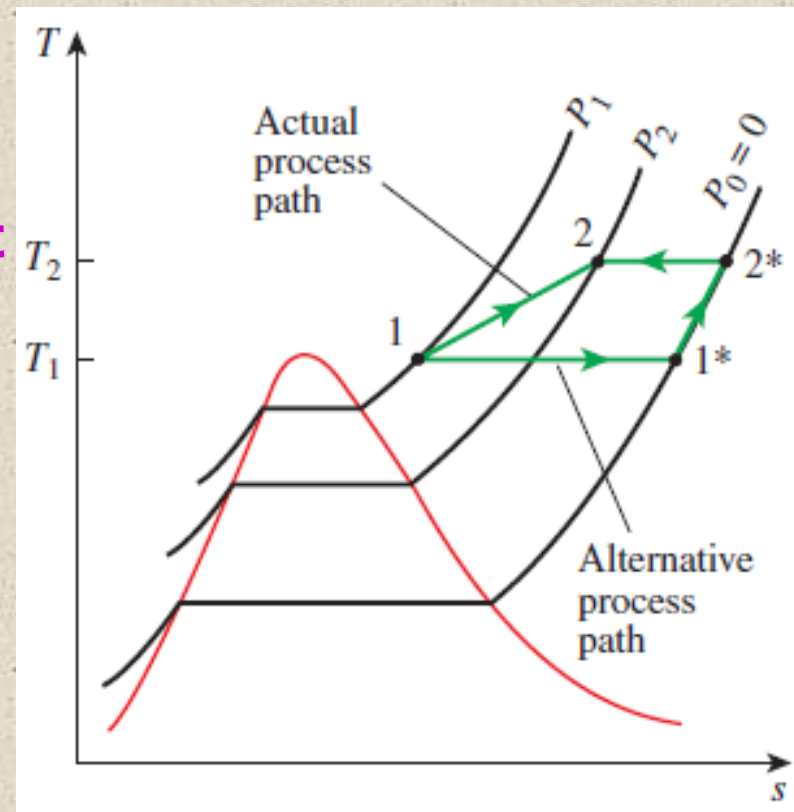
(Isothermal:

1-1*, dT = 0)

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



- 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



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

Constant temperature (T) **use: $v = ZRT/P$**

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

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

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

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

Enthalpy departure factor
(non-dimensional)

overbar represents molar
specific enthalpy, kJ/kmol

- 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**. Note that T_{cr} is the critical temperature and P_{cr} is the critical pressure
- 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

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

Molar specific
enthalpy (kJ/kmol)

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

Specific enthalpy
(kJ/kg)

$$(h_2 - h_1)_{ideal}$$

from ideal
gas tables

Enthalpy departure chart (Appendix: Fig A-29)

