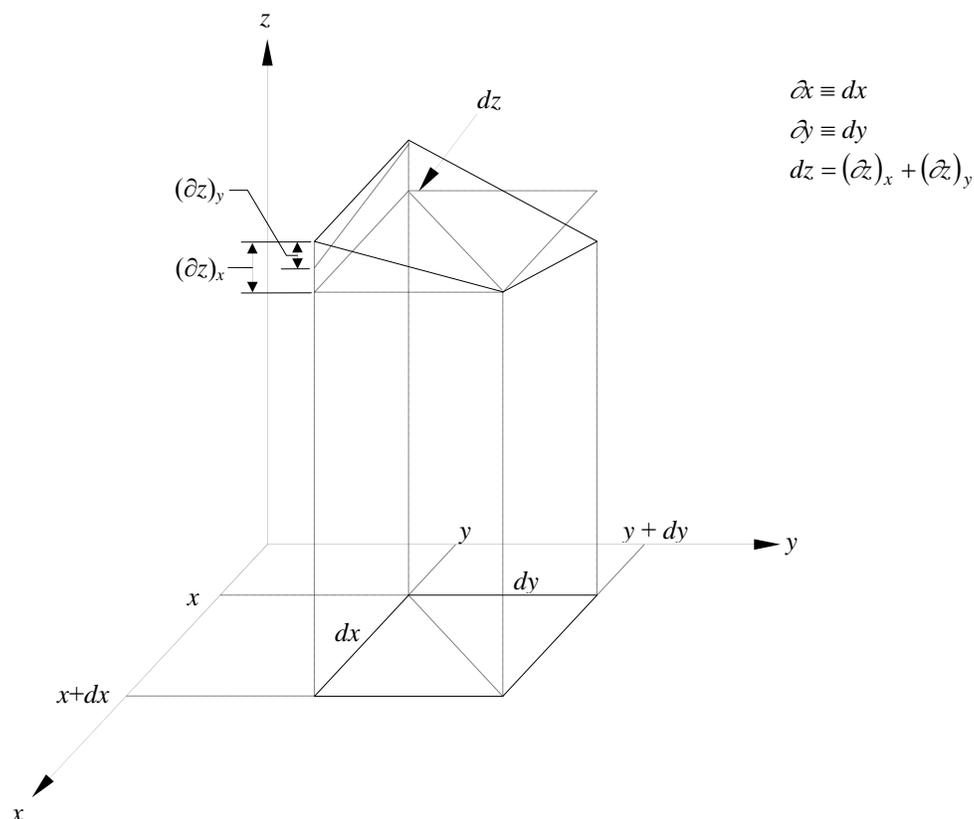


# Chapter 12

## THERMODYNAMIC PROPERTY RELATIONS

### Partial Derivatives and Associated Relations

#### 12-1C



**12-2C** For functions that depend on one variable, they are identical. For functions that depend on two or more variables, the partial differential represents the change in the function with one of the variables as the other variables are held constant. The ordinary differential for such functions represents the total change as a result of differential changes in all variables.

**12-3C** (a)  $(\partial x)_y = dx$ ; (b)  $(\partial z)_y \leq dz$ ; and (c)  $dz = (\partial z)_x + (\partial z)_y$

**12-4C** Yes.

**12-5C** Yes.

**12-6** Air at a specified temperature and specific volume is considered. The changes in pressure corresponding to a certain increase of different properties are to be determined.

**Assumptions** Air is an ideal gas.

**Properties** The gas constant of air is  $R = 0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}$  (Table A-1).

**Analysis** An ideal gas equation can be expressed as  $P = RT/\nu$ . Noting that  $R$  is a constant and  $P = P(T, \nu)$ ,

$$dP = \left( \frac{\partial P}{\partial T} \right)_{\nu} dT + \left( \frac{\partial P}{\partial \nu} \right)_{T} d\nu = \frac{RdT}{\nu} - \frac{RTd\nu}{\nu^2}$$

(a) The change in  $T$  can be expressed as  $dT \cong \Delta T = 400 \times 0.01 = 4.0 \text{ K}$ . At  $\nu = \text{constant}$ ,

$$(dP)_{\nu} = \frac{RdT}{\nu} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(4.0 \text{ K})}{0.90 \text{ m}^3/\text{kg}} = \mathbf{1.276 \text{ kPa}}$$

(b) The change in  $\nu$  can be expressed as  $d\nu \cong \Delta \nu = 0.90 \times 0.01 = 0.009 \text{ m}^3/\text{kg}$ . At  $T = \text{constant}$ ,

$$(dP)_{T} = -\frac{RTd\nu}{\nu^2} = -\frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(400\text{K})(0.009 \text{ m}^3/\text{kg})}{(0.90 \text{ m}^3/\text{kg})^2} = \mathbf{-1.276 \text{ kPa}}$$

(c) When both  $\nu$  and  $T$  increases by 1%, the change in  $P$  becomes

$$dP = (dP)_{\nu} + (dP)_{T} = 1.276 + (-1.276) = \mathbf{0}$$

Thus the changes in  $T$  and  $\nu$  balance each other.

**12-7** Helium at a specified temperature and specific volume is considered. The changes in pressure corresponding to a certain increase of different properties are to be determined.

**Assumptions** Helium is an ideal gas

**Properties** The gas constant of helium is  $R = 2.0769 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}$  (Table A-1).

**Analysis** An ideal gas equation can be expressed as  $P = RT/\nu$ . Noting that  $R$  is a constant and  $P = P(T, \nu)$ ,

$$dP = \left( \frac{\partial P}{\partial T} \right)_{\nu} dT + \left( \frac{\partial P}{\partial \nu} \right)_{T} d\nu = \frac{RdT}{\nu} - \frac{RTd\nu}{\nu^2}$$

(a) The change in  $T$  can be expressed as  $dT \cong \Delta T = 400 \times 0.01 = 4.0 \text{ K}$ . At  $\nu = \text{constant}$ ,

$$(dP)_{\nu} = \frac{RdT}{\nu} = \frac{(2.0769 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(4.0 \text{ K})}{0.90 \text{ m}^3/\text{kg}} = \mathbf{9.231 \text{ kPa}}$$

(b) The change in  $\nu$  can be expressed as  $d\nu \cong \Delta \nu = 0.90 \times 0.01 = 0.009 \text{ m}^3/\text{kg}$ . At  $T = \text{constant}$ ,

$$(dP)_{T} = -\frac{RTd\nu}{\nu^2} = -\frac{(2.0769 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(400 \text{ K})(0.009 \text{ m}^3/\text{kg})}{(0.90 \text{ m}^3/\text{kg})^2} = \mathbf{-9.231 \text{ kPa}}$$

(c) When both  $\nu$  and  $T$  increases by 1%, the change in  $P$  becomes

$$dP = (dP)_{\nu} + (dP)_{T} = 9.231 + (-9.231) = \mathbf{0}$$

Thus the changes in  $T$  and  $\nu$  balance each other.

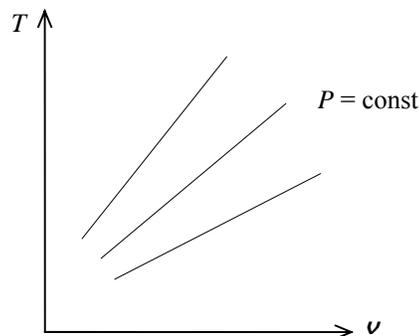
**12-8** It is to be proven for an ideal gas that the  $P = \text{constant}$  lines on a  $T$ - $v$  diagram are straight lines and that the high pressure lines are steeper than the low-pressure lines.

**Analysis** (a) For an ideal gas  $Pv = RT$  or  $T = Pv/R$ . Taking the partial derivative of  $T$  with respect to  $v$  holding  $P$  constant yields

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

which remains constant at  $P = \text{constant}$ . Thus the derivative  $(\partial T/\partial v)_P$ , which represents the slope of the  $P = \text{const.}$  lines on a  $T$ - $v$  diagram, remains constant. That is, the  $P = \text{const.}$  lines are straight lines on a  $T$ - $v$  diagram.

(b) The slope of the  $P = \text{const.}$  lines on a  $T$ - $v$  diagram is equal to  $P/R$ , which is proportional to  $P$ . Therefore, the high pressure lines are steeper than low pressure lines on the  $T$ - $v$  diagram.



**12-9** A relation is to be derived for the slope of the  $v = \text{constant}$  lines on a  $T$ - $P$  diagram for a gas that obeys the van der Waals equation of state.

**Analysis** The van der Waals equation of state can be expressed as

$$T = \frac{1}{R} \left( P + \frac{a}{v^2} \right) (v - b)$$

Taking the derivative of  $T$  with respect to  $P$  holding  $v$  constant,

$$\left(\frac{\partial T}{\partial P}\right)_v = \frac{1}{R} (1 + 0)(v - b) = \frac{v - b}{R}$$

which is the slope of the  $v = \text{constant}$  lines on a  $T$ - $P$  diagram.

**12-10** Nitrogen gas at a specified state is considered. The  $c_p$  and  $c_v$  of the nitrogen are to be determined using Table A-18, and to be compared to the values listed in Table A-2b.

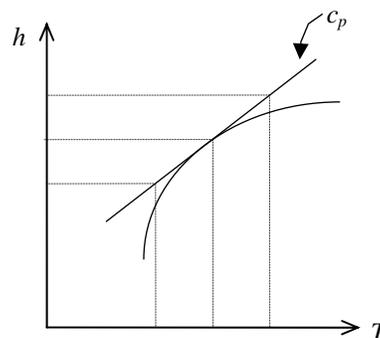
**Analysis** The  $c_p$  and  $c_v$  of ideal gases depends on temperature only, and are expressed as  $c_p(T) = dh(T)/dT$  and  $c_v(T) = du(T)/dT$ . Approximating the differentials as differences about 400 K, the  $c_p$  and  $c_v$  values are determined to be

$$\begin{aligned} c_p(400\text{ K}) &= \left( \frac{dh(T)}{dT} \right)_{T=400\text{ K}} \cong \left( \frac{\Delta h(T)}{\Delta T} \right)_{T \cong 400\text{ K}} \\ &= \frac{h(410\text{ K}) - h(390\text{ K})}{(410 - 390)\text{K}} \\ &= \frac{(11,932 - 11,347)/28.0\text{ kJ/kg}}{(410 - 390)\text{K}} \\ &= \mathbf{1.045\text{ kJ/kg} \cdot \text{K}} \end{aligned}$$

(Compare: Table A-2b at 400 K  $\rightarrow c_p = 1.044\text{ kJ/kg} \cdot \text{K}$ )

$$\begin{aligned} c_v(400\text{ K}) &= \left( \frac{du(T)}{dT} \right)_{T=400\text{ K}} \cong \left( \frac{\Delta u(T)}{\Delta T} \right)_{T \cong 400\text{ K}} \\ &= \frac{u(410\text{ K}) - u(390\text{ K})}{(410 - 390)\text{K}} \\ &= \frac{(8,523 - 8,104)/28.0\text{ kJ/kg}}{(410 - 390)\text{K}} = \mathbf{0.748\text{ kJ/kg} \cdot \text{K}} \end{aligned}$$

(Compare: Table A-2b at 400 K  $\rightarrow c_v = 0.747\text{ kJ/kg} \cdot \text{K}$ )



**12-11E** Nitrogen gas at a specified state is considered. The  $c_p$  and  $c_v$  of the nitrogen are to be determined using Table A-18E, and to be compared to the values listed in Table A-2Eb.

**Analysis** The  $c_p$  and  $c_v$  of ideal gases depends on temperature only, and are expressed as  $c_p(T) = dh(T)/dT$  and  $c_v(T) = du(T)/dT$ . Approximating the differentials as differences about 600 R, the  $c_p$  and  $c_v$  values are determined to be

$$\begin{aligned} c_p(600 \text{ R}) &= \left( \frac{dh(T)}{dT} \right)_{T=600 \text{ R}} \cong \left( \frac{\Delta h(T)}{\Delta T} \right)_{T \cong 600 \text{ R}} \\ &= \frac{h(620 \text{ R}) - h(580 \text{ R})}{(620 - 580) \text{ R}} \\ &= \frac{(4,307.1 - 4,028.7) \text{ Btu/lbm}}{(620 - 580) \text{ R}} = \mathbf{0.249 \text{ Btu/lbm} \cdot \text{R}} \end{aligned}$$

(Compare: Table A-2Eb at 600 R  $\rightarrow c_p = 0.248 \text{ Btu/lbm} \cdot \text{R}$ )

$$\begin{aligned} c_v(600 \text{ R}) &= \left( \frac{du(T)}{dT} \right)_{T=600 \text{ R}} \cong \left( \frac{\Delta u(T)}{\Delta T} \right)_{T \cong 600 \text{ R}} \\ &= \frac{u(620 \text{ R}) - u(580 \text{ R})}{(620 - 580) \text{ R}} \\ &= \frac{(3,075.9 - 2,876.9) \text{ Btu/lbm}}{(620 - 580) \text{ R}} = \mathbf{0.178 \text{ Btu/lbm} \cdot \text{R}} \end{aligned}$$

(Compare: Table A-2Eb at 600 R  $\rightarrow c_v = 0.178 \text{ Btu/lbm} \cdot \text{R}$ )

**12-12** The state of an ideal gas is altered slightly. The change in the specific volume of the gas is to be determined using differential relations and the ideal-gas relation at each state.

**Assumptions** The gas is air and air is an ideal gas.

**Properties** The gas constant of air is  $R = 0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}$  (Table A-1).

**Analysis** (a) The changes in  $T$  and  $P$  can be expressed as

$$dT \cong \Delta T = (404 - 400)\text{K} = 4 \text{ K}$$

$$dP \cong \Delta P = (96 - 100)\text{kPa} = -4 \text{ kPa}$$

The ideal gas relation  $P\nu = RT$  can be expressed as  $\nu = RT/P$ . Note that  $R$  is a constant and  $\nu = \nu(T, P)$ . Applying the total differential relation and using average values for  $T$  and  $P$ ,

$$\begin{aligned} d\nu &= \left(\frac{\partial \nu}{\partial T}\right)_P dT + \left(\frac{\partial \nu}{\partial P}\right)_T dP = \frac{RdT}{P} - \frac{RT dP}{P^2} \\ &= (0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K}) \left( \frac{4 \text{ K}}{98 \text{ kPa}} - \frac{(402 \text{ K})(-4 \text{ kPa})}{(98 \text{ kPa})^2} \right) \\ &= (0.0117 \text{ m}^3/\text{kg}) + (0.04805 \text{ m}^3/\text{kg}) = \mathbf{0.0598 \text{ m}^3/\text{kg}} \end{aligned}$$

(b) Using the ideal gas relation at each state,

$$\nu_1 = \frac{RT_1}{P_1} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(400 \text{ K})}{100 \text{ kPa}} = 1.1480 \text{ m}^3/\text{kg}$$

$$\nu_2 = \frac{RT_2}{P_2} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(404 \text{ K})}{96 \text{ kPa}} = 1.2078 \text{ m}^3/\text{kg}$$

Thus,

$$\Delta \nu = \nu_2 - \nu_1 = 1.2078 - 1.1480 = \mathbf{0.0598 \text{ m}^3/\text{kg}}$$

The two results are identical.

**12-13** Using the equation of state  $P(\nu - a) = RT$ , the cyclic relation, and the reciprocity relation at constant  $\nu$  are to be verified.

**Analysis** (a) This equation of state involves three variables  $P$ ,  $\nu$ , and  $T$ . Any two of these can be taken as the independent variables, with the remaining one being the dependent variable. Replacing  $x$ ,  $y$ , and  $z$  by  $P$ ,  $\nu$ , and  $T$ , the cyclic relation can be expressed as

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

where

$$\begin{aligned} P &= \frac{RT}{\nu - a} \longrightarrow \left(\frac{\partial P}{\partial \nu}\right)_T = \frac{-RT}{(\nu - a)^2} = -\frac{P}{\nu - a} \\ \nu &= \frac{RT}{P} + a \longrightarrow \left(\frac{\partial \nu}{\partial T}\right)_P = \frac{R}{P} \\ T &= \frac{P(\nu - a)}{R} \longrightarrow \left(\frac{\partial T}{\partial P}\right)_\nu = \frac{\nu - a}{R} \end{aligned}$$

Substituting,

$$\left(\frac{\partial P}{\partial \nu}\right)_T \left(\frac{\partial \nu}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_\nu = \left(-\frac{P}{\nu - a}\right) \left(\frac{R}{P}\right) \left(\frac{\nu - a}{R}\right) = -1$$

which is the desired result.

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

$$\begin{aligned} \left(\frac{\partial P}{\partial T}\right)_\nu &= \frac{1}{(\partial T / \partial P)_\nu} \\ T &= \frac{P(\nu - a)}{R} \longrightarrow \left(\frac{\partial T}{\partial P}\right)_\nu = \frac{\nu - a}{R} \\ P &= \frac{RT}{\nu - a} \longrightarrow \left(\frac{\partial P}{\partial T}\right)_\nu = \frac{R}{\nu - a} \end{aligned}$$

We observe that the first differential is the inverse of the second one. Thus the proof is complete.

## The Maxwell Relations

**12-14** The validity of the last Maxwell relation for refrigerant-134a at a specified state is to be verified.

**Analysis** We do not have exact analytical property relations for refrigerant-134a, and thus we need to replace the differential quantities in the last Maxwell relation with the corresponding finite quantities. Using property values from the tables about the specified state,

$$\begin{aligned} \left(\frac{\partial s}{\partial P}\right)_T &\stackrel{?}{=} -\left(\frac{\partial v}{\partial T}\right)_P \\ \left(\frac{\Delta s}{\Delta P}\right)_{T=80^\circ\text{C}} &\stackrel{?}{\cong} -\left(\frac{\Delta v}{\Delta T}\right)_{P=1200\text{kPa}} \\ \left(\frac{s_{1400\text{ kPa}} - s_{1000\text{ kPa}}}{(1400 - 1000)\text{kPa}}\right)_{T=80^\circ\text{C}} &\stackrel{?}{\cong} -\left(\frac{v_{100^\circ\text{C}} - v_{60^\circ\text{C}}}{(100 - 60)^\circ\text{C}}\right)_{P=1200\text{kPa}} \\ \frac{(1.0056 - 1.0458)\text{kJ/kg} \cdot \text{K}}{(1400 - 1000)\text{kPa}} &\stackrel{?}{\cong} -\frac{(0.022442 - 0.018404)\text{m}^3/\text{kg}}{(100 - 60)^\circ\text{C}} \\ &\cong -1.005 \times 10^{-4} \text{ m}^3/\text{kg} \cdot \text{K} \cong -1.0095 \times 10^{-4} \text{ m}^3/\text{kg} \cdot \text{K} \end{aligned}$$

since  $\text{kJ} \equiv \text{kPa} \cdot \text{m}^3$ , and  $\text{K} \equiv ^\circ\text{C}$  for temperature differences. Thus the last Maxwell relation is satisfied.

**12-15 EES** Problem 12-14 is reconsidered. The validity of the last Maxwell relation for refrigerant 134a at the specified state is to be verified.

**Analysis** The problem is solved using EES, and the solution is given below.

"Input Data:"

```
T=80 [C]
P=1200 [kPa]
P_increment = 200 [kPa]
T_increment = 20 [C]
P[2]=P+P_increment
P[1]=P-P_increment
T[2]=T+T_increment
T[1]=T-T_increment
```

```
DELTAP = P[2]-P[1]
DELTAT = T[2]-T[1]
```

```
v[1]=volume(R134a,T=T[1],P=P)
v[2]=volume(R134a,T=T[2],P=P)
s[1]=entropy(R134a,T=T,P=P[1])
s[2]=entropy(R134a,T=T,P=P[2])
```

```
DELTAs=s[2] - s[1]
DELTAv=v[2] - v[1]
```

"The partial derivatives in the last Maxwell relation (Eq. 11-19) is associated with the Gibbs function and are approximated by the ratio of ordinary differentials:"

```
LeftSide =DELTAs/DELTAP*Convert(kJ,m^3-kPa) "[m^3/kg-K]" "at T = Const."
RightSide=-DELTAv/DELTAT "[m^3/kg-K]" "at P = Const."
```

SOLUTION

DELTAP=400 [kPa]	RightSide=-0.000101 [m^3/kg-K]
DELTAs=-0.04026 [kJ/kg-K]	s[1]=1.046 [kJ/kg-K]
DELTAT=40 [C]	s[2]=1.006 [kJ/kg-K]
DELTAv=0.004038 [m^3/kg]	T=80 [C]
LeftSide=-0.0001007 [m^3/kg-K]	T[1]=60 [C]
P=1200 [kPa]	T[2]=100 [C]
P[1]=1000 [kPa]	T_increment=20 [C]
P[2]=1400 [kPa]	v[1]=0.0184 [m^3/kg]
P_increment=200 [kPa]	v[2]=0.02244 [m^3/kg]

**12-16E** The validity of the last Maxwell relation for steam at a specified state is to be verified.

**Analysis** We do not have exact analytical property relations for steam, and thus we need to replace the differential quantities in the last Maxwell relation with the corresponding finite quantities. Using property values from the tables about the specified state,

$$\begin{aligned} \left(\frac{\partial s}{\partial P}\right)_T &\stackrel{?}{=} -\left(\frac{\partial \nu}{\partial T}\right)_P \\ \left(\frac{\Delta s}{\Delta P}\right)_{T=800^\circ\text{F}} &\stackrel{?}{\cong} -\left(\frac{\Delta \nu}{\Delta T}\right)_{P=400\text{psia}} \\ \left(\frac{s_{450\text{psia}} - s_{350\text{psia}}}{(450 - 350)\text{psia}}\right)_{T=800^\circ\text{F}} &\stackrel{?}{\cong} -\left(\frac{\nu_{900^\circ\text{F}} - \nu_{700^\circ\text{F}}}{(900 - 700)^\circ\text{F}}\right)_{P=400\text{psia}} \\ \frac{(1.6706 - 1.7009)\text{Btu/lbm}\cdot\text{R}}{(450 - 350)\text{psia}} &\stackrel{?}{\cong} -\frac{(1.9777 - 1.6507)\text{ft}^3/\text{lbm}}{(900 - 700)^\circ\text{F}} \\ -1.639 \times 10^{-3} \text{ft}^3/\text{lbm}\cdot\text{R} &\cong -1.635 \times 10^{-3} \text{ft}^3/\text{lbm}\cdot\text{R} \end{aligned}$$

since  $1 \text{ Btu} \cong 5.4039 \text{ psia}\cdot\text{ft}^3$ , and  $\text{R} \cong ^\circ\text{F}$  for temperature differences. Thus the fourth Maxwell relation is satisfied.

**12-17** Using the Maxwell relations, a relation for  $(\partial s/\partial P)_T$  for a gas whose equation of state is  $P(\nu - b) = RT$  is to be obtained.

**Analysis** This equation of state can be expressed as  $\nu = \frac{RT}{P} + b$ . Then,

$$\left(\frac{\partial \nu}{\partial T}\right)_P = \frac{R}{P}$$

From the fourth Maxwell relation,

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

**12-18** Using the Maxwell relations, a relation for  $(\partial s/\partial v)_T$  for a gas whose equation of state is  $(P-a/v^2)(v-b) = RT$  is to be obtained.

**Analysis** This equation of state can be expressed as  $P = \frac{RT}{v-b} + \frac{a}{v^2}$ . Then,

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

From the third Maxwell relation,

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

**12-19** Using the Maxwell relations and the ideal-gas equation of state, a relation for  $(\partial s/\partial v)_T$  for an ideal gas is to be obtained.

**Analysis** The ideal gas equation of state can be expressed as  $P = \frac{RT}{v}$ . Then,

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

From the third Maxwell relation,

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

**12-20** It is to be proven that  $\left(\frac{\partial P}{\partial T}\right)_s = \frac{k}{k-1} \left(\frac{\partial P}{\partial T}\right)_v$

**Analysis** Using the definition of  $c_v$ ,

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

Substituting the first Maxwell relation  $\left(\frac{\partial s}{\partial P}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_s$ ,

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

Using the definition of  $c_p$ ,

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

Substituting the second Maxwell relation  $\left(\frac{\partial s}{\partial v}\right)_p = \left(\frac{\partial P}{\partial T}\right)_s$ ,

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

From Eq. 12-46,

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

Also,

$$\frac{k}{k-1} = \frac{c_p}{c_p - c_v}$$

Then,

$$\frac{k}{k-1} = -\frac{\left(\frac{\partial P}{\partial T}\right)_s \left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial P}{\partial v}\right)_T} = -\left(\frac{\partial P}{\partial T}\right)_s \left(\frac{\partial T}{\partial v}\right)_p \left(\frac{\partial v}{\partial P}\right)_T$$

Substituting this into the original equation in the problem statement produces

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

But, according to the cyclic relation, the last three terms are equal to  $-1$ . Then,

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

**12-21** It is to be shown how  $T$ ,  $\nu$ ,  $u$ ,  $a$ , and  $g$  could be evaluated from the thermodynamic function  $h = h(s, P)$ .

**Analysis** Forming the differential of the given expression for  $h$  produces

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

Solving the  $dh$  Gibbs equation gives

$$dh = Tds + \nu dP$$

Comparing the coefficient of these two expressions

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

$$\nu = \left( \frac{\partial h}{\partial P} \right)_s$$

both of which can be evaluated for a given  $P$  and  $s$ .

From the definition of the enthalpy,

$$u = h - P\nu = h - P \left( \frac{\partial h}{\partial P} \right)_s$$

Similarly, the definition of the Helmholtz function,

$$a = u - Ts = h - P \left( \frac{\partial h}{\partial P} \right)_s - s \left( \frac{\partial h}{\partial s} \right)_P$$

while the definition of the Gibbs function gives

$$g = h - Ts = h - s \left( \frac{\partial h}{\partial s} \right)_P$$

All of these can be evaluated for a given  $P$  and  $s$  and the fundamental  $h(s, P)$  equation.

## The Clapeyron Equation

**12-22C** It enables us to determine the enthalpy of vaporization from  $h_{fg}$  at a given temperature from the  $P$ ,  $v$ ,  $T$  data alone.

**12-23C** It is assumed that  $v_g \cong v_g \cong RT/P$ , and  $h_{fg} \cong$  constant for small temperature intervals.

**12-24** Using the Clapeyron equation, the enthalpy of vaporization of steam at a specified pressure is to be estimated and to be compared to the tabulated data.

**Analysis** From the Clapeyron equation,

$$\begin{aligned}
 h_{fg} &= T v_{fg} \left( \frac{dP}{dT} \right)_{\text{sat}} \\
 &\cong T (v_g - v_f)_{@300 \text{ kPa}} \left( \frac{\Delta P}{\Delta T} \right)_{\text{sat}, 300 \text{ kPa}} \\
 &= T_{\text{sat}@300 \text{ kPa}} (v_g - v_f)_{@300 \text{ kPa}} \left( \frac{(325 - 275) \text{ kPa}}{T_{\text{sat}@325 \text{ kPa}} - T_{\text{sat}@275 \text{ kPa}}} \right) \\
 &= (133.52 + 273.15 \text{ K})(0.60582 - 0.001073 \text{ m}^3/\text{kg}) \left( \frac{50 \text{ kPa}}{(136.27 - 130.58)^\circ\text{C}} \right) \\
 &= \mathbf{2159.9 \text{ kJ/kg}}
 \end{aligned}$$

The tabulated value of  $h_{fg}$  at 300 kPa is **2163.5 kJ/kg**.

**12-25** The  $h_{fg}$  and  $s_{fg}$  of steam at a specified temperature are to be calculated using the Clapeyron equation and to be compared to the tabulated data.

**Analysis** From the Clapeyron equation,

$$\begin{aligned}
 h_{fg} &= T \nu_{fg} \left( \frac{dP}{dT} \right)_{\text{sat}} \\
 &\cong T(\nu_g - \nu_f)_{@120^\circ\text{C}} \left( \frac{\Delta P}{\Delta T} \right)_{\text{sat}, 120^\circ\text{C}} \\
 &= T(\nu_g - \nu_f)_{@120^\circ\text{C}} \left( \frac{P_{\text{sat}@125^\circ\text{C}} - P_{\text{sat}@115^\circ\text{C}}}{125^\circ\text{C} - 115^\circ\text{C}} \right) \\
 &= (120 + 273.15 \text{ K})(0.89133 - 0.001060 \text{ m}^3/\text{kg}) \left( \frac{(232.23 - 169.18) \text{ kPa}}{10 \text{ K}} \right) \\
 &= \mathbf{2206.8 \text{ kJ/kg}}
 \end{aligned}$$

Also,

$$s_{fg} = \frac{h_{fg}}{T} = \frac{2206.8 \text{ kJ/kg}}{(120 + 273.15) \text{ K}} = \mathbf{5.6131 \text{ kJ/kg} \cdot \text{K}}$$

The tabulated values at  $120^\circ\text{C}$  are  $h_{fg} = \mathbf{2202.1 \text{ kJ/kg}}$  and  $s_{fg} = \mathbf{5.6013 \text{ kJ/kg} \cdot \text{K}}$ .

**12-26E** [Also solved by EES on enclosed CD] The  $h_{fg}$  of refrigerant-134a at a specified temperature is to be calculated using the Clapeyron equation and Clapeyron-Clausius equation and to be compared to the tabulated data.

**Analysis** (a) From the Clapeyron equation,

$$\begin{aligned}
 h_{fg} &= T \nu_{fg} \left( \frac{dP}{dT} \right)_{\text{sat}} \\
 &\cong T (\nu_g - \nu_f)_{@ 50^\circ\text{F}} \left( \frac{\Delta P}{\Delta T} \right)_{\text{sat}, 50^\circ\text{F}} \\
 &= T (\nu_g - \nu_f)_{@ 50^\circ\text{F}} \left( \frac{P_{\text{sat}@ 60^\circ\text{F}} - P_{\text{sat}@ 40^\circ\text{F}}}{60^\circ\text{F} - 40^\circ\text{F}} \right) \\
 &= (50 + 459.67 \text{ R})(0.79136 - 0.01270 \text{ ft}^3/\text{lbm}) \left( \frac{(72.152 - 49.776) \text{ psia}}{20 \text{ R}} \right) \\
 &= 444.0 \text{ psia} \cdot \text{ft}^3/\text{lbm} = \mathbf{82.16 \text{ Btu/lbm}} \quad (0.2\% \text{ error})
 \end{aligned}$$

since  $1 \text{ Btu} = 5.4039 \text{ psia} \cdot \text{ft}^3$ .

(b) From the Clapeyron-Clausius equation,

$$\begin{aligned}
 \ln \left( \frac{P_2}{P_1} \right)_{\text{sat}} &\cong \frac{h_{fg}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)_{\text{sat}} \\
 \ln \left( \frac{72.152 \text{ psia}}{49.776 \text{ psia}} \right) &\cong \frac{h_{fg}}{0.01946 \text{ Btu/lbm} \cdot \text{R}} \left( \frac{1}{40 + 459.67 \text{ R}} - \frac{1}{60 + 459.67 \text{ R}} \right) \\
 h_{fg} &= \mathbf{93.80 \text{ Btu/lbm}} \quad (14.4\% \text{ error})
 \end{aligned}$$

The tabulated value of  $h_{fg}$  at  $50^\circ\text{F}$  is **82.00 Btu/lbm**.

**12-27 EES** The enthalpy of vaporization of steam as a function of temperature using Clapeyron equation and steam data in EES is to be plotted.

**Analysis** The enthalpy of vaporization is determined using Clapeyron equation from

$$h_{fg, \text{Clapeyron}} = T \nu_{fg} \frac{\Delta P}{\Delta T}$$

At 100°C, for an increment of 5°C, we obtain

$$\begin{aligned} T_1 &= T - T_{\text{increment}} = 100 - 5 = 95^\circ\text{C} \\ T_2 &= T + T_{\text{increment}} = 100 + 5 = 105^\circ\text{C} \\ P_1 &= P_{\text{sat}@95^\circ\text{C}} = 84.61 \text{ kPa} \\ P_2 &= P_{\text{sat}@105^\circ\text{C}} = 120.90 \text{ kPa} \\ \Delta T &= T_2 - T_1 = 105 - 95 = 10^\circ\text{C} \\ \Delta P &= P_2 - P_1 = 120.90 - 84.61 = 36.29 \text{ kPa} \\ \nu_{f@100^\circ\text{C}} &= 0.001043 \text{ m}^3/\text{kg} \\ \nu_{g@100^\circ\text{C}} &= 1.6720 \text{ m}^3/\text{kg} \\ \nu_{fg} &= \nu_g - \nu_f = 1.6720 - 0.001043 = 1.6710 \text{ m}^3/\text{kg} \end{aligned}$$

Substituting,

$$h_{fg, \text{Clapeyron}} = T \nu_{fg} \frac{\Delta P}{\Delta T} = (100 + 273.15 \text{ K})(1.6710 \text{ m}^3/\text{kg}) \frac{36.29 \text{ kPa}}{10 \text{ K}} = \mathbf{2262.8 \text{ kJ/kg}}$$

The enthalpy of vaporization from steam table is

$$h_{fg@100^\circ\text{C}} = \mathbf{2256.4 \text{ m}^3/\text{kg}}$$

The percent error in using Clapeyron equation is

$$\text{PercentError} = \frac{2262.8 - 2256.4}{2256.4} \times 100 = \mathbf{0.28\%}$$