$$Z_h = \frac{(\bar{h}^* - \bar{h})_T}{R_u T_{cr}}$$

**Molar specific
enthalpy (kJ/kmol)**

$$Z_h = \frac{(h^* - h)_T}{R T_{cr}}$$

**Specific enthalpy
(kJ/kg)**

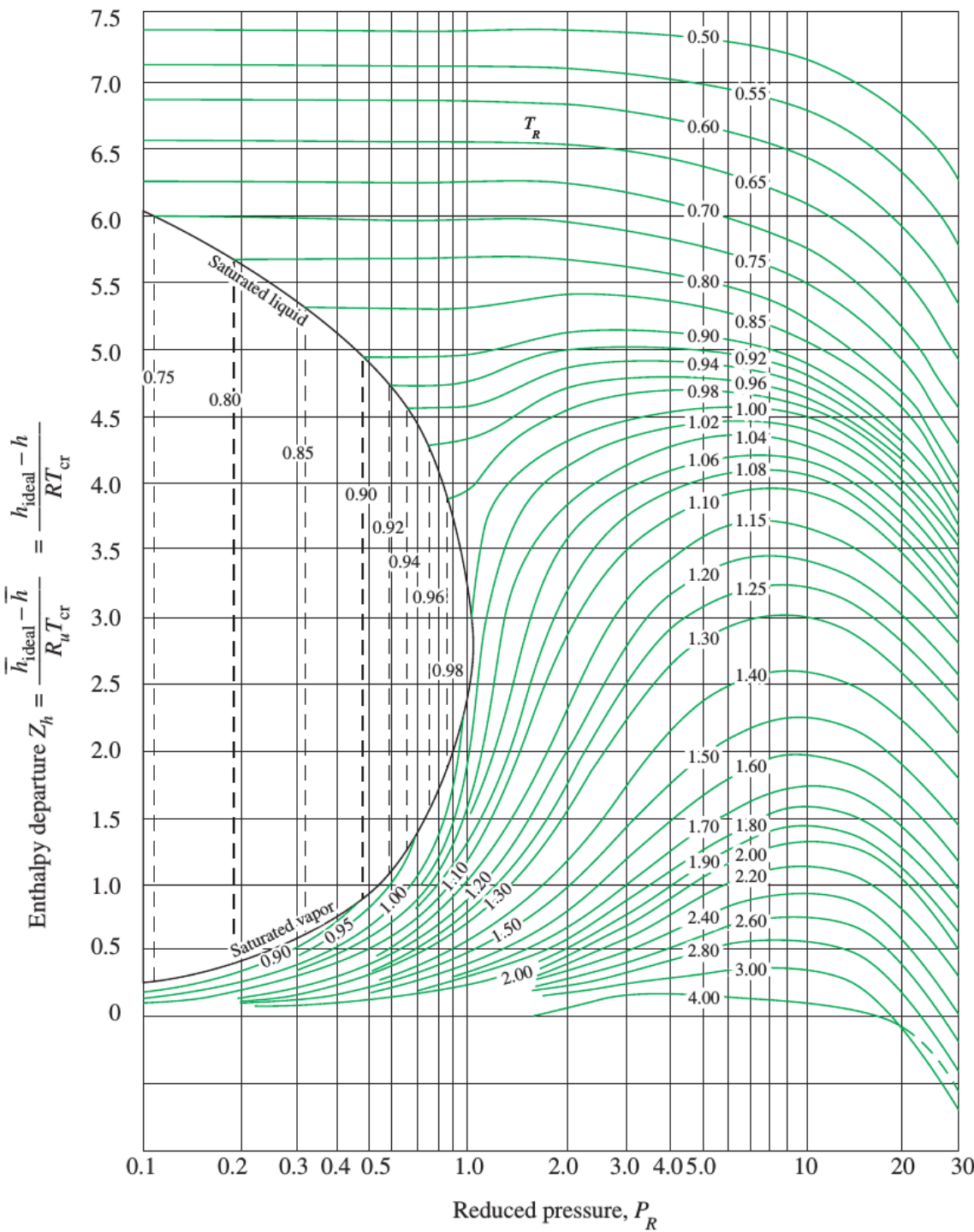
R: gas constant (kJ/kg-K)

R_u: universal gas constant
(8.314 kJ/kmol-K)

M: molar mass (kg/kmol)

$$R = \frac{R_u}{M}$$

$$\bar{h} = h \times M$$



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

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

using the definition

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

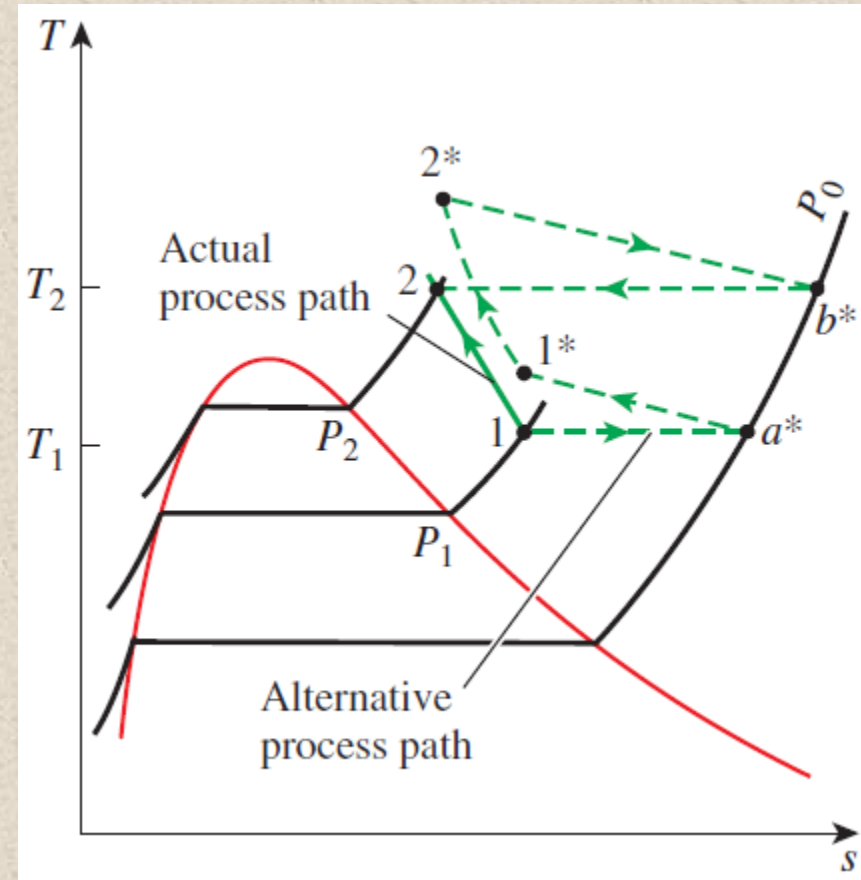
Molar specific internal energy (kJ/kmol)