We repeat the analysis over the temperature range 10 to 200°C using EES. Below, the copy of EES solution is provided:

```
"Input Data:"
"T=100" "[C]"
T_increment = 5 "[C]"
T[2]=T+T_increment "[C]"
T[1]=T-T_increment "[C]"
P[1] = pressure(Steam_iapws,T=T[1],x=0) "[kPa]"
P[2] = pressure(Steam_iapws,T=T[2],x=0) "[kPa]"
DELTAP = P[2]-P[1] "[kPa]"
DELTAT = T[2]-T[1] "[C]"

v_f=volume(Steam_iapws,T=T,x=0) "[m^3/kg]"
v_g=volume(Steam_iapws,T=T,x=1) "[m^3/kg]"
h_f=enthalpy(Steam_iapws,T=T,x=0) "[kJ/kg]"
h_g=enthalpy(Steam_iapws,T=T,x=1) "[kJ/kg]"

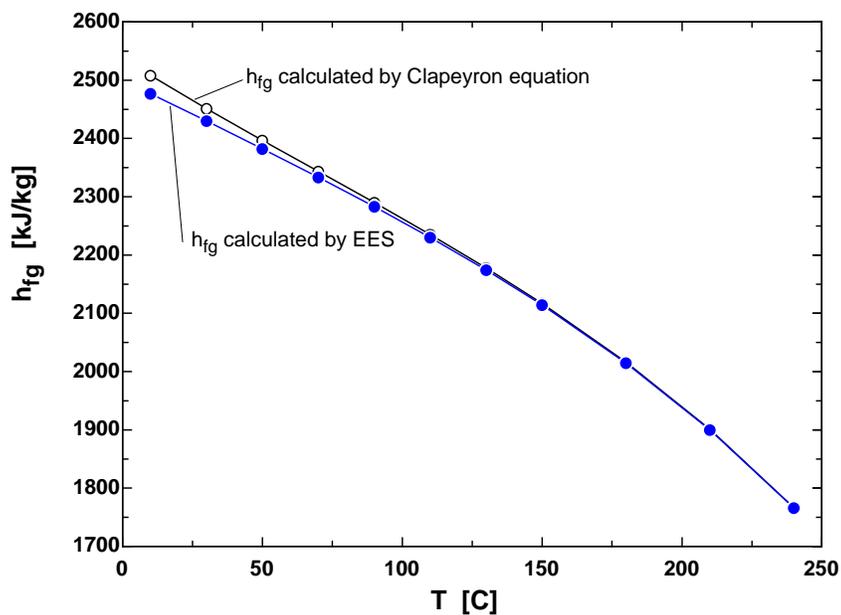
h_fg=h_g - h_f "[kJ/kg-K]"
v_fg=v_g - v_f "[m^3/kg]"
```

"The Clapeyron equation (Eq. 11-22) provides a means to calculate the enthalpy of vaporization,  $h_{fg}$  at a given temperature by determining the slope of the saturation curve on a P-T diagram and the specific volume of the saturated liquid and saturated vapor at the temperature."

$$h_{fg\_Clapeyron} = (T + 273.15) \cdot v_{fg} \cdot \Delta P / \Delta T \cdot \text{Convert}(m^3\text{-kPa}, kJ) \text{ [kJ/kg]}$$

$$\text{PercentError} = \text{ABS}(h_{fg\_Clapeyron} - h_{fg}) / h_{fg} \cdot 100 \text{ [%]}$$

$h_{fg}$ [kJ/kg]	$h_{fg, Clapeyron}$ [kJ/kg]	PercentError [%]	T [C]
2477.20	2508.09	1.247	10
2429.82	2451.09	0.8756	30
2381.95	2396.69	0.6188	50
2333.04	2343.47	0.4469	70
2282.51	2290.07	0.3311	90
2229.68	2235.25	0.25	110
2173.73	2177.86	0.1903	130
2113.77	2116.84	0.1454	150
2014.17	2016.15	0.09829	180
1899.67	1900.98	0.06915	210
1765.50	1766.38	0.05015	240



**12-28** A substance is heated in a piston-cylinder device until it turns from saturated liquid to saturated vapor at a constant pressure and temperature. The boiling temperature of this substance at a different pressure is to be estimated.

**Analysis** From the Clapeyron equation,

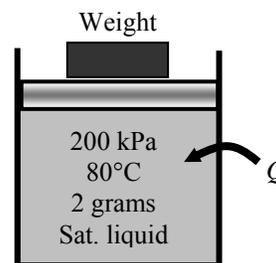
$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T v_{fg}} = \frac{(5 \text{ kPa} \cdot \text{m}^3)/(0.002 \text{ kg})}{(353 \text{ K})(1 \times 10^{-3} \text{ m}^3)/(0.002 \text{ kg})} = 14.16 \text{ kPa/K}$$

Using the finite difference approximation,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} \approx \left(\frac{P_2 - P_1}{T_2 - T_1}\right)_{\text{sat}}$$

Solving for  $T_2$ ,

$$T_2 = T_1 + \frac{P_2 - P_1}{dP/dT} = 353 \text{ K} + \frac{(180 - 200) \text{ kPa}}{14.16 \text{ kPa/K}} = \mathbf{351.6 \text{ K}}$$



**12-29** A substance is heated in a piston-cylinder device until it turns from saturated liquid to saturated vapor at a constant pressure and temperature. The saturation pressure of this substance at a different temperature is to be estimated.

**Analysis** From the Clapeyron equation,

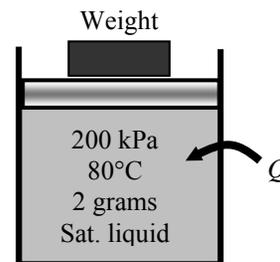
$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T v_{fg}} = \frac{(5 \text{ kPa} \cdot \text{m}^3)/(0.002 \text{ kg})}{(353 \text{ K})(1 \times 10^{-3} \text{ m}^3)/(0.002 \text{ kg})} = 14.16 \text{ kPa/K}$$

Using the finite difference approximation,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} \approx \left(\frac{P_2 - P_1}{T_2 - T_1}\right)_{\text{sat}}$$

Solving for  $P_2$ ,

$$P_2 = P_1 + \frac{dP}{dT}(T_2 - T_1) = 200 \text{ kPa} + (14.16 \text{ kPa/K})(373 - 353) \text{ K} = \mathbf{483.2 \text{ kPa}}$$



**12-30** A substance is heated in a piston-cylinder device until it turns from saturated liquid to saturated vapor at a constant pressure and temperature. The  $s_{fg}$  of this substance at a different temperature is to be estimated.

**Analysis** From the Clapeyron equation,

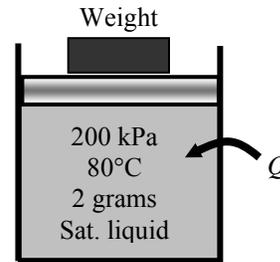
$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T\nu_{fg}} = \frac{s_{fg}}{\nu_{fg}}$$

Solving for  $s_{fg}$ ,

$$s_{fg} = \frac{h_{fg}}{T} = \frac{(5 \text{ kJ})/(0.002 \text{ kg})}{353 \text{ K}} = \mathbf{7.082 \text{ kJ/kg} \cdot \text{K}}$$

Alternatively,

$$s_{fg} = \left(\frac{dP}{dT}\right)_{\text{sat}} \nu_{fg} = (14.16 \text{ kPa/K}) \frac{1 \times 10^{-3} \text{ m}^3}{0.002 \text{ kg}} = 7.08 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K} = 7.08 \text{ kJ/kg} \cdot \text{K}$$



**12-31** It is to be shown that  $c_{p,g} - c_{p,f} = T \left( \frac{\partial(h_{fg}/T)}{\partial T} \right)_P + \nu_{fg} \left( \frac{\partial P}{\partial T} \right)_{\text{sat}}$ .

**Analysis** The definition of specific heat and Clapeyron equation are

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

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

According to the definition of the enthalpy of vaporization,

$$\frac{h_{fg}}{T} = \frac{h_g}{T} - \frac{h_f}{T}$$

Differentiating this expression gives

$$\begin{aligned} \left( \frac{\partial(h_{fg}/T)}{\partial T} \right)_P &= \left( \frac{\partial h_g/T}{\partial T} \right)_P - \left( \frac{\partial h_f/T}{\partial T} \right)_P \\ &= \frac{1}{T} \left( \frac{\partial h_g}{\partial T} \right)_P - \frac{h_g}{T^2} - \frac{1}{T} \left( \frac{\partial h_f}{\partial T} \right)_P + \frac{h_f}{T^2} \\ &= \frac{c_{p,g}}{T} - \frac{c_{p,f}}{T} - \frac{h_g - h_f}{T^2} \end{aligned}$$

Using Clausius-Clapeyron to replace the last term of this expression and solving for the specific heat difference gives

$$c_{p,g} - c_{p,f} = T \left( \frac{\partial(h_{fg}/T)}{\partial T} \right)_P + \nu_{fg} \left( \frac{\partial P}{\partial T} \right)_{\text{sat}}$$

**12-32E** A table of properties for methyl chloride is given. The saturation pressure is to be estimated at two different temperatures.

**Analysis** The Clapeyron equation is

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

Using the finite difference approximation,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} \approx \left(\frac{P_2 - P_1}{T_2 - T_1}\right)_{\text{sat}} = \frac{h_{fg}}{T\nu_{fg}}$$

Solving this for the second pressure gives for  $T_2 = 110^\circ\text{F}$

$$\begin{aligned} P_2 &= P_1 + \frac{h_{fg}}{T\nu_{fg}}(T_2 - T_1) \\ &= 116.7 \text{ psia} + \frac{154.85 \text{ Btu/lbm}}{(560 \text{ R})(0.86332 \text{ ft}^3/\text{lbm})} \left( \frac{5.404 \text{ psia} \cdot \text{ft}^3}{1 \text{ Btu}} \right) (110 - 100) \text{ R} \\ &= \mathbf{134.0 \text{ psia}} \end{aligned}$$

When  $T_2 = 90^\circ\text{F}$

$$\begin{aligned} P_2 &= P_1 + \frac{h_{fg}}{T\nu_{fg}}(T_2 - T_1) \\ &= 116.7 \text{ psia} + \frac{154.85 \text{ Btu/lbm}}{(560 \text{ R})(0.86332 \text{ ft}^3/\text{lbm})} \left( \frac{5.404 \text{ psia} \cdot \text{ft}^3}{1 \text{ Btu}} \right) (90 - 100) \text{ R} \\ &= \mathbf{99.4 \text{ psia}} \end{aligned}$$

**12-33** Saturation properties for R-134a at a specified temperature are given. The saturation pressure is to be estimated at two different temperatures.

**Analysis** From the Clapeyron equation,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T v_{fg}} = \frac{225.86 \text{ kPa} \cdot \text{m}^3/\text{kg}}{(233 \text{ K})(0.36010 \text{ m}^3/\text{kg})} = 2.692 \text{ kPa/K}$$

Using the finite difference approximation,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} \approx \left(\frac{P_2 - P_1}{T_2 - T_1}\right)_{\text{sat}}$$

Solving for  $P_2$  at  $-50^\circ\text{C}$

$$P_2 = P_1 + \frac{dP}{dT}(T_2 - T_1) = 51.25 \text{ kPa} + (2.692 \text{ kPa/K})(223 - 233)\text{K} = \mathbf{24.33 \text{ kPa}}$$

Solving for  $P_2$  at  $-30^\circ\text{C}$

$$P_2 = P_1 + \frac{dP}{dT}(T_2 - T_1) = 51.25 \text{ kPa} + (2.692 \text{ kPa/K})(243 - 233)\text{K} = \mathbf{78.17 \text{ kPa}}$$

**General Relations for du, dh, ds, c<sub>v</sub>, and c<sub>p</sub>**

**12-34C** Yes, through the relation

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

**12-35** General expressions for  $\Delta u$ ,  $\Delta h$ , and  $\Delta s$  for a gas whose equation of state is  $P(\nu - a) = RT$  for an isothermal process are to be derived.

**Analysis (a)** A relation for  $\Delta u$  is obtained from the general relation

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

The equation of state for the specified gas can be expressed as

$$P = \frac{RT}{\nu - a} \longrightarrow \left( \frac{\partial P}{\partial T} \right)_\nu = \frac{R}{\nu - a}$$

Thus,

$$T \left( \frac{\partial P}{\partial T} \right)_\nu - P = \frac{RT}{\nu - a} - P = P - P = 0$$

Substituting, 
$$\Delta u = \int_{T_1}^{T_2} c_\nu dT$$

(b) A relation for  $\Delta h$  is obtained from the general relation

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

The equation of state for the specified gas can be expressed as

$$\nu = \frac{RT}{P} + a \longrightarrow \left( \frac{\partial \nu}{\partial T} \right)_P = \frac{R}{P}$$

Thus,

$$\nu - T \left( \frac{\partial \nu}{\partial T} \right)_P = \nu - T \frac{R}{P} = \nu - (\nu - a) = a$$

Substituting,

$$\Delta h = \int_{T_1}^{T_2} c_p dT + \int_{P_1}^{P_2} a dP = \int_{T_1}^{T_2} c_p dT + a(P_2 - P_1)$$

(c) A relation for  $\Delta s$  is obtained from the general relation

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

Substituting  $(\partial \nu / \partial T)_P = R/T$ ,

$$\Delta s = \int_{T_1}^{T_2} \frac{c_p}{T} dT - \int_{P_1}^{P_2} \left( \frac{R}{P} \right)_P dP = \int_{T_1}^{T_2} \frac{c_p}{T} dT - R \ln \frac{P_2}{P_1}$$

For an isothermal process  $dT = 0$  and these relations reduce to

$$\Delta u = 0, \quad \Delta h = a(P_2 - P_1), \quad \text{and} \quad \Delta s = -R \ln \frac{P_2}{P_1}$$

**12-36** General expressions for  $(\partial u/\partial P)_T$  and  $(\partial h/\partial \nu)_T$  in terms of  $P$ ,  $\nu$ , and  $T$  only are to be derived.

**Analysis** The general relation for  $du$  is

$$du = c_\nu dT + \left( T \left( \frac{\partial P}{\partial T} \right)_\nu - P \right) d\nu$$

Differentiating each term in this equation with respect to  $P$  at  $T = \text{constant}$  yields

$$\left( \frac{\partial u}{\partial P} \right)_T = 0 + \left( T \left( \frac{\partial P}{\partial T} \right)_\nu - P \right) \left( \frac{\partial \nu}{\partial P} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_\nu \left( \frac{\partial \nu}{\partial P} \right)_T - P \left( \frac{\partial \nu}{\partial P} \right)_T$$

Using the properties  $P$ ,  $T$ ,  $\nu$ , the cyclic relation can be expressed as

$$\left( \frac{\partial P}{\partial T} \right)_\nu \left( \frac{\partial T}{\partial \nu} \right)_P \left( \frac{\partial \nu}{\partial P} \right)_T = -1 \longrightarrow \left( \frac{\partial P}{\partial T} \right)_\nu \left( \frac{\partial \nu}{\partial P} \right)_T = - \left( \frac{\partial \nu}{\partial T} \right)_P$$

Substituting, we get

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

The general relation for  $dh$  is

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

Differentiating each term in this equation with respect to  $\nu$  at  $T = \text{constant}$  yields

$$\left( \frac{\partial h}{\partial \nu} \right)_T = 0 + \left( \nu - T \left( \frac{\partial \nu}{\partial T} \right)_P \right) \left( \frac{\partial P}{\partial \nu} \right)_T = \nu \left( \frac{\partial P}{\partial \nu} \right)_T - T \left( \frac{\partial \nu}{\partial T} \right)_P \left( \frac{\partial P}{\partial \nu} \right)_T$$

Using the properties  $\nu$ ,  $T$ ,  $P$ , the cyclic relation can be expressed as

$$\left( \frac{\partial \nu}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_\nu \left( \frac{\partial P}{\partial \nu} \right)_T = -1 \longrightarrow \left( \frac{\partial \nu}{\partial T} \right)_P \left( \frac{\partial P}{\partial \nu} \right)_T = - \left( \frac{\partial T}{\partial P} \right)_\nu$$

Substituting, we get

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

**12-37E** The specific heat difference  $c_p - c_v$  for liquid water at 1000 psia and 150°F is to be estimated.

**Analysis** The specific heat difference  $c_p - c_v$  is given as

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

Approximating differentials by differences about the specified state,

$$\begin{aligned} c_p - c_v &\cong -T \left( \frac{\Delta v}{\Delta T} \right)_{P=1000 \text{ psia}} \left( \frac{\Delta P}{\Delta v} \right)_{T=150^\circ \text{F}} \\ &= -(150 + 459.67 \text{ R}) \left( \frac{v_{175^\circ \text{F}} - v_{125^\circ \text{F}}}{(175 - 125)^\circ \text{F}} \right)_{P=1000 \text{ psia}} \left( \frac{(1500 - 500) \text{ psia}}{v_{1500 \text{ psia}} - v_{500 \text{ psia}}} \right)_{T=150^\circ \text{F}} \\ &= -(609.67 \text{ R}) \left( \frac{(0.016427 - 0.016177) \text{ ft}^3/\text{lbm}}{50 \text{ R}} \right)^2 \left( \frac{1000 \text{ psia}}{(0.016267 - 0.016317) \text{ ft}^3/\text{lbm}} \right) \\ &= 0.3081 \text{ psia} \cdot \text{ft}^3/\text{lbm} \cdot \text{R} \\ &= \mathbf{0.0570 \text{ Btu/lbm} \cdot \text{R}} \quad (1 \text{ Btu} = 5.4039 \text{ psia} \cdot \text{ft}^3) \end{aligned}$$

**12-38** The volume expansivity  $\beta$  and the isothermal compressibility  $\alpha$  of refrigerant-134a at 200 kPa and 30°C are to be estimated.

**Analysis** The volume expansivity and isothermal compressibility are expressed as

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

Approximating differentials by differences about the specified state,

$$\begin{aligned} \beta &\cong \frac{1}{v} \left( \frac{\Delta v}{\Delta T} \right)_{P=200 \text{ kPa}} = \frac{1}{v} \left( \frac{v_{40^\circ \text{C}} - v_{20^\circ \text{C}}}{(40 - 20)^\circ \text{C}} \right)_{P=200 \text{ kPa}} \\ &= \frac{1}{0.11874 \text{ m}^3/\text{kg}} \left( \frac{(0.12322 - 0.11418) \text{ m}^3/\text{kg}}{20 \text{ K}} \right) \\ &= \mathbf{0.00381 \text{ K}^{-1}} \end{aligned}$$

and

$$\begin{aligned} \alpha &\cong -\frac{1}{v} \left( \frac{\Delta v}{\Delta P} \right)_{T=30^\circ \text{C}} = -\frac{1}{v} \left( \frac{v_{240 \text{ kPa}} - v_{180 \text{ kPa}}}{(240 - 180) \text{ kPa}} \right)_{T=30^\circ \text{C}} \\ &= -\frac{1}{0.11874 \text{ m}^3/\text{kg}} \left( \frac{(0.09812 - 0.13248) \text{ m}^3/\text{kg}}{60 \text{ kPa}} \right) \\ &= \mathbf{0.00482 \text{ kPa}^{-1}} \end{aligned}$$

**12-39** It is to be shown that  $c_p - c_v = T \left( \frac{\partial P}{\partial T} \right)_v \left( \frac{\partial v}{\partial T} \right)_p$ .

**Analysis** We begin by taking the entropy to be a function of specific volume and temperature. The differential of the entropy is then

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

Substituting  $\left( \frac{\partial s}{\partial T} \right)_v = \frac{c_v}{T}$  from Eq. 12-28 and the third Maxwell equation changes this to

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

Taking the entropy to be a function of pressure and temperature,

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

Combining this result with  $\left( \frac{\partial s}{\partial T} \right)_P = \frac{c_p}{T}$  from Eq. 12-34 and the fourth Maxwell equation produces

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

Equating the two previous  $ds$  expressions and solving the result for the specific heat difference,

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

Taking the pressure to be a function of temperature and volume,

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

When this is substituted into the previous expression, the result is

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

According to the cyclic relation, the term in the bracket is zero. Then, canceling the common  $dT$  term,

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

**12-40** It is to be proven that the definition for temperature  $T = (\partial u / \partial s)_v$  reduces the net entropy change of two constant-volume systems filled with simple compressible substances to zero as the two systems approach thermal equilibrium.

**Analysis** The two constant-volume systems form an isolated system shown here

For the isolated system

$$dS_{\text{tot}} = dS_A + dS_B \geq 0$$

Assume  $S = S(u, v)$

Then,

$$ds = \left( \frac{\partial s}{\partial u} \right)_v du + \left( \frac{\partial s}{\partial v} \right)_u dv$$

Since  $v = \text{const.}$  and  $dv = 0$ ,

$$ds = \left( \frac{\partial s}{\partial u} \right)_v du$$

and from the definition of temperature from the problem statement,

$$\frac{du}{(\partial u / \partial s)_v} = \frac{du}{T}$$

Then,

$$dS_{\text{tot}} = m_A \frac{du_A}{T_A} + m_B \frac{du_B}{T_B}$$

The first law applied to the isolated system yields

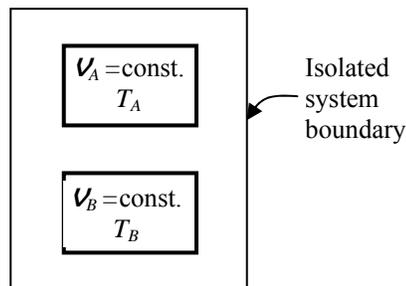
$$\begin{aligned} E_{\text{in}} - E_{\text{out}} &= dU \\ 0 &= dU \longrightarrow m_A du_A + m_B du_B = 0 \longrightarrow m_B du_B = -m_A du_A \end{aligned}$$

Now, the entropy change may be expressed as

$$dS_{\text{tot}} = m_A du_A \left( \frac{1}{T_A} - \frac{1}{T_B} \right) = m_A du_A \left( \frac{T_B - T_A}{T_A T_B} \right)$$

As the two systems approach thermal equilibrium,

$$\begin{aligned} \lim dS_{\text{tot}} &= 0 \\ T_A &\rightarrow T_B \end{aligned}$$



**12-41** The internal energy change of air between two specified states is to be compared for two equations of states.

**Assumptions** Constant specific heats for air can be used.

**Properties** For air at the average temperature  $(20+300)/2=160^\circ\text{C}=433\text{ K}$ ,  $c_v = 0.731\text{ kJ/kg}\cdot\text{K}$  (Table A-2b).

**Analysis** Solving the equation of state for  $P$  gives

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

Then,

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

Using equation 12-29,

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

Substituting,

$$\begin{aligned} du &= c_v dT + \left( \frac{RT}{v - a} - \frac{RT}{v - a} \right) dv \\ &= c_v dT \end{aligned}$$

Integrating this result between the two states with constant specific heats gives

$$u_2 - u_1 = c_v (T_2 - T_1) = (0.731\text{ kJ/kg}\cdot\text{K})(300 - 20)\text{K} = \mathbf{205\text{ kJ/kg}}$$

The ideal gas model for the air gives

$$du = c_v dT$$

which gives the same answer.

**12-42** The enthalpy change of air between two specified states is to be compared for two equations of states.

**Assumptions** Constant specific heats for air can be used.

**Properties** For air at the average temperature  $(20+300)/2=160^\circ\text{C}=433\text{ K}$ ,  $c_p = 1.018\text{ kJ/kg}\cdot\text{K}$  (Table A-2b).

**Analysis** Solving the equation of state for  $\nu$  gives

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

Then,

$$\left(\frac{\partial \nu}{\partial T}\right)_P = \frac{R}{P}$$

Using equation 12-35,

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

Substituting,

$$\begin{aligned} dh &= c_p dT + \left( \frac{RT}{P} + a - \frac{RT}{P} \right) dP \\ &= c_p dT + a dP \end{aligned}$$

Integrating this result between the two states with constant specific heats gives

$$\begin{aligned} h_2 - h_1 &= c_p (T_2 - T_1) + a(P_2 - P_1) \\ &= (1.018\text{ kJ/kg}\cdot\text{K})(300 - 20)\text{K} + (0.10\text{ m}^3/\text{kg})(600 - 100)\text{kPa} \\ &= \mathbf{335.0\text{ kJ/kg}} \end{aligned}$$

For an ideal gas,

$$dh = c_p dT$$

which when integrated gives

$$h_2 - h_1 = c_p (T_2 - T_1) = (1.018\text{ kJ/kg}\cdot\text{K})(300 - 20)\text{K} = \mathbf{285.0\text{ kJ/kg}}$$

**12-43** The entropy change of air between two specified states is to be compared for two equations of states.

**Assumptions** Constant specific heats for air can be used.

**Properties** For air at the average temperature  $(20+300)/2=160^\circ\text{C}=433\text{ K}$ ,  $c_p = 1.018\text{ kJ/kg}\cdot\text{K}$  (Table A-2b) and  $R = 0.287\text{ kJ/kg}\cdot\text{K}$  (Table A-1).

**Analysis** Solving the equation of state for  $\nu$  gives

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

Then,

$$\left(\frac{\partial \nu}{\partial T}\right)_P = \frac{R}{P}$$

The entropy differential is

$$\begin{aligned} ds &= c_p \frac{dT}{T} - \left(\frac{\partial \nu}{\partial T}\right)_P dP \\ &= c_p \frac{dT}{T} - R \frac{dP}{P} \end{aligned}$$

which is the same as that of an ideal gas. Integrating this result between the two states with constant specific heats gives

$$\begin{aligned} s_2 - s_1 &= c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\ &= (1.018\text{ kJ/kg}\cdot\text{K}) \ln \frac{573\text{ K}}{293\text{ K}} - (0.287\text{ kJ/kg}\cdot\text{K}) \ln \frac{600\text{ kPa}}{100\text{ kPa}} \\ &= \mathbf{0.1686\text{ kJ/kg}\cdot\text{K}} \end{aligned}$$

**12-44** The internal energy change of helium between two specified states is to be compared for two equations of states.

**Properties** For helium,  $c_v = 3.1156 \text{ kJ/kg}\cdot\text{K}$  (Table A-2a).

**Analysis** Solving the equation of state for  $P$  gives

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

Then,

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

Using equation 12-29,

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

Substituting,

$$\begin{aligned} du &= c_\nu dT + \left( \frac{RT}{\nu - a} - \frac{RT}{\nu - a} \right) d\nu \\ &= c_\nu dT \end{aligned}$$

Integrating this result between the two states gives

$$u_2 - u_1 = c_\nu (T_2 - T_1) = (3.1156 \text{ kJ/kg}\cdot\text{K})(300 - 20)\text{K} = \mathbf{872.4 \text{ kJ/kg}}$$

The ideal gas model for the helium gives

$$du = c_\nu dT$$

which gives the same answer.

**12-45** The enthalpy change of helium between two specified states is to be compared for two equations of states.

**Properties** For helium,  $c_p = 5.1926 \text{ kJ/kg}\cdot\text{K}$  (Table A-2a).

**Analysis** Solving the equation of state for  $\nu$  gives

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

Then,

$$\left(\frac{\partial \nu}{\partial T}\right)_P = \frac{R}{P}$$

Using equation 12-35,

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

Substituting,

$$\begin{aligned} dh &= c_p dT + \left( \frac{RT}{P} + a - \frac{RT}{P} \right) dP \\ &= c_p dT + a dP \end{aligned}$$

Integrating this result between the two states gives

$$\begin{aligned} h_2 - h_1 &= c_p (T_2 - T_1) + a(P_2 - P_1) \\ &= (5.1926 \text{ kJ/kg}\cdot\text{K})(300 - 20)\text{K} + (0.10 \text{ m}^3/\text{kg})(600 - 100)\text{kPa} \\ &= \mathbf{1504 \text{ kJ/kg}} \end{aligned}$$

For an ideal gas,

$$dh = c_p dT$$

which when integrated gives

$$h_2 - h_1 = c_p (T_2 - T_1) = (5.1926 \text{ kJ/kg}\cdot\text{K})(300 - 20)\text{K} = \mathbf{1454 \text{ kJ/kg}}$$

**12-46** The entropy change of helium between two specified states is to be compared for two equations of states.

**Properties** For helium,  $c_p = 5.1926 \text{ kJ/kg}\cdot\text{K}$  and  $R = 2.0769 \text{ kJ/kg}\cdot\text{K}$  (Table A-2a).

**Analysis** Solving the equation of state for  $\nu$  gives

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

Then,

$$\left(\frac{\partial \nu}{\partial T}\right)_P = \frac{R}{P}$$

The entropy differential is

$$\begin{aligned} ds &= c_p \frac{dT}{T} - \left(\frac{\partial \nu}{\partial T}\right)_P dP \\ &= c_p \frac{dT}{T} - R \frac{dP}{P} \end{aligned}$$

which is the same as that of an ideal gas. Integrating this result between the two states gives

$$\begin{aligned} s_2 - s_1 &= c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \\ &= (5.1926 \text{ kJ/kg}\cdot\text{K}) \ln \frac{573 \text{ K}}{293 \text{ K}} - (2.0769 \text{ kJ/kg}\cdot\text{K}) \ln \frac{600 \text{ kPa}}{100 \text{ kPa}} \\ &= \mathbf{-0.2386 \text{ kJ/kg}\cdot\text{K}} \end{aligned}$$

**12-47** An expression for the volume expansivity of a substance whose equation of state is  $P(\nu - a) = RT$  is to be derived.

**Analysis** Solving the equation of state for  $\nu$  gives

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

The specific volume derivative is then

$$\left(\frac{\partial \nu}{\partial T}\right)_P = \frac{R}{P}$$

The definition for volume expansivity is

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

Combining these two equations gives

$$\beta = \frac{R}{RT + aP}$$

**12-48** The Helmholtz function of a substance has the form  $a = -RT \ln \frac{\nu}{\nu_0} - cT_0 \left( 1 - \frac{T}{T_0} + \frac{T}{T_0} \ln \frac{T}{T_0} \right)$ . It is to be shown how to obtain  $P$ ,  $h$ ,  $s$ ,  $c_\nu$  and  $c_p$  from this expression.

**Analysis** Taking the Helmholtz function to be a function of temperature and specific volume yields

$$da = \left( \frac{\partial a}{\partial T} \right)_\nu dT + \left( \frac{\partial a}{\partial \nu} \right)_T d\nu$$

while the applicable Helmholtz equation is

$$da = -Pd\nu - sdT$$

Equating the coefficients of the two results produces

$$P = - \left( \frac{\partial a}{\partial \nu} \right)_T$$

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

Taking the indicated partial derivatives of the Helmholtz function given in the problem statement reduces these expressions to

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

$$s = R \ln \frac{\nu}{\nu_0} + c \ln \frac{T}{T_0}$$

The definition of the enthalpy ( $h = u + P\nu$ ) and Helmholtz function ( $a = u - Ts$ ) may be combined to give

$$\begin{aligned} h &= u + P\nu \\ &= a + Ts + P\nu \\ &= a - T \left( \frac{\partial a}{\partial T} \right)_\nu - \nu \left( \frac{\partial a}{\partial \nu} \right)_T \\ &= -RT \ln \frac{\nu}{\nu_0} - cT_0 \left( 1 - \frac{T}{T_0} + \frac{T}{T_0} \ln \frac{T}{T_0} \right) + RT \ln \frac{\nu}{\nu_0} - cT \ln \frac{T}{T_0} + RT \\ &= cT_0 + cT + RT \end{aligned}$$

According to  $\left( \frac{\partial s}{\partial T} \right)_\nu = \frac{c_\nu}{T}$  given in the text (Eq. 12-28),

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

The preceding expression for the temperature indicates that the equation of state for the substance is the same as that of an ideal gas. Then,

$$c_p = R + c_\nu = R + c$$

**12-49** An expression for the volume expansivity of a substance whose equation of state

is  $P = \frac{RT}{\nu - b} - \frac{a}{\nu(\nu + b)T^{1/2}}$  is to be derived.

**Analysis** The definition for volume expansivity is

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

According to the cyclic relation,

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

which on rearrangement becomes

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

Proceeding to perform the differentiations gives

$$\left( \frac{\partial P}{\partial T} \right)_\nu = \frac{R}{\nu - b} + \frac{a}{2\nu(\nu + b)T^{3/2}}$$

and

$$\begin{aligned} \left( \frac{\partial P}{\partial \nu} \right)_T &= -\frac{RT}{(\nu - b)^2} + \frac{a}{bT^{1/2}} \left[ \frac{1}{\nu^2} - \frac{1}{(\nu + b)^2} \right] \\ &= -\frac{RT}{(\nu - b)^2} + \frac{a}{T^{1/2}} \frac{2\nu + b}{\nu^2(\nu + b)^2} \end{aligned}$$

Substituting these results into the definition of the volume expansivity produces

$$\beta = -\frac{1}{\nu} \frac{\frac{R}{\nu - b} + \frac{a}{2\nu(\nu + b)T^{3/2}}}{-\frac{RT}{(\nu - b)^2} + \frac{a}{T^{1/2}} \frac{2\nu + b}{\nu^2(\nu + b)^2}}$$

**12-50** An expression for the specific heat difference of a substance whose equation of state

is  $P = \frac{RT}{v-b} - \frac{a}{v(v+b)T^{1/2}}$  is to be derived.

**Analysis** The specific heat difference is expressed by

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

According to the cyclic relation,

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

which on rearrangement becomes

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

Substituting this result into the expression for the specific heat difference gives

$$c_p - c_v = -T \left( \frac{\partial P}{\partial T} \right)_v^2 \left( \frac{\partial P}{\partial v} \right)_T^{-1}$$

The appropriate partial derivatives of the equation of state are

$$\begin{aligned} \left( \frac{\partial P}{\partial T} \right)_v &= \frac{R}{v-b} + \frac{a/2}{v(v+b)T^{3/2}} \\ \left( \frac{\partial P}{\partial v} \right)_T &= -\frac{RT}{(v-b)^2} + \frac{a}{bT^{1/2}} \left[ \frac{1}{v^2} - \frac{1}{(v+b)^2} \right] \\ &= -\frac{RT}{(v-b)^2} + \frac{a}{T^{1/2}} \frac{2v+b}{v^2(v+b)^2} \end{aligned}$$

The difference in the specific heats is then

$$c_p - c_v = \frac{-T \left[ \frac{R}{v-b} + \frac{a/2}{v(v+b)T^{3/2}} \right]^2}{-\frac{RT}{(v-b)^2} + \frac{a}{T^{1/2}} \frac{2v+b}{v^2(v+b)^2}}$$

**12-51** An expression for the volume expansivity of a substance whose equation of state is  $P = \frac{RT}{v-b} - \frac{a}{v^2T}$  is to be derived.

**Analysis** The definition for volume expansivity is

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

According to the cyclic relation,

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

which on rearrangement becomes

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

Proceeding to perform the differentiations gives

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

and

$$\left( \frac{\partial P}{\partial v} \right)_T = - \frac{RT}{(v-b)^2} + \frac{2a}{v^3T}$$

Substituting these results into the definition of the volume expansivity produces

$$\beta = - \frac{1}{v} \frac{\frac{R}{v-b} + \frac{a}{v^2T^2}}{\frac{-RT}{(v-b)^2} + \frac{2a}{v^3T}}$$

**12-52** An expression for the isothermal compressibility of a substance whose equation of state

is  $P = \frac{RT}{v-b} - \frac{a}{v^2T}$  is to be derived.