Entropy Changes of Real Gases

General relation for ds

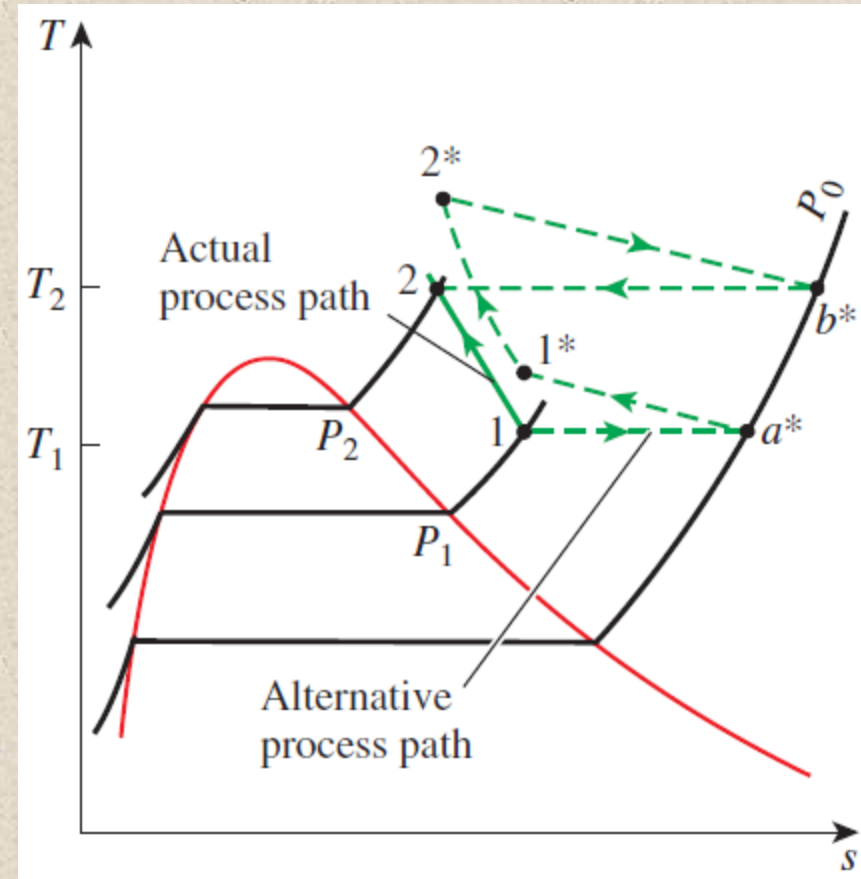
$$s_2 - s_1 = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial v}{\partial T} \right)_P dP$$

- One way is to perform the integrations first along a $T_1 =$ constant line to zero pressure ($1-a^*$), then along the $P = 0$ line to T_2 (a^*-b^*), and finally along the $T_2 =$ constant line to P_2 (b^*-2), as we did for the enthalpy
- However, this approach is not suitable for entropy-change calculations, since it involves the value of entropy at zero pressure, which is infinity



Entropy Changes of Real Gases

- We can avoid this difficulty by choosing a different (but more complex) path between the two states
- 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



Entropy Changes of Real Gases

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

- 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 $*$)