**Analysis** The definition for the isothermal compressibility is

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

Now,

$$\left( \frac{\partial P}{\partial v} \right)_T = \frac{-RT}{(v-b)^2} + \frac{2a}{v^3T}$$

Using the partial derivative properties,

$$\alpha = -\frac{1}{v \left( \frac{\partial P}{\partial v} \right)_T} = -\frac{1}{\frac{-RTv}{(v-b)^2} + \frac{2a}{v^2T}}$$

**12-53** It is to be shown that  $\beta = \alpha \left( \frac{\partial P}{\partial T} \right)_v$ .

**Analysis** The definition for the volume expansivity is

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

The definition for the isothermal compressibility is

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

According to the cyclic relation,

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

which on rearrangement becomes

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

When this is substituted into the definition of the volume expansivity, the result is

$$\begin{aligned} \beta &= -\frac{1}{v} \left( \frac{\partial v}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_v \\ &= -\alpha \left( \frac{\partial P}{\partial T} \right)_v \end{aligned}$$

**12-54** It is to be demonstrated that  $k = \frac{c_p}{c_v} = -\frac{\nu\alpha}{(\partial\nu/\partial P)_s}$ .

**Analysis** The relations for entropy differential are

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

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

For fixed  $s$ , these basic equations reduce to

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

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

Also, when  $s$  is fixed,

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

Forming the specific heat ratio from these expressions gives

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

The cyclic relation is

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

Solving this for the numerator of the specific heat ratio expression and substituting the result into this numerator produces

$$k = \frac{\left(\frac{\partial \nu}{\partial P}\right)_T}{\left(\frac{\partial \nu}{\partial P}\right)_s} = -\frac{\nu\alpha}{\left(\frac{\partial \nu}{\partial P}\right)_s}$$

**12-55** An expression for the specific heat difference of a substance whose equation of state is  $P = \frac{RT}{\nu - b} - \frac{a}{\nu^2 T}$  is to be derived.

**Analysis** The specific heat difference is expressed by

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

According to the cyclic relation,

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

which on rearrangement becomes

$$\left( \frac{\partial \nu}{\partial T} \right)_P = - \left( \frac{\partial P}{\partial T} \right)_\nu \left( \frac{\partial P}{\partial \nu} \right)_T^{-1}$$

Substituting this result into the expression for the specific heat difference gives

$$c_p - c_\nu = -T \left( \frac{\partial P}{\partial T} \right)_\nu^2 \left( \frac{\partial P}{\partial \nu} \right)_T^{-1}$$

The appropriate partial derivatives of the equation of state are

$$\left( \frac{\partial P}{\partial T} \right)_\nu = \frac{R}{\nu - b} + \frac{a}{\nu^2 T^2}$$

$$\left( \frac{\partial P}{\partial \nu} \right)_T = - \frac{RT}{(\nu - b)^2} + \frac{2a}{\nu^3 T}$$

The difference in the specific heats is then

$$c_p - c_\nu = -T \frac{\left[ \frac{R}{\nu - b} + \frac{a}{\nu^2 T^2} \right]^2}{-\frac{RT}{(\nu - b)^2} + \frac{2a}{\nu^3 T}}$$

### The Joule-Thomson Coefficient

**12-56C** It represents the variation of temperature with pressure during a throttling process.

**12-57C** The line that passes through the peak points of the constant enthalpy lines on a  $T$ - $P$  diagram is called the inversion line. The maximum inversion temperature is the highest temperature a fluid can be cooled by throttling.

**12-58C** No. The temperature may even increase as a result of throttling.

**12-59C** Yes.

**12-60C** No. Helium is an ideal gas and  $h = h(T)$  for ideal gases. Therefore, the temperature of an ideal gas remains constant during a throttling ( $h = \text{constant}$ ) process.

**12-61E** [Also solved by EES on enclosed CD] The Joule-Thomson coefficient of nitrogen at two states is to be estimated.

**Analysis** (a) The enthalpy of nitrogen at 200 psia and 500 R is, from EES,  $h = -10.564$  Btu/lbm. Note that in EES, by default, the reference state for specific enthalpy and entropy is 0 at 25°C (77°F) and 1 atm. Approximating differentials by differences about the specified state, the Joule-Thomson coefficient is expressed as

$$\mu = \left( \frac{\partial T}{\partial P} \right)_h \cong \left( \frac{\Delta T}{\Delta P} \right)_{h=-10.564 \text{ Btu/lbm}}$$

Considering a throttling process from 210 psia to 190 psia at  $h = -10.564$  Btu/lbm, the Joule-Thomson coefficient is determined to be

$$\mu = \left( \frac{T_{190 \text{ psia}} - T_{210 \text{ psia}}}{(190 - 210) \text{ psia}} \right)_{h=-10.564 \text{ Btu/lbm}} = \frac{(499.703 - 500.296) \text{ R}}{(190 - 210) \text{ psia}} = \mathbf{0.0297 \text{ R/psia}}$$

(b) The enthalpy of nitrogen at 2000 psia and 400 R is, from EES,  $h = -55.321$  Btu/lbm. Approximating differentials by differences about the specified state, the Joule-Thomson coefficient is expressed as

$$\mu = \left( \frac{\partial T}{\partial P} \right)_h \cong \left( \frac{\Delta T}{\Delta P} \right)_{h=-55.321 \text{ Btu/lbm}}$$

Considering a throttling process from 2010 psia to 1990 psia at  $h = -55.321$  Btu/lbm, the Joule-Thomson coefficient is determined to be

$$\mu = \left( \frac{T_{1999 \text{ psia}} - T_{2001 \text{ psia}}}{(1990 - 2010) \text{ psia}} \right)_{h=-55.321 \text{ Btu/lbm}} = \frac{(399.786 - 400.213) \text{ R}}{(1990 - 2010) \text{ psia}} = \mathbf{0.0213 \text{ R/psia}}$$

**12-62E EES** Problem 12-61E is reconsidered. The Joule-Thompson coefficient for nitrogen over the pressure range 100 to 1500 psia at the enthalpy values 100, 175, and 225 Btu/lbm is to be plotted.

**Analysis** The problem is solved using EES, and the results are tabulated and plotted below.

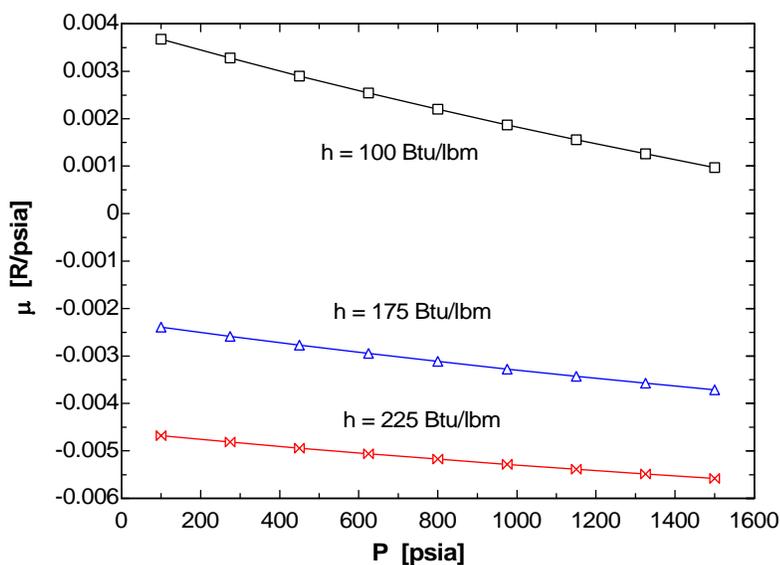
```

Gas$ = 'Nitrogen'
{P_ref=200 [psia]
T_ref=500 [R]
P= P_ref}
h=50 [Btu/lbm]
{h=enthalpy(Gas$, T=T_ref, P=P_ref)}
dP = 10 [psia]
T = temperature(Gas$, P=P, h=h)
P[1] = P + dP
P[2] = P - dP
T[1] = temperature(Gas$, P=P[1], h=h)
T[2] = temperature(Gas$, P=P[2], h=h)
Mu = DELTAT/DELTAP "Approximate the differential by differences about the state at h=const."
DELTAT=T[2]-T[1]
DELTAP=P[2]-P[1]

```

**h = 100 Btu/lbm**

P [psia]	$\mu$ [R/psia]
100	0.003675
275	0.003277
450	0.002899
625	0.00254
800	0.002198
975	0.001871
1150	0.001558
1325	0.001258
1500	0.0009699



**12-63** The Joule-Thomson coefficient of refrigerant-134a at a specified state is to be estimated.

**Analysis** The enthalpy of refrigerant-134a at 0.7 MPa and  $T = 50^\circ\text{C}$  is  $h = 288.53$  kJ/kg. Approximating differentials by differences about the specified state, the Joule-Thomson coefficient is expressed as

$$\mu = \left( \frac{\partial T}{\partial P} \right)_h \cong \left( \frac{\Delta T}{\Delta P} \right)_{h=288.53 \text{ kJ/kg}}$$

Considering a throttling process from 0.8 MPa to 0.6 MPa at  $h = 288.53$  kJ/kg, the Joule-Thomson coefficient is determined to be

$$\mu = \left( \frac{T_{0.8 \text{ MPa}} - T_{0.6 \text{ MPa}}}{(0.8 - 0.6) \text{ MPa}} \right)_{h=288.53 \text{ kJ/kg}} = \frac{(51.81 - 48.19)^\circ\text{C}}{(0.8 - 0.6) \text{ MPa}} = \mathbf{18.1^\circ\text{C/MPa}}$$

**12-64** Steam is throttled slightly from 1 MPa and  $300^\circ\text{C}$ . It is to be determined if the temperature of the steam will increase, decrease, or remain the same during this process.

**Analysis** The enthalpy of steam at 1 MPa and  $T = 300^\circ\text{C}$  is  $h = 3051.6$  kJ/kg. Now consider a throttling process from this state to 0.8 MPa, which is the next lowest pressure listed in the tables. The temperature of the steam at the end of this throttling process will be

$$\left. \begin{array}{l} P = 0.8 \text{ MPa} \\ h = 3051.6 \text{ kJ/kg} \end{array} \right\} T_2 = 297.52^\circ\text{C}$$

Therefore, the temperature will **decrease**.

**12-65** It is to be demonstrated that the Joule-Thomson coefficient is given by  $\mu = \frac{T^2}{c_p} \left( \frac{\partial(\nu/T)}{\partial T} \right)_P$ .

**Analysis** From Eq. 12-52 of the text,

$$c_p = \frac{1}{\mu} \left[ T \left( \frac{\partial \nu}{\partial T} \right)_P - \nu \right]$$

Expanding the partial derivative of  $\nu/T$  produces

$$\left( \frac{\partial(\nu/T)}{\partial T} \right)_P = \frac{1}{T} \left( \frac{\partial \nu}{\partial T} \right)_P - \frac{\nu}{T^2}$$

When this is multiplied by  $T^2$ , the right-hand side becomes the same as the bracketed quantity above. Then,

$$\mu = \frac{T^2}{c_p} \left( \frac{\partial(\nu/T)}{\partial T} \right)_P$$

**12-66** The most general equation of state for which the Joule-Thomson coefficient is always zero is to be determined.

**Analysis** From Eq. 12-52 of the text,

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

When  $\mu = 0$ , this equation becomes

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

This can only be satisfied by an equation of state of the form

$$\frac{v}{T} = f(P)$$

where  $f(P)$  is an arbitrary function of the pressure.

**12-67E** The Joule-Thomson coefficient of refrigerant-134a at a given state is to be estimated.

**Analysis** The Joule-Thomson coefficient is defined as

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

We use a finite difference approximation as

$$\mu \cong \frac{T_2 - T_1}{P_2 - P_1} \quad (\text{at constant enthalpy})$$

At the given state (we call it state 1), the enthalpy of R-134a is

$$\left. \begin{array}{l} P_1 = 30 \text{ psia} \\ T_1 = 20^\circ\text{F} \end{array} \right\} h_1 = 106.27 \text{ Btu/lbm} \quad (\text{Table A-13E})$$

The second state will be selected for a pressure of 20 psia. At this pressure and the same enthalpy, we have

$$\left. \begin{array}{l} P_2 = 20 \text{ psia} \\ h_2 = h_1 = 106.27 \text{ Btu/lbm} \end{array} \right\} T_2 = 15.65^\circ\text{F} \quad (\text{Table A-13E})$$

Substituting,

$$\mu \cong \frac{T_2 - T_1}{P_2 - P_1} = \frac{(15.65 - 20)\text{R}}{(20 - 30)\text{psia}} = \mathbf{0.435 \text{ R/psia}}$$

**12-68** The Joule-Thomson coefficient of refrigerant-134a at a given state is to be estimated.

**Analysis** The Joule-Thomson coefficient is defined as

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

We use a finite difference approximation as

$$\mu \cong \frac{T_2 - T_1}{P_2 - P_1} \quad (\text{at constant enthalpy})$$

At the given state (we call it state 1), the enthalpy of R-134a is

$$\left. \begin{array}{l} P_1 = 200 \text{ kPa} \\ T_1 = 20^\circ\text{C} \end{array} \right\} h_1 = 270.18 \text{ kJ/kg} \quad (\text{Table A - 13})$$

The second state will be selected for a pressure of 180 kPa. At this pressure and the same enthalpy, we have

$$\left. \begin{array}{l} P_2 = 180 \text{ kPa} \\ h_2 = h_1 = 270.18 \text{ kJ/kg} \end{array} \right\} T_2 = 19.51^\circ\text{C} \quad (\text{Table A - 13})$$

Substituting,

$$\mu \cong \frac{T_2 - T_1}{P_2 - P_1} = \frac{(19.51 - 20)\text{K}}{(180 - 200)\text{kPa}} = \mathbf{0.0245 \text{ K/kPa}}$$

**12-69** The equation of state of a gas is given by  $\nu = \frac{RT}{P} - \frac{a}{T} + b$ . An equation for the Joule-Thomson coefficient inversion line using this equation is to be derived.

**Analysis** From Eq. 12-52 of the text,

$$c_p = \frac{1}{\mu} \left[ T \left( \frac{\partial \nu}{\partial T} \right)_P - \nu \right]$$

When  $\mu = 0$  as it does on the inversion line, this equation becomes

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

Using the equation of state to evaluate the partial derivative,

$$\left( \frac{\partial \nu}{\partial T} \right)_P = \frac{R}{P} + \frac{a}{T^2}$$

Substituting this result into the previous expression produces

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

Solving this for the temperature gives

$$T = \frac{2a}{b}$$

as the condition along the inversion line.

### The $\Delta h$ , $\Delta u$ , and $\Delta s$ of Real Gases

**12-70C** It is the variation of enthalpy with pressure at a fixed temperature.

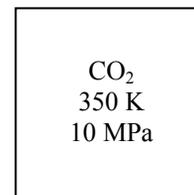
**12-71C** As  $P_R$  approaches zero, the gas approaches ideal gas behavior. As a result, the deviation from ideal gas behavior diminishes.

**12-72C** So that a single chart can be used for all gases instead of a single particular gas.

**12-73** The errors involved in the enthalpy and internal energy of  $\text{CO}_2$  at 350 K and 10 MPa if it is assumed to be an ideal gas are to be determined.

**Analysis** (a) The enthalpy departure of  $\text{CO}_2$  at the specified state is determined from the generalized chart to be (Fig. A-29)

$$\text{and } \left. \begin{aligned} T_R &= \frac{T}{T_{\text{cr}}} = \frac{350}{304.2} = 1.151 \\ P_R &= \frac{P}{P_{\text{cr}}} = \frac{10}{7.39} = 1.353 \end{aligned} \right\} \longrightarrow Z_h = \frac{(\bar{h}_{\text{ideal}} - \bar{h})_{T,P}}{R_u T_{\text{cr}}} = 1.5$$



Thus,

$$\bar{h} = \bar{h}_{\text{ideal}} - Z_h R_u T_{\text{cr}} = 11,351 - [(1.5)(8.314)(304.2)] = 7,557 \text{ kJ/kmol}$$

and,

$$\text{Error} = \frac{(\bar{h}_{\text{ideal}} - \bar{h})_{T,P}}{\bar{h}} = \frac{11,351 - 7,557}{7,557} = \mathbf{50.2\%}$$

(b) At the calculated  $T_R$  and  $P_R$  the compressibility factor is determined from the compressibility chart to be  $Z = 0.65$ . Then using the definition of enthalpy, the internal energy is determined to be

$$\bar{u} = \bar{h} - P\bar{v} = \bar{h} - ZR_u T = 7557 - [(0.65)(8.314)(350)] = 5,666 \text{ kJ/kmol}$$

and,

$$\text{Error} = \frac{\bar{u}_{\text{ideal}} - \bar{u}}{\bar{u}} = \frac{8,439 - 5,666}{5,666} = \mathbf{48.9\%}$$

**12-74** The enthalpy and entropy changes of nitrogen during a process are to be determined assuming ideal gas behavior and using generalized charts.

**Analysis** (a) Using data from the ideal gas property table of nitrogen (Table A-18),

$$(\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \bar{h}_{2,\text{ideal}} - \bar{h}_{1,\text{ideal}} = 9306 - 6,537 = \mathbf{2769 \text{ kJ/kmol}}$$

and

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = s_2^\circ - s_1^\circ - R_u \ln \frac{P_2}{P_1} = 193.562 - 183.289 - 8.314 \times \ln \frac{12}{6} = \mathbf{4.510 \text{ kJ/kmol} \cdot \text{K}}$$

(b) The enthalpy and entropy departures of nitrogen at the specified states are determined from the generalized charts to be (Figs. A-29, A-30)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{225}{126.2} = 1.783 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{6}{3.39} = 1.770 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.6 \text{ and } Z_{s1} = 0.25$$

and

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{320}{126.2} = 2.536 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{12}{3.39} = 2.540 \end{aligned} \right\} \longrightarrow Z_{h2} = 0.4 \text{ and } Z_{s2} = 0.15$$

Substituting,

$$\begin{aligned} \bar{h}_2 - \bar{h}_1 &= R_u T_{\text{cr}} (Z_{h1} - Z_{h2}) + (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} \\ &= (8.314)(126.2)(0.6 - 0.4) + 2769 \\ &= \mathbf{2979 \text{ kJ/kmol}} \end{aligned}$$

$$\begin{aligned} \bar{s}_2 - \bar{s}_1 &= R_u (Z_{s1} - Z_{s2}) + (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} \\ &= (8.314)(0.25 - 0.15) + 4.510 \\ &= \mathbf{5.341 \text{ kJ/kmol} \cdot \text{K}} \end{aligned}$$

**12-75** Methane is compressed adiabatically by a steady-flow compressor. The required power input to the compressor is to be determined using the generalized charts.

**Assumptions** 1 Steady operating conditions exist. 2 Kinetic and potential energy changes are negligible.

**Analysis** The steady-flow energy balance equation for this compressor can be expressed as

$$\dot{E}_{\text{in}} - \dot{E}_{\text{out}} = \Delta \dot{E}_{\text{system}} \overset{\text{steady}}{\neq 0} = 0$$

$$\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$$

$$\dot{W}_{\text{C,in}} + \dot{m}h_1 = \dot{m}h_2$$

$$\dot{W}_{\text{C,in}} = \dot{m}(h_2 - h_1)$$

The enthalpy departures of CH<sub>4</sub> at the specified states are determined from the generalized charts to be (Fig. A-29)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{263}{191.1} = 1.376 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{2}{4.64} = 0.431 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.21$$

and

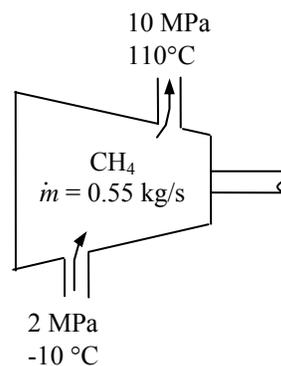
$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{383}{191.1} = 2.00 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{10}{4.64} = 2.155 \end{aligned} \right\} \longrightarrow Z_{h2} = 0.50$$

Thus,

$$\begin{aligned} h_2 - h_1 &= RT_{\text{cr}}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{\text{ideal}} \\ &= (0.5182)(191.1)(0.21 - 0.50) + 2.2537(110 - (-10)) \\ &= 241.7 \text{ kJ/kg} \end{aligned}$$

Substituting,

$$\dot{W}_{\text{C,in}} = (0.55 \text{ kg/s})(241.7 \text{ kJ/kg}) = \mathbf{133 \text{ kW}}$$



**12-76E** The enthalpy and entropy changes of water vapor during a change of state are to be determined using the departure charts and the property tables.

**Properties** The properties of water are (Table A-1E)

$$M = 18.015 \text{ lbm/lbmol}, T_{\text{cr}} = 1164.8 \text{ R}, P_{\text{cr}} = 3200 \text{ psia}$$

**Analysis** (a) Using data from the ideal gas property table of water vapor (Table A-23E),

$$(\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \bar{h}_{2,\text{ideal}} - \bar{h}_{1,\text{ideal}} = 12,178.8 - 17,032.5 = -4853.7 \text{ Btu/lbmol}$$

and

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = s_2^\circ - s_1^\circ - R_u \ln \frac{P_2}{P_1} = 53.556 - 56.411 - 1.9858 \times \ln \frac{1000}{3000} = -0.6734 \text{ Btu/lbmol} \cdot \text{R}$$

The enthalpy and entropy departures of water vapor at the specified states are determined from the generalized charts to be (Figs. A-29, A-30 or from EES)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{1960}{1164.8} = 1.683 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{3000}{3200} = 0.9375 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.387 \text{ and } Z_{s1} = 0.188$$

and

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{1460}{1164.8} = 1.253 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{1000}{3200} = 0.3125 \end{aligned} \right\} \longrightarrow Z_{h2} = 0.233 \text{ and } Z_{s2} = 0.134$$

The enthalpy and entropy changes per mole basis are

$$\begin{aligned} \bar{h}_2 - \bar{h}_1 &= (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} - R_u T_{\text{cr}} (Z_{h2} - Z_{h1}) \\ &= -4853.7 - (1.9858)(1164.8)(0.233 - 0.387) = -4497.5 \text{ Btu/lbmol} \end{aligned}$$

$$\begin{aligned} \bar{s}_2 - \bar{s}_1 &= (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} - R_u (Z_{s2} - Z_{s1}) \\ &= -0.6734 - (1.9858)(0.134 - 0.188) = -0.5662 \text{ Btu/lbmol} \cdot \text{R} \end{aligned}$$

The enthalpy and entropy changes per mass basis are

$$\begin{aligned} h_2 - h_1 &= \frac{\bar{h}_2 - \bar{h}_1}{M} = \frac{-4497.5 \text{ Btu/lbmol}}{18.015 \text{ lbm/lbmol}} = \mathbf{-249.7 \text{ Btu/lbm}} \\ s_2 - s_1 &= \frac{\bar{s}_2 - \bar{s}_1}{M} = \frac{-0.5662 \text{ Btu/lbmol} \cdot \text{R}}{18.015 \text{ lbm/lbmol}} = \mathbf{-0.0314 \text{ Btu/lbm} \cdot \text{R}} \end{aligned}$$

(b) Using water tables (Table A-6E)

$$\left. \begin{aligned} P_1 &= 3000 \text{ psia} \\ T_1 &= 1500^\circ\text{F} \end{aligned} \right\} \begin{aligned} h_1 &= 1764.6 \text{ Btu/lbm} \\ s_1 &= 1.6883 \text{ Btu/lbm} \cdot \text{R} \end{aligned}$$

$$\left. \begin{aligned} P_2 &= 1000 \text{ psia} \\ T_2 &= 1000^\circ\text{F} \end{aligned} \right\} \begin{aligned} h_2 &= 1506.2 \text{ Btu/lbm} \\ s_2 &= 1.6535 \text{ Btu/lbm} \cdot \text{R} \end{aligned}$$

The enthalpy and entropy changes are

$$\begin{aligned} h_2 - h_1 &= 1506.2 - 1764.6 = \mathbf{-258.4 \text{ Btu/lbm}} \\ s_2 - s_1 &= 1.6535 - 1.6883 = \mathbf{-0.0348 \text{ Btu/lbm} \cdot \text{R}} \end{aligned}$$

**12-77** The enthalpy and entropy changes of water vapor during a change of state are to be determined using the departure charts and the property tables.

**Properties** The properties of water are (Table A-1)

$$M = 18.015 \text{ kg/kmol}, T_{\text{cr}} = 647.1 \text{ K}, P_{\text{cr}} = 22.06 \text{ MPa}$$

**Analysis** Using data from the ideal gas property table of water vapor (Table A-23),

$$(\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \bar{h}_{2,\text{ideal}} - \bar{h}_{1,\text{ideal}} = 23,082 - 30,754 = -7672 \text{ kJ/kmol}$$

and

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = s_2^\circ - s_1^\circ - R_u \ln \frac{P_2}{P_1} = 217.141 - 227.109 - 8.314 \times \ln \frac{500}{1000} = -4.2052 \text{ kJ/kmol} \cdot \text{K}$$

The enthalpy and entropy departures of water vapor at the specified states are determined from the generalized charts to be (Figs. A-29, A-30 or from EES)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{873}{647.1} = 1.349 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{1}{22.06} = 0.0453 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.0288 \text{ and } Z_{s1} = 0.0157$$

and

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{673}{647.1} = 1.040 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{0.5}{22.06} = 0.0227 \end{aligned} \right\} \longrightarrow Z_{h2} = 0.0223 \text{ and } Z_{s2} = 0.0146$$

The enthalpy and entropy changes per mole basis are

$$\begin{aligned} \bar{h}_2 - \bar{h}_1 &= (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} - R_u T_{\text{cr}} (Z_{h2} - Z_{h1}) \\ &= -7672 - (8.314)(647.1)(0.0223 - 0.0288) = -7637 \text{ kJ/kmol} \end{aligned}$$

$$\begin{aligned} \bar{s}_2 - \bar{s}_1 &= (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} - R_u (Z_{s2} - Z_{s1}) \\ &= -4.2052 - (8.314)(0.0146 - 0.0157) = -4.1961 \text{ kJ/kmol} \cdot \text{K} \end{aligned}$$

The enthalpy and entropy changes per mass basis are

$$\begin{aligned} h_2 - h_1 &= \frac{\bar{h}_2 - \bar{h}_1}{M} = \frac{-7637 \text{ kJ/kmol}}{18.015 \text{ kg/kmol}} = \mathbf{-423.9 \text{ kJ/kg}} \\ s_2 - s_1 &= \frac{\bar{s}_2 - \bar{s}_1}{M} = \frac{-4.1961 \text{ kJ/kmol} \cdot \text{K}}{18.015 \text{ kg/kmol}} = \mathbf{-0.2329 \text{ kJ/kg} \cdot \text{K}} \end{aligned}$$

The inlet and exit state properties of water vapor from Table A-6 are

$$\left. \begin{aligned} P_1 &= 1000 \text{ kPa} \\ T_1 &= 600^\circ\text{C} \end{aligned} \right\} \begin{aligned} h_1 &= 3698.6 \text{ kJ/kg} \\ s_1 &= 8.0311 \text{ kJ/kg} \cdot \text{K} \end{aligned}$$

$$\left. \begin{aligned} P_2 &= 500 \text{ kPa} \\ T_2 &= 400^\circ\text{C} \end{aligned} \right\} \begin{aligned} h_2 &= 3272.4 \text{ kJ/kg} \\ s_2 &= 7.7956 \text{ kJ/kg} \cdot \text{K} \end{aligned}$$

The enthalpy and entropy changes are

$$\begin{aligned} h_2 - h_1 &= 3272.4 - 3698.6 = \mathbf{-426.2 \text{ kJ/kg}} \\ s_2 - s_1 &= 7.7956 - 8.0311 = \mathbf{-0.2355 \text{ kJ/kg} \cdot \text{K}} \end{aligned}$$

**12-78** The enthalpy and entropy changes of water vapor during a change of state are to be determined using the departure charts and the property tables.

**Properties** The properties of water are (Table A-1)

$$M = 18.015 \text{ kg/kmol}, T_{\text{cr}} = 647.1 \text{ K}, P_{\text{cr}} = 22.06 \text{ MPa}$$

**Analysis (a)** The pressure of water vapor during this process is

$$P_1 = P_2 = P_{\text{sat}@300^\circ\text{C}} = 8588 \text{ kPa}$$

Using data from the ideal gas property table of water vapor (Table A-23),

$$(\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \bar{h}_{2,\text{ideal}} - \bar{h}_{1,\text{ideal}} = 34,775 - 19,426 = 15,349 \text{ kJ/kmol}$$

and

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = s_2^\circ - s_1^\circ - R_u \ln \frac{P_2}{P_1} = 231.473 - 211.263 - 0 = 20.210 \text{ kJ/kmol} \cdot \text{K}$$

The enthalpy and entropy departures of water vapor at the specified states are determined from the generalized charts to be (Figs. A-29, A-30 or from EES)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{573}{647.1} = 0.885 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{8.588}{22.06} = 0.389 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.609 \text{ and } Z_{s1} = 0.481$$

and

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{973}{647.1} = 1.504 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{8.588}{22.06} = 0.389 \end{aligned} \right\} \longrightarrow Z_{h2} = 0.204 \text{ and } Z_{s2} = 0.105$$

The enthalpy and entropy changes per mole basis are

$$\begin{aligned} \bar{h}_2 - \bar{h}_1 &= (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} - R_u T_{\text{cr}} (Z_{h2} - Z_{h1}) \\ &= 15,349 - (8.314)(647.1)(0.204 - 0.609) = 17,528 \text{ kJ/kmol} \end{aligned}$$

$$\begin{aligned} \bar{s}_2 - \bar{s}_1 &= (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} - R_u (Z_{s2} - Z_{s1}) \\ &= 20.210 - (8.314)(0.105 - 0.481) = 23.336 \text{ kJ/kmol} \cdot \text{K} \end{aligned}$$

The enthalpy and entropy changes per mass basis are

$$\begin{aligned} h_2 - h_1 &= \frac{\bar{h}_2 - \bar{h}_1}{M} = \frac{17,528 \text{ kJ/kmol}}{18.015 \text{ kg/kmol}} = \mathbf{973.0 \text{ kJ/kg}} \\ s_2 - s_1 &= \frac{\bar{s}_2 - \bar{s}_1}{M} = \frac{23.336 \text{ kJ/kmol} \cdot \text{K}}{18.015 \text{ kg/kmol}} = \mathbf{1.2954 \text{ kJ/kg} \cdot \text{K}} \end{aligned}$$

(b) The inlet and exit state properties of water vapor from Table A-6 are

$$\begin{aligned} T_1 = 300^\circ\text{C} \left\{ \begin{array}{l} h_1 = 2749.6 \text{ kJ/kg} \\ x_1 = 1 \quad \left. \vphantom{\begin{array}{l} h_1 = 2749.6 \text{ kJ/kg} \\ x_1 = 1 \end{array}} \right\} s_1 = 5.7059 \text{ kJ/kg} \cdot \text{K} \end{array} \right. \\ P_2 = 8588 \text{ kPa} \left\{ \begin{array}{l} h_2 = 3878.6 \text{ kJ/kg} \\ T_2 = 700^\circ\text{C} \quad \left. \vphantom{\begin{array}{l} h_2 = 3878.6 \text{ kJ/kg} \\ T_2 = 700^\circ\text{C} \end{array}} \right\} s_2 = 7.2465 \text{ kJ/kg} \cdot \text{K} \end{array} \right. \quad (\text{from EES}) \end{aligned}$$

The enthalpy and entropy changes are

$$\begin{aligned} h_2 - h_1 &= 3878.6 - 2749.6 = \mathbf{1129 \text{ kJ/kg}} \\ s_2 - s_1 &= 7.2465 - 5.7059 = \mathbf{1.5406 \text{ kJ/kg} \cdot \text{K}} \end{aligned}$$

**12-79** Propane is to be adiabatically and reversibly compressed in a steady-flow device. The specific work required for this compression is to be determined using the departure charts and treating the propane as an ideal gas with temperature variable specific heats.

**Properties** The properties of propane are (Table A-1)

$$M = 44.097 \text{ kg/kmol}, R = 0.1885 \text{ kJ/kg} \cdot \text{K}, T_{\text{cr}} = 370 \text{ K}, P_{\text{cr}} = 4.26 \text{ MPa}$$

**Analysis** The temperature at the exit state may be determined by the fact that the process is isentropic and the molar entropy change between the inlet and exit is zero. When the entropy change equation is integrated with variable specific heats, it becomes

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = \int_1^2 \frac{c_p}{T} dT - R_u \ln \frac{P_2}{P_1}$$

When the expression of Table A-2c is substituted for  $c_p$  and the integration performed, we obtain

$$\begin{aligned} (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} &= \int_1^2 \frac{c_p}{T} dT - R_u \ln \frac{P_2}{P_1} = \int_1^2 \left( \frac{a}{T} + b + cT + dT^2 \right) dT - R_u \ln \frac{P_2}{P_1} \\ &= a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) + \frac{d}{3}(T_2^3 - T_1^3) - R_u \ln \frac{P_2}{P_1} \\ 0 &= -4.04 \ln \frac{T_2}{373} + 30.48 \left( \frac{T_2}{100} - 3.73 \right) - 0.786 \left[ \left( \frac{T_2}{100} \right)^2 - 3.73^2 \right] + 0.01058 \left[ \left( \frac{T_2}{100} \right)^3 - 3.73^3 \right] \\ &\quad - (8.314) \ln \frac{4000}{500} \end{aligned}$$

Solving this equation by EES or an iterative solution by hand gives

$$T_2 = 446 \text{ K}$$

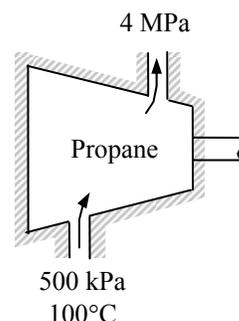
When an energy balance is applied to the compressor, it becomes

$$\begin{aligned} \bar{w}_{\text{in}} &= (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \int_1^2 c_p dT = \int_1^2 (a + bT + cT^2 + dT^3) dT \\ &= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4) \\ &= -4.04(446 - 373) + 0.1524(446^2 - 373^2) - 52.4(4.46^3 - 3.73^3) + 0.7935(4.46^4 - 3.73^4) \\ &= 7048 \text{ kJ/kmol} \end{aligned}$$

The work input per unit mass basis is

$$w_{\text{in}} = \frac{\bar{w}_{\text{in}}}{M} = \frac{7048 \text{ kJ/kmol}}{44.097 \text{ kg/kmol}} = \mathbf{159.8 \text{ kJ/kg}}$$

The enthalpy departures of propane at the specified states are determined from the generalized charts to be (Fig. A-29 or from EES)



$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{cr}} = \frac{373}{370} = 1.008 \\ P_{R1} &= \frac{P_1}{P_{cr}} = \frac{0.5}{4.26} = 0.117 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.124$$

and

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{cr}} = \frac{446}{370} = 1.205 \\ P_{R2} &= \frac{P_2}{P_{cr}} = \frac{4}{4.26} = 0.939 \end{aligned} \right\} \longrightarrow Z_{h2} = 0.826$$

The work input (i.e., enthalpy change) is determined to be

$$\begin{aligned} w_{in} &= h_2 - h_1 = (h_2 - h_1)_{ideal} - RT_{cr}(Z_{h2} - Z_{h1}) \\ &= 159.8 - (0.1885)(370)(0.826 - 0.124) \\ &= \mathbf{110.8 \text{ kJ/kg}} \end{aligned}$$

**12-80E** Oxygen is to be adiabatically and reversibly expanded in a nozzle. The exit velocity is to be determined using the departure charts and treating the oxygen as an ideal gas with temperature variable specific heats.