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

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

$$V = ZRT/P$$

$$V^* = V_{\text{ideal}} = RT/P$$

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

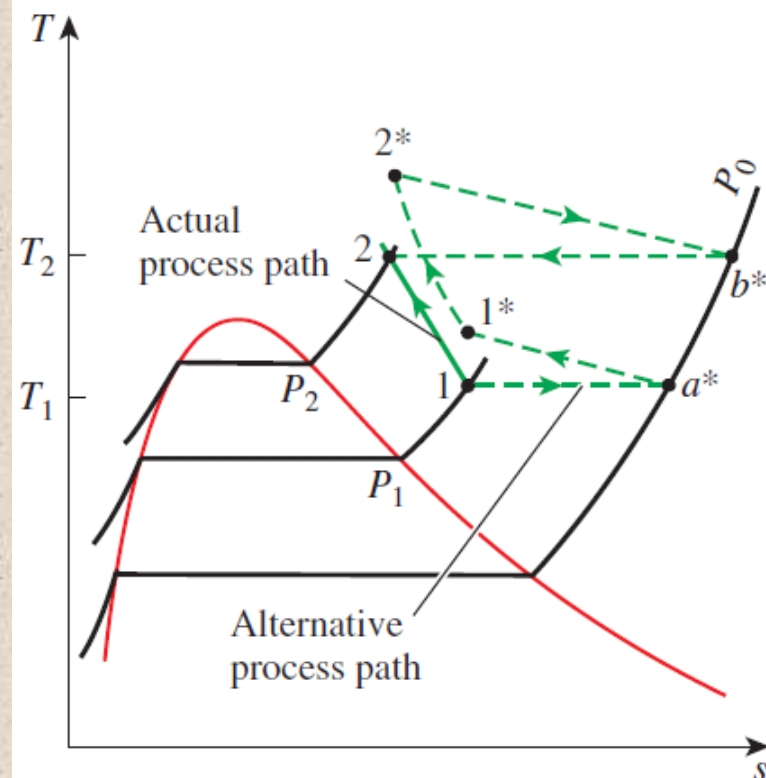


FIGURE 12-16

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

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

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

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

Enthalpy departure factor (non-dimensional)

overbar represents molar specific enthalpy, kJ/kmol

- 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

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

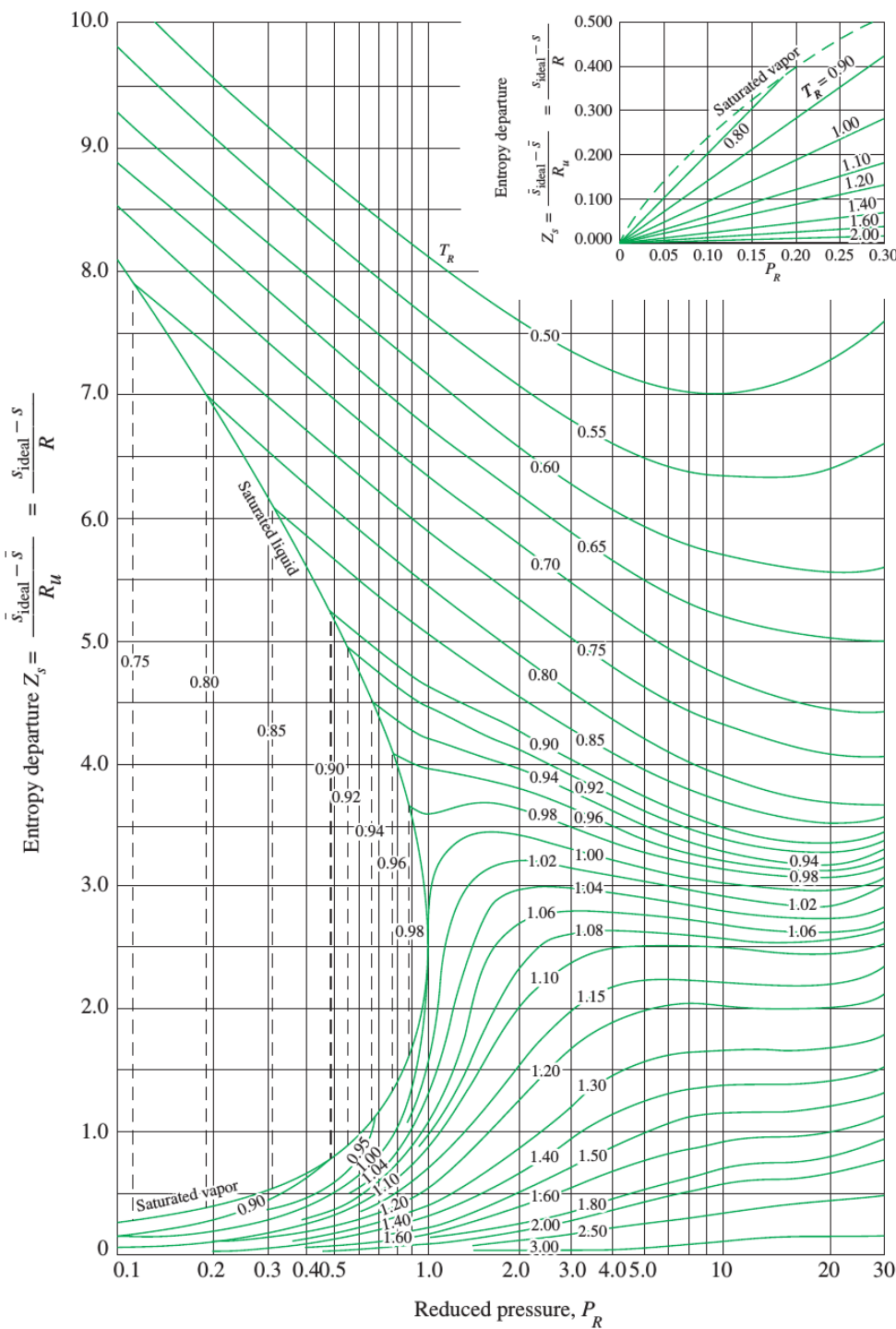
Molar specific entropy (kJ/kmol-K)