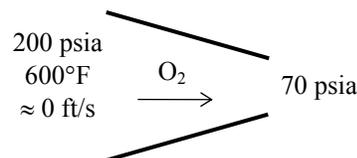
**Properties** The properties of oxygen are (Table A-1)

$$M = 31.999 \text{ lbm/lbmol}, R = 0.06206 \text{ Btu/lbm} \cdot \text{R}, T_{\text{cr}} = 278.6 \text{ R}, P_{\text{cr}} = 736 \text{ psia}$$

**Analysis** The temperature at the exit state may be determined by the fact that the process is isentropic and the molar entropy change between the inlet and exit is zero. From the entropy change equation for an ideal gas with variable specific heats:

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = 0$$

$$s_2^\circ - s_1^\circ = R_u \ln \frac{P_2}{P_1} = (1.9858) \ln \frac{70}{200} = -2.085 \text{ Btu/lbmol} \cdot \text{R}$$



Then from Table A-19E,

$$T_1 = 1060 \text{ R} \longrightarrow \bar{h}_{1,\text{ideal}} = 7543.6 \text{ Btu/lbmol}, s_1^\circ = 53.921 \text{ Btu/lbmol} \cdot \text{R}$$

$$s_2^\circ = s_1^\circ - 2.085 = 53.921 - 2.085 = 51.836 \text{ Btu/lbmol} \cdot \text{R}$$

$$s_2^\circ = 51.836 \text{ Btu/lbmol} \cdot \text{R} \longrightarrow T_2 = 802 \text{ R}, \bar{h}_{2,\text{ideal}} = 5614.1 \text{ Btu/lbmol}$$

The enthalpy change per mole basis is

$$(\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \bar{h}_{2,\text{ideal}} - \bar{h}_{1,\text{ideal}} = 5614.1 - 7543.6 = -1929.5 \text{ Btu/lbmol}$$

The enthalpy change per mass basis is

$$(h_2 - h_1)_{\text{ideal}} = \frac{(\bar{h}_2 - \bar{h}_1)_{\text{ideal}}}{M} = \frac{-1929.5 \text{ Btu/lbmol}}{31.999 \text{ lbm/lbmol}} = -60.30 \text{ Btu/lbm}$$

An energy balance on the nozzle gives

$$\dot{E}_{\text{in}} = \dot{E}_{\text{out}}$$

$$\dot{m}(h_1 + V_1^2 / 2) = \dot{m}(h_2 + V_2^2 / 2)$$

$$h_1 + V_1^2 / 2 = h_2 + V_2^2 / 2$$

Solving for the exit velocity,

$$V_2 = [V_1^2 + 2(h_1 - h_2)]^{0.5} = \left[ (0 \text{ ft/s})^2 + 2(60.30 \text{ Btu/lbm}) \left( \frac{25,037 \text{ ft}^2/\text{s}^2}{1 \text{ Btu/lbm}} \right) \right]^{0.5} = \mathbf{1738 \text{ ft/s}}$$

The enthalpy departures of oxygen at the specified states are determined from the generalized charts to be (Fig. A-29 or from EES)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{1060}{278.6} = 3.805 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{200}{736} = 0.272 \end{aligned} \right\} Z_{h1} = 0.000759$$

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{802}{278.6} = 2.879 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{70}{736} = 0.0951 \end{aligned} \right\} Z_{h2} = 0.00894$$

The enthalpy change is

$$\begin{aligned} h_2 - h_1 &= (h_2 - h_1)_{\text{ideal}} - RT_{\text{cr}}(Z_{h2} - Z_{h1}) \\ &= -60.30 \text{ Btu/lbm} - (0.06206 \text{ Btu/lbm} \cdot \text{R})(278.6 \text{ R})(0.00894 - 0.000759) \\ &= -60.44 \text{ Btu/lbm} \end{aligned}$$

The exit velocity is

$$V_2 = [V_1^2 + 2(h_1 - h_2)]^{0.5} = \left[ (0 \text{ ft/s})^2 + 2(60.44 \text{ Btu/lbm}) \left( \frac{25,037 \text{ ft}^2/\text{s}^2}{1 \text{ Btu/lbm}} \right) \right]^{0.5} = \mathbf{1740 \text{ ft/s}}$$

**12-81** [Also solved by EES on enclosed CD] Propane is compressed isothermally by a piston-cylinder device. The work done and the heat transfer are to be determined using the generalized charts.

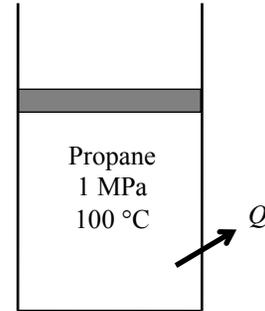
**Assumptions 1** The compression process is quasi-equilibrium. **2** Kinetic and potential energy changes are negligible.

**Analysis (a)** The enthalpy departure and the compressibility factors of propane at the initial and the final states are determined from the generalized charts to be (Figs. A-29, A-15)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{cr}} = \frac{373}{370} = 1.008 \\ P_{R1} &= \frac{P_1}{P_{cr}} = \frac{1}{4.26} = 0.235 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.28 \text{ and } Z_1 = 0.92$$

and

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{cr}} = \frac{373}{370} = 1.008 \\ P_{R2} &= \frac{P_2}{P_{cr}} = \frac{4}{4.26} = 0.939 \end{aligned} \right\} \longrightarrow Z_{h2} = 1.8 \text{ and } Z_2 = 0.50$$



Treating propane as a real gas with  $Z_{\text{avg}} = (Z_1 + Z_2)/2 = (0.92 + 0.50)/2 = 0.71$ ,

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

Then the boundary work becomes

$$\begin{aligned} w_{b,\text{in}} &= -\int_1^2 P d\nu = -\int_1^2 \frac{C}{\nu} d\nu = -C \ln \frac{\nu_2}{\nu_1} = Z_{\text{avg}} RT \ln \frac{Z_2 RT / P_2}{Z_1 RT / P_1} = -Z_{\text{ave}} RT \ln \frac{Z_2 P_1}{Z_1 P_2} \\ &= -(0.71)(0.1885 \text{ kJ/kg} \cdot \text{K})(373 \text{ K}) \ln \frac{(0.50)(1)}{(0.92)(4)} = \mathbf{99.6 \text{ kJ/kg}} \end{aligned}$$

Also,

$$\begin{aligned} h_2 - h_1 &= RT_{cr}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{\text{ideal}} = (0.1885)(370)(0.28 - 1.8) + 0 = -106 \text{ kJ/kg} \\ u_2 - u_1 &= (h_2 - h_1) - R(Z_2 T_2 - Z_1 T_1) = -106 - (0.1885)[(0.5)(373) - (0.92)(373)] = -76.5 \text{ kJ/kg} \end{aligned}$$

Then the heat transfer for this process is determined from the closed system energy balance to be

$$\begin{aligned} E_{\text{in}} - E_{\text{out}} &= \Delta E_{\text{system}} \\ q_{\text{in}} + w_{b,\text{in}} &= \Delta u = u_2 - u_1 \\ q_{\text{in}} &= (u_2 - u_1) - w_{b,\text{in}} = -76.5 - 99.6 = -176.1 \text{ kJ/kg} \quad \rightarrow \quad q_{\text{out}} = 176.1 \text{ kJ/kg} \end{aligned}$$

**12-82 EES** Problem 12-81 is reconsidered. This problem is to be extended to compare the solutions based on the ideal gas assumption, generalized chart data and real fluid (EES) data. Also, the solution is to be extended to carbon dioxide, nitrogen and methane.

**Analysis** The problem is solved using EES, and the solution is given below.

```

Procedure INFO(Name$, T[1] : Fluid$, T_critical, p_critical)
If Name$='Propane' then
    T_critical=370 ; p_critical=4620 ; Fluid$='C3H8'; goto 10
endif
If Name$='Methane' then
    T_critical=191.1 ; p_critical=4640 ; Fluid$='CH4'; goto 10
endif
If Name$='Nitrogen' then
    T_critical=126.2 ; p_critical=3390 ; Fluid$='N2'; goto 10
endif
If Name$='Oxygen' then
    T_critical=154.8 ; p_critical=5080 ; Fluid$='O2'; goto 10
endif
If Name$='CarbonDioxide' then
    T_critical=304.2 ; p_critical=7390 ; Fluid$='CO2' ; goto 10
endif
If Name$='n-Butane' then
    T_critical=425.2 ; p_critical=3800 ; Fluid$='C4H10' ; goto 10
endif

10:
    If T[1]<=T_critical then
    CALL ERROR('The supplied temperature must be greater than the critical temperature for the
fluid. A value of XXXF1 K was supplied',T[1])
    endif

end

{"Data from the Diagram Window"
T[1]=100+273.15
p[1]=1000
p[2]=4000
Name$='Propane'
Fluid$='C3H8' }

Call INFO(Name$, T[1] : Fluid$, T_critical, p_critical)
R_u=8.314
M=molarmass(Fluid$)
R=R_u/M

***** IDEAL GAS SOLUTION *****
"State 1"
h_ideal[1]=enthalpy(Fluid$, T=T[1]) "Enthalpy of ideal gas"
s_ideal[1]=entropy(Fluid$, T=T[1], p=p[1]) "Entropy of ideal gas"
u_ideal[1]=h_ideal[1]-R*T[1] "Internal energy of ideal gas"
"State 2"
h_ideal[2]=enthalpy(Fluid$, T=T[2]) "Enthalpy of ideal gas"
s_ideal[2]=entropy(Fluid$, T=T[2], p=p[2]) "Entropy of ideal gas"
u_ideal[2]=h_ideal[2]-R*T[2] "Internal energy of ideal gas"

```

"Work is the integral of  $p \, dv$ , which can be done analytically."

$$w_{\text{ideal}} = R \cdot T[1] \cdot \ln(p[1]/p[2])$$

"First Law - note that  $u_{\text{ideal}}[2]$  is equal to  $u_{\text{ideal}}[1]$ "

$$q_{\text{ideal}} - w_{\text{ideal}} = u_{\text{ideal}}[2] - u_{\text{ideal}}[1]$$

"Entropy change"

$$\Delta s_{\text{ideal}} = s_{\text{ideal}}[2] - s_{\text{ideal}}[1]$$

\*\*\*\*\* COMPRESSABILITY CHART SOLUTION \*\*\*\*\*

"State 1"

$$Tr[1] = T[1]/T_{\text{critical}}$$

$$pr[1] = p[1]/p_{\text{critical}}$$

$$Z[1] = \text{COMPRESS}(Tr[1], Pr[1])$$

$$\Delta h[1] = \text{ENTHDEP}(Tr[1], Pr[1]) \cdot R \cdot T_{\text{critical}} \quad \text{"Enthalpy departure"}$$

$$h[1] = h_{\text{ideal}}[1] - \Delta h[1] \quad \text{"Enthalpy of real gas using charts"}$$

$$u[1] = h[1] - Z[1] \cdot R \cdot T[1]$$

"Internal energy of gas using charts"

$$\Delta s[1] = \text{ENTRDEP}(Tr[1], Pr[1]) \cdot R \quad \text{"Entropy departure"}$$

$$s[1] = s_{\text{ideal}}[1] - \Delta s[1] \quad \text{"Entropy of real gas using charts"}$$

"State 2"

$$T[2] = T[1]$$

$$Tr[2] = Tr[1]$$

$$pr[2] = p[2]/p_{\text{critical}}$$

$$Z[2] = \text{COMPRESS}(Tr[2], Pr[2])$$

$$\Delta h[2] = \text{ENTHDEP}(Tr[2], Pr[2]) \cdot R \cdot T_{\text{critical}} \quad \text{"Enthalpy departure"}$$

$$\Delta s[2] = \text{ENTRDEP}(Tr[2], Pr[2]) \cdot R \quad \text{"Entropy departure"}$$

$$h[2] = h_{\text{ideal}}[2] - \Delta h[2] \quad \text{"Enthalpy of real gas using charts"}$$

$$s[2] = s_{\text{ideal}}[2] - \Delta s[2] \quad \text{"Entropy of real gas using charts"}$$

$$u[2] = h[2] - Z[2] \cdot R \cdot T[2] \quad \text{"Internal energy of gas using charts"}$$

"Work using charts - note use of EES integral function to evaluate the integral of  $p \, dv$ ."

$$w_{\text{chart}} = \text{Integral}(p, v, v[1], v[2])$$

"We need an equation to relate  $p$  and  $v$  in the above INTEGRAL function. "

$$p \cdot v = \text{COMPRESS}(Tr[2], p/p_{\text{critical}}) \cdot R \cdot T[1] \quad \text{"To specify relationship between } p \text{ and } v"$$

"Find the limits of integration"

$$p[1] \cdot v[1] = Z[1] \cdot R \cdot T[1] \quad \text{"to get } v[1], \text{ the lower bound"}$$

$$p[2] \cdot v[2] = Z[2] \cdot R \cdot T[2] \quad \text{"to get } v[2], \text{ the upper bound"}$$

"First Law - note that  $u[2]$  is not equal to  $u[1]$ "

$$q_{\text{chart}} - w_{\text{chart}} = u[2] - u[1]$$

"Entropy Change"

$$\Delta s_{\text{chart}} = s[2] - s[1]$$

\*\*\*\*\* SOLUTION USING EES BUILT-IN PROPERTY DATA \*\*\*\*\*

"At state 1"

$$u_{\text{ees}}[1] = \text{intEnergy}(\text{Name}\$, T=T[1], p=p[1])$$

$$s_{\text{ees}}[1] = \text{entropy}(\text{Name}\$, T=T[1], p=p[1])$$

"At state 2"

$$u_{\text{ees}}[2] = \text{intEnergy}(\text{Name}\$, T=T[2], p=p[2])$$

$$s_{\text{ees}}[2] = \text{entropy}(\text{Name}\$, T=T[2], p=p[2])$$

"Work using EES built-in properties- note use of EES Integral function to evaluate the integral of  $p \, dv$ ."

$$w_{\text{ees}} = \text{integral}(p_{\text{ees}}, v_{\text{ees}}, v_{\text{ees}}[1], v_{\text{ees}}[2])$$

"The following equation relates  $p$  and  $v$  in the above INTEGRAL"

$p_{ees}$ =pressure(Name\$, T=T[1], v=v\_ees) "To specify relationship between p and v"

"Find the limits of integration"

$v_{ees}[1]$ =volume(Name\$, T=T[1], p=p[1]) "to get lower bound"

$v_{ees}[2]$ =volume(Name\$, T=T[2], p=p[2]) "to get upper bound"

"First law - note that  $u_{ees}[2]$  is not equal to  $u_{ees}[1]$ "

$q_{ees}-w_{ees}=u_{ees}[2]-u_{ees}[1]$

"Entropy change"

$\Delta s_{ees}=s_{ees}[2]-s_{ees}[1]$

"Note: In all three solutions to this problem we could have calculated the heat transfer by  $q/T=\Delta s$  since T is constant. Then the first law could have been used to find the work. The use of integral of  $p dv$  to find the work is a more fundamental approach and can be used if T is not constant."