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

Specific entropy (kJ/kg-K)

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

Entropy departure chart (Appendix: Fig A-30)



$$Z_s = \frac{(\bar{s}^* - \bar{s})_{T,P}}{R_u}$$

**Molar specific entropy
(kJ/kmol-K)**

$$Z_s = \frac{(s^* - s)_{T,P}}{R}$$

**Specific entropy
(kJ/kg-K)**

R : gas constant (kJ/kg-K)

**R_u : universal gas constant
(8.314 kJ/kmol-K)**

M : molar mass (kg/kmol)

$$R = \frac{R_u}{M}$$

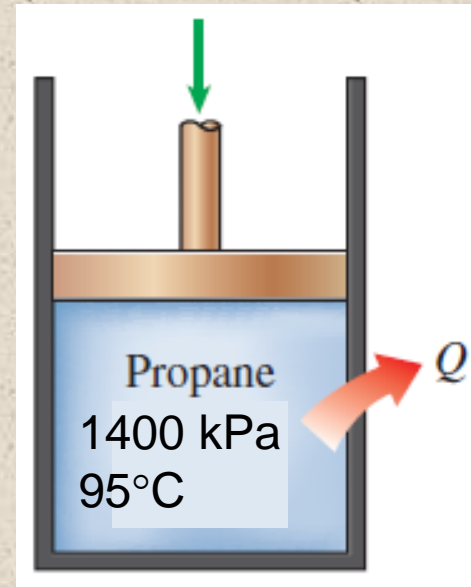
$$\bar{s} = s \times M$$

Thermodynamic Analysis with Non-Ideal Gas properties

Propane is compressed isothermally by a piston–cylinder device from 95°C and 1400 kPa to 5500 kPa. Using the generalized charts, determine the work done and the heat transfer per unit mass of propane. For propane: $R = 0.1885 \text{ kJ/kg}\cdot\text{K}$

Assumptions **1** The compression process is quasi-equilibrium. **2** Kinetic and potential energy changes are negligible.

Analysis The critical temperature and pressure of propane are $T_{\text{cr}} = 370 \text{ K}$ and $P_{\text{cr}} = 4.26 \text{ MPa}$ (Table A–1), respectively. Propane remains close to its critical temperature, and is compressed to a pressure above its critical value. Therefore, propane is expected to deviate from the ideal-gas behavior, and thus it should be treated as a real gas.



$$\left. \begin{aligned} T_{R_1} &= \frac{T_1}{T_{\text{cr}}} = \frac{368 \text{ K}}{370 \text{ K}} = 0.995 \\ P_{R_1} &= \frac{P_1}{P_{\text{cr}}} = \frac{1400 \text{ kPa}}{4260 \text{ kPa}} = 0.329 \end{aligned} \right\} \rightarrow Z_{h_1} = 0.37 \text{ and } Z_1 = 0.88$$

$$\left. \begin{aligned} T_{R_2} &= \frac{T_2}{T_{cr}} = \frac{368 \text{ K}}{370 \text{ K}} = 0.995 \\ P_{R_2} &= \frac{P_2}{P_{cr}} = \frac{5500 \text{ kPa}}{4260 \text{ kPa}} = 1.291 \end{aligned} \right\} \rightarrow Z_{h_2} = 4.2 \text{ and } Z_2 = 0.22$$

As an approximation, treating propane as a real gas with $Z_{\text{avg}} = (Z_1 + Z_2)/2 = (0.88 + 0.22)/2 = 0.55$ gives

$$Pv = ZRT \cong Z_{\text{avg}}RT = C = \text{constant}$$

$$\begin{aligned} w_{b,\text{in}} &= -\int_1^2 P dv = -\int_1^2 \frac{C}{v} dv = -C \ln \frac{v_2}{v_1} = -Z_{\text{avg}}RT \ln \frac{Z_2 RT/P_2}{Z_1 RT/P_1} \\ &= -Z_{\text{avg}}RT \ln \frac{Z_2 P_1}{Z_1 P_2} = \mathbf{105.1 \text{ kJ/kg}} \end{aligned}$$

$$h_2 - h_1 = RT_{cr}(Z_{h_1} - Z_{h_2}) + (h_2 - h_1)_{\text{ideal}} \nearrow^0 = \mathbf{-267.1 \text{ kJ/kg}}$$

$$u_2 - u_1 = (h_2 - h_1) - R(Z_2 T_2 - Z_1 T_1) = \mathbf{-221.3 \text{ kJ/kg}}$$

Then the heat transfer during this process is determined from the closed-system energy balance equation for the piston-cylinder device to be

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}}$$

$$q_{\text{in}} + w_{b,\text{in}} = \Delta u = u_2 - u_1$$

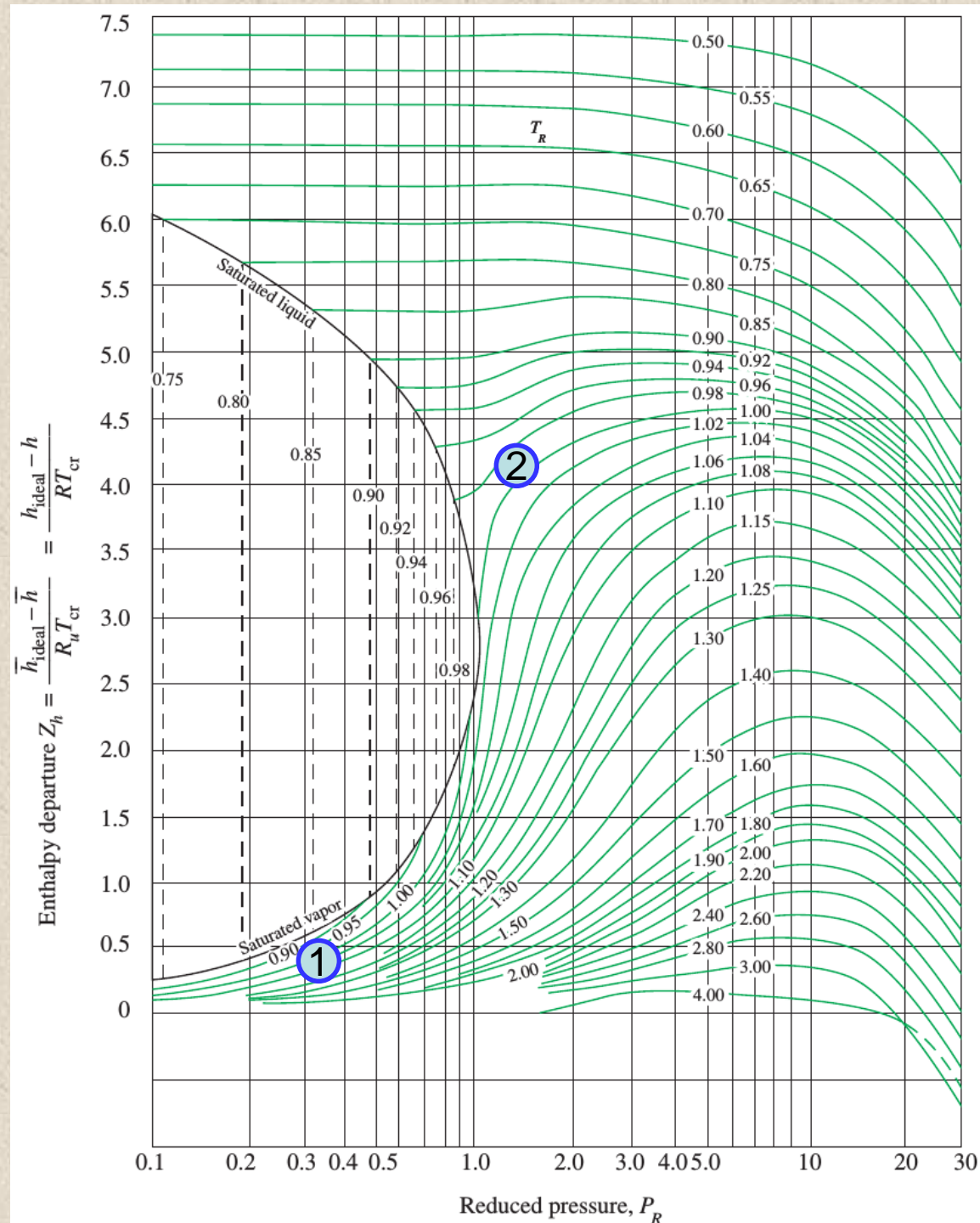
$$q_{\text{in}} = (u_2 - u_1) - w_{b,\text{in}} = -221.3 - 105.1 = -326.4 \text{ kJ/kg}$$

The negative sign indicates heat rejection. Therefore, heat transfer out of the system during this process is

$$q_{\text{out}} = 326.4 \text{ kJ/kg}$$

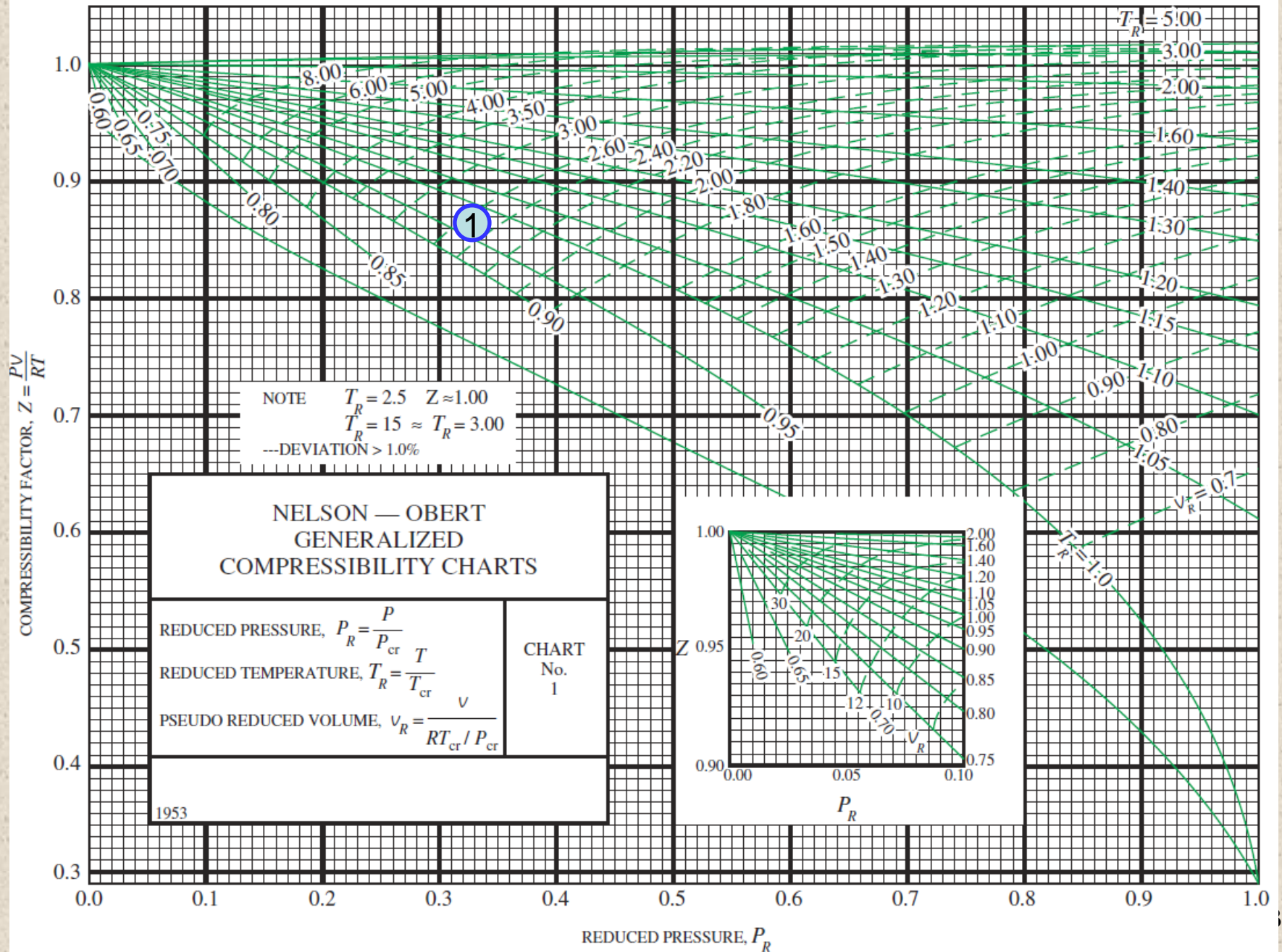
Discussion Note that if the ideal-gas assumption were used for propane, the magnitudes of boundary work and heat transfer would have been the same (94.9 kJ/kg). Therefore, the ideal-gas approximation would underestimate boundary work by 10 percent, and the heat transfer by 71 percent.

Appendix: Fig. A-29



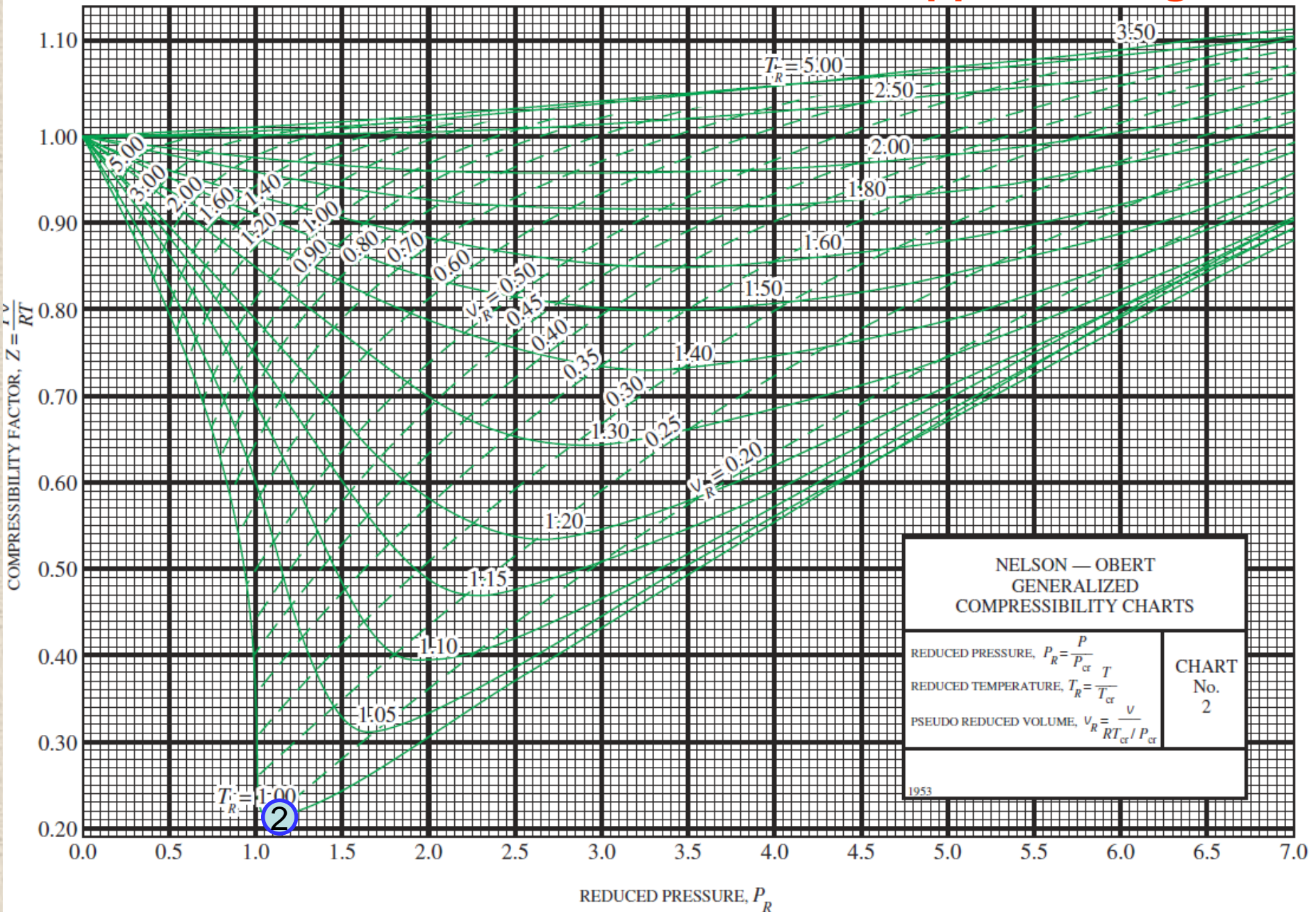
(a) Low pressures, $0 < P_R < 1.0$

Appendix: Fig. A-15



(b) Intermediate pressures, $0 < P_R < 7$

Appendix: Fig. A-15



$$\begin{aligned} du &= T ds - P dv \\ dh &= T ds + v dP \\ da &= -s dT - P dv \\ dg &= -s dT + v dP \end{aligned}$$

$$\begin{aligned} \left(\frac{\partial T}{\partial v}\right)_s &= -\left(\frac{\partial P}{\partial s}\right)_v \\ \left(\frac{\partial T}{\partial P}\right)_s &= \left(\frac{\partial v}{\partial s}\right)_P \\ \left(\frac{\partial s}{\partial v}\right)_T &= \left(\frac{\partial P}{\partial T}\right)_v \\ \left(\frac{\partial s}{\partial P}\right)_T &= -\left(\frac{\partial v}{\partial T}\right)_P \end{aligned}$$

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

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

$$\begin{aligned} du &= c_v dT + \left[T\left(\frac{\partial P}{\partial T}\right)_v - P\right] dv \\ dh &= c_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dP \\ ds &= \frac{c_v}{T} dT + \left(\frac{\partial P}{\partial T}\right)_v dv \\ ds &= \frac{c_p}{T} dT - \left(\frac{\partial v}{\partial T}\right)_P dP \end{aligned}$$

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

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

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

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

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

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

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

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

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

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

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

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