## SOLUTION

$\Delta h[1]=16.48$ [kJ/kg]	$s[2]=5.657$ [kJ/kg-K]
$\Delta h[2]=91.96$ [kJ/kg]	$s_{ees}[1]=2.797$ [kJ/kg-K]
$\Delta s[1]=0.03029$ [kJ/kg-K]	$s_{ees}[2]=2.326$ [kJ/kg-K]
$\Delta s[2]=0.1851$ [kJ/kg-K]	$s_{ideal}[1]=6.103$ [kJ/kg-K]
$\Delta s_{chart}=-0.4162$ [kJ/kg-K]	$s_{ideal}[2]=5.842$ [kJ/kg-K]
$\Delta s_{ees}=-0.4711$ [kJ/kg-K]	$T[1]=373.2$ [K]
$\Delta s_{ideal}=-0.2614$ [kJ/kg-K]	$T[2]=373.2$ [K]
Fluid\$='C3H8'	$T_r[1]=1.009$
$h[1]=-2232$ [kJ/kg]	$T_r[2]=1.009$
$h[2]=-2308$ [kJ/kg]	$T_{critical}=370$ [K]
$h_{ideal}[1]=-2216$ [kJ/kg]	$u[1]=-2298$ [kJ/kg]
$h_{ideal}[2]=-2216$ [kJ/kg]	$u[2]=-2351$ [kJ/kg]
M=44.1	$u_{ees}[1]=688.4$ [kJ/kg]
Name\$='Propane'	$u_{ees}[2]=617.1$ [kJ/kg]
p=4000	$u_{ideal}[1]=-2286$ [kJ/kg]
$p[1]=1000$ [kPa]	$u_{ideal}[2]=-2286$ [kJ/kg]
$p[2]=4000$ [kPa]	$v=0.01074$
$pr[1]=0.2165$	$v[1]=0.06506$ [m <sup>3</sup> /kg]
$pr[2]=0.8658$	$v[2]=0.01074$ [m <sup>3</sup> /kg]
$p_{critical}=4620$ [kPa]	$v_{ees}=0.009426$
$p_{ees}=4000$	$v_{ees}[1]=0.0646$ [m <sup>3</sup> /kg]
$q_{chart}=-155.3$ [kJ/kg]	$v_{ees}[2]=0.009426$ [m <sup>3</sup> /kg]
$q_{ees}=-175.8$ [kJ/kg]	$w_{chart}=-101.9$ [kJ/kg]
$q_{ideal}=-97.54$ [kJ/kg]	$w_{ees}=-104.5$ [kJ/kg]
$R=0.1885$ [kJ/kg-K]	$w_{ideal}=-97.54$ [kJ/kg]
$R_u=8.314$ [kJ/mole-K]	$Z[1]=0.9246$
$s[1]=6.073$ [kJ/kg-K]	$Z[2]=0.6104$

**12-83** Propane is compressed isothermally by a piston-cylinder device. The exergy destruction associated with this process is to be determined.

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

**Properties** The gas constant of propane is  $R = 0.1885 \text{ kJ/kg}\cdot\text{K}$  (Table A-1).

**Analysis** The exergy destruction is determined from its definition  $x_{\text{destroyed}} = T_0 s_{\text{gen}}$  where the entropy generation is determined from an entropy balance on the contents of the cylinder. It gives

$$S_{\text{in}} - S_{\text{out}} + S_{\text{gen}} = \Delta S_{\text{system}}$$

$$-\frac{Q_{\text{out}}}{T_{b,\text{surr}}} + S_{\text{gen}} = m(s_2 - s_1) \rightarrow s_{\text{gen}} = (s_2 - s_1) + \frac{q_{\text{out}}}{T_{\text{surr}}}$$

where

$$\Delta s_{\text{sys}} = s_2 - s_1 = R(Z_{s1} - Z_{s2}) + (s_2 - s_1)_{\text{ideal}}$$

$$(s_2 - s_1)_{\text{ideal}} = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} = 0 - 0.1885 \ln \frac{4}{1} = -0.261 \text{ kJ/kg}\cdot\text{K}$$

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{373}{370} = 1.008 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{1}{4.26} = 0.235 \end{aligned} \right\} \longrightarrow Z_{s1} = 0.21$$

and

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{373}{370} = 1.008 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{4}{4.26} = 0.939 \end{aligned} \right\} \longrightarrow Z_{s2} = 1.5$$

Thus,

$$\Delta s_{\text{sys}} = s_2 - s_1 = R(Z_{s1} - Z_{s2}) + (s_2 - s_1)_{\text{ideal}} = (0.1885)(0.21 - 1.5) - 0.261 = -0.504 \text{ kJ/kg}\cdot\text{K}$$

and

$$x_{\text{destroyed}} = T_0 s_{\text{gen}} = T_0 \left( (s_2 - s_1) + \frac{q_{\text{out}}}{T_{\text{surr}}} \right)$$

$$= (303 \text{ K}) \left( -0.504 + \frac{176.1 \text{ kJ/kg}}{303 \text{ K}} \right) \text{kJ/kg}\cdot\text{K}$$

$$= \mathbf{23.4 \text{ kJ/kg}}$$

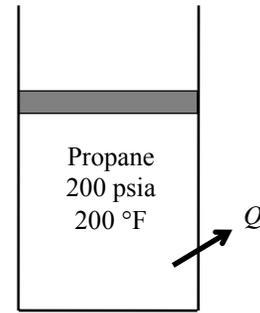
**12-84E** Propane is compressed isothermally by a piston-cylinder device. The work done and the heat transfer are to be determined using the generalized charts.

**Assumptions** **1**The compression process is quasi-equilibrium. **2** Kinetic and potential energy changes are negligible. **3** The device is well-insulated and thus heat transfer is negligible

**Analysis** (a) The enthalpy departure and the compressibility factors of propane at the initial and the final states are determined from the generalized charts to be (Figs. A-29, A-15)

$$\text{and } \left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{cr}} = \frac{660}{665.9} = 0.991 \\ P_{R1} &= \frac{P_1}{P_{cr}} = \frac{200}{617} = 0.324 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.37 \text{ and } Z_1 = 0.88$$

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{cr}} = \frac{660}{665.9} = 0.991 \\ P_{R2} &= \frac{P_2}{P_{cr}} = \frac{800}{617} = 1.297 \end{aligned} \right\} \longrightarrow Z_{h2} = 4.2 \text{ and } Z_2 = 0.22$$



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

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

Then the boundary work becomes

$$\begin{aligned} w_{b,\text{in}} &= -\int_1^2 P d\nu = -\int_1^2 \frac{C}{\nu} d\nu = -C \ln \frac{\nu_2}{\nu_1} = -Z_{\text{avg}}RT \ln \frac{Z_2 RT / P_2}{Z_1 RT / P_1} = -Z_{\text{avg}}RT \ln \frac{Z_2 P_1}{Z_1 P_2} \\ &= -(0.55)(0.04504 \text{ Btu/lbm} \cdot \text{R})(660 \text{ R}) \ln \frac{(0.22)(200)}{(0.88)(800)} \\ &= \mathbf{45.3 \text{ Btu/lbm}} \end{aligned}$$

Also,

$$\begin{aligned} h_2 - h_1 &= RT_{cr}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{\text{ideal}}^{\phi=0} \\ &= (0.04504)(665.9)(0.37 - 4.2) + 0 = -114.9 \text{ Btu/lbm} \end{aligned}$$

$$\begin{aligned} u_2 - u_1 &= (h_2 - h_1) - R(Z_2 T_2 - Z_1 T_1) \\ &= -114.9 - (0.04504)[(0.22)(660) - (0.88)(660)] = -95.3 \text{ Btu/lbm} \end{aligned}$$

Then the heat transfer for this process is determined from the closed system energy balance equation to be

$$\begin{aligned} E_{\text{in}} - E_{\text{out}} &= \Delta E_{\text{system}} \\ q_{\text{in}} + w_{b,\text{in}} &= \Delta u = u_2 - u_1 \\ q_{\text{in}} &= (u_2 - u_1) - w_{b,\text{in}} = -95.3 - 45.3 = -140.6 \text{ Btu/lbm} \rightarrow q_{\text{out}} = \mathbf{140.6 \text{ Btu/lbm}} \end{aligned}$$

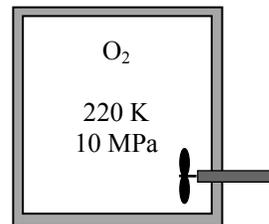
**12-85** A paddle-wheel placed in a well-insulated rigid tank containing oxygen is turned on. The final pressure in the tank and the paddle-wheel work done during this process are to be determined.

**Assumptions** **1**The tank is well-insulated and thus heat transfer is negligible. **2** Kinetic and potential energy changes are negligible.

**Properties** The gas constant of  $O_2$  is  $R = 0.2598 \text{ kJ/kg}\cdot\text{K}$  (Table A-1).

**Analysis** (a) The compressibility factor of oxygen at the initial state is determined from the generalized chart to be

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{cr}} = \frac{220}{154.8} = 1.42 \\ P_{R1} &= \frac{P_1}{P_{cr}} = \frac{10}{5.08} = 1.97 \end{aligned} \right\} \longrightarrow Z_1 = 0.80 \text{ and } Z_{h1} = 1.15$$



Then,

$$P\nu = ZRT \longrightarrow \nu_1 = \frac{(0.8)(0.2598 \text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(220 \text{ K})}{10,000 \text{ kPa}} = 0.00457 \text{ m}^3/\text{kg}$$

$$m = \frac{\nu}{\nu_1} = \frac{0.08 \text{ m}^3}{0.00457 \text{ m}^3/\text{kg}} = 17.5 \text{ kg}$$

The specific volume of oxygen remains constant during this process,  $\nu_2 = \nu_1$ . Thus,

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{cr}} = \frac{250}{154.8} = 1.615 \\ \nu_{R2} &= \frac{\nu_2}{RT_{cr}/P_{cr}} = \frac{0.00457 \text{ m}^3/\text{kg}}{(0.2598 \text{ kPa}\cdot\text{m}^3/\text{kg}\cdot\text{K})(154.8 \text{ K})/(5080 \text{ kPa})} = 0.577 \end{aligned} \right\} \begin{aligned} Z_2 &= 0.87 \\ Z_{h2} &= 1.0 \\ P_{R2} &= 2.4 \end{aligned}$$

$$P_2 = P_{R2}P_{cr} = (2.4)(5080) = \mathbf{12,190 \text{ kPa}}$$

(b) The energy balance relation for this closed system can be expressed as

$$\begin{aligned} E_{in} - E_{out} &= \Delta E_{\text{system}} \\ W_{in} &= \Delta U = m(u_2 - u_1) \\ W_{in} &= m[h_2 - h_1 - (P_2\nu_2 - P_1\nu_1)] = m[h_2 - h_1 - R(Z_2T_2 - Z_1T_1)] \end{aligned}$$

where

$$\begin{aligned} h_2 - h_1 &= RT_{cr}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{\text{ideal}} \\ &= (0.2598)(154.8)(1.15 - 1) + (7275 - 6404) / 32 \\ &= 33.25 \text{ kJ/kg} \end{aligned}$$

Substituting,

$$W_{in} = (17.5 \text{ kg})[33.25 - (0.2598 \text{ kJ/kg}\cdot\text{K})\{(0.87)(250) - (0.80)(220)\}\text{K}] = \mathbf{393 \text{ kJ}}$$

**12-86** The heat transfer and entropy changes of CO<sub>2</sub> during a process are to be determined assuming ideal gas behavior, using generalized charts, and real fluid (EES) data.

**Analysis** The temperature at the final state is

$$T_2 = T_1 \frac{P_2}{P_1} = (100 + 273 \text{ K}) \frac{8 \text{ MPa}}{1 \text{ MPa}} = 2984 \text{ K}$$

Using data from the ideal gas property table of CO<sub>2</sub> (Table A-20),

$$(\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \bar{h}_{2,\text{ideal}} - \bar{h}_{1,\text{ideal}} = 161,293 - 12,269 = 149,024 \text{ kJ/kmol}$$

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = s_2^\circ - s_1^\circ - R_u \ln \frac{P_2}{P_1} = 333.770 - 222.367 - 8.314 \times \ln \frac{8}{1} = 94.115 \text{ kJ/kmol} \cdot \text{K}$$

$$(h_2 - h_1)_{\text{ideal}} = \frac{(\bar{h}_2 - \bar{h}_1)_{\text{ideal}}}{M} = \frac{149,024 \text{ kJ/kmol}}{44 \text{ kg/kmol}} = 3386.9 \text{ kJ/kg}$$

The heat transfer is determined from an energy balance noting that there is no work interaction

$$\begin{aligned} q_{\text{ideal}} &= (u_2 - u_1)_{\text{ideal}} = (h_2 - h_1)_{\text{ideal}} - R(T_2 - T_1) \\ &= 3386.9 \text{ kJ/kg} - (0.1889 \text{ kJ/kg} \cdot \text{K})(2984 - 373) = \mathbf{2893.7 \text{ kJ/kg}} \end{aligned}$$

The entropy change is

$$\Delta s_{\text{ideal}} = (s_2 - s_1)_{\text{ideal}} = \frac{(\bar{s}_2 - \bar{s}_1)_{\text{ideal}}}{M} = \frac{94.115 \text{ kJ/kmol}}{44 \text{ kg/kmol}} = \mathbf{2.1390 \text{ kJ/kg} \cdot \text{K}}$$

The compressibility factor and the enthalpy and entropy departures of CO<sub>2</sub> at the specified states are determined from the generalized charts to be (we used EES)

$$\text{and } \left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{373}{304.2} = 1.226 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{1}{7.39} = 0.135 \end{aligned} \right\} \longrightarrow Z_1 = 0.976, Z_{h1} = 0.1028 \text{ and } Z_{s1} = 0.05987$$

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{2985}{304.2} = 9.813 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{8}{7.39} = 1.083 \end{aligned} \right\} \longrightarrow Z_2 = 1.009, Z_{h2} = -0.1144 \text{ and } Z_{s2} = -0.002685$$

Thus,

$$\begin{aligned} q_{\text{chart}} &= u_2 - u_1 = (h_2 - h_1)_{\text{ideal}} - RT_{\text{cr}}(Z_{h2} - Z_{h1}) - Z_1 R(T_2 - T_1) \\ &= 3386.9 - (0.1889)(304.2)(-0.1144 - 0.1028) - (0.976)(0.1889)(2887 - 373) = \mathbf{2935.9 \text{ kJ/kg}} \end{aligned}$$

$$\begin{aligned} \Delta s_{\text{chart}} &= (s_2 - s_1)_{\text{chart}} = R(Z_{s1} - Z_{s2}) + (s_2 - s_1)_{\text{ideal}} \\ &= (0.1889)(0.05987 - (-0.002685)) + 2.1390 = \mathbf{2.151 \text{ kJ/kg} \cdot \text{K}} \end{aligned}$$

Note that the temperature at the final state in this case was determined from

$$T_2 = T_1 \frac{P_2}{P_1} \frac{Z_1}{Z_2} = (100 + 273 \text{ K}) \frac{8 \text{ MPa}}{1 \text{ MPa}} \frac{0.976}{1.009} = 2888 \text{ K}$$

The solution using EES built-in property data is as follows:

$$\left. \begin{aligned} T_1 &= 373 \text{ K} \\ P_1 &= 1 \text{ MPa} \end{aligned} \right\} \begin{aligned} v_1 &= 0.06885 \text{ m}^3/\text{kg} \\ u_1 &= -8.614 \text{ kJ/kg} \\ s_1 &= -0.2464 \text{ kJ/kg} \cdot \text{K} \end{aligned} \quad \left. \begin{aligned} P_2 &= 8 \text{ MPa} \\ v_2 &= v_1 = 0.06885 \text{ m}^3/\text{kg} \end{aligned} \right\} \begin{aligned} T_2 &= 2879 \text{ K} \\ u_2 &= 2754 \text{ kJ/kg} \\ s_2 &= 1.85 \text{ kJ/kg} \cdot \text{K} \end{aligned}$$

Then

$$q_{\text{EES}} = u_2 - u_1 = 2754 - (-8.614) = \mathbf{2763 \text{ kJ/kg}}$$

$$\Delta s_{\text{EES}} = (s_2 - s_1)_{\text{EES}} = s_2 - s_1 = 1.85 - (-0.2464) = \mathbf{2.097 \text{ kJ/kg} \cdot \text{K}}$$

## Review Problems

**12-87** For  $\beta \geq 0$ , it is to be shown that at every point of a single-phase region of an  $h$ - $s$  diagram, the slope of a constant-pressure line is greater than the slope of a constant-temperature line, but less than the slope of a constant-volume line.

**Analysis** It is given that  $\beta > 0$ .

Using the  $Tds$  relation:  $dh = T ds + \nu dP \longrightarrow \frac{dh}{ds} = T + \nu \frac{dP}{ds}$

$$(1) P = \text{constant:} \quad \left( \frac{\partial h}{\partial s} \right)_P = T$$

$$(2) T = \text{constant:} \quad \left( \frac{\partial h}{\partial s} \right)_T = T + \nu \left( \frac{\partial P}{\partial s} \right)_T$$

But the 4th Maxwell relation:  $\left( \frac{\partial P}{\partial s} \right)_T = - \left( \frac{\partial T}{\partial \nu} \right)_P$

Substituting:  $\left( \frac{\partial h}{\partial s} \right)_T = T - \nu \left( \frac{\partial T}{\partial \nu} \right)_P = T - \frac{1}{\beta}$

Therefore, the slope of  $P = \text{constant}$  lines is **greater** than the slope of  $T = \text{constant}$  lines.

$$(3) \nu = \text{constant:} \quad \left( \frac{\partial h}{\partial s} \right)_\nu = T + \nu \left( \frac{\partial P}{\partial s} \right)_\nu \quad (a)$$

From the  $ds$  relation:  $ds = \frac{c_\nu}{T} dT + \left( \frac{\partial P}{\partial T} \right)_\nu d\nu$

Divide by  $dP$  holding  $\nu$  constant:  $\left( \frac{\partial s}{\partial P} \right)_\nu = \frac{c_\nu}{T} \left( \frac{\partial T}{\partial P} \right)_\nu$  or  $\left( \frac{\partial P}{\partial s} \right)_\nu = \frac{T}{c_\nu} \left( \frac{\partial P}{\partial T} \right)_\nu$  (b)

Using the properties  $P$ ,  $T$ ,  $\nu$ , the cyclic relation can be expressed as

$$\left( \frac{\partial P}{\partial T} \right)_\nu \left( \frac{\partial T}{\partial \nu} \right)_P \left( \frac{\partial \nu}{\partial P} \right)_T = -1 \longrightarrow \left( \frac{\partial P}{\partial T} \right)_\nu = - \left( \frac{\partial \nu}{\partial T} \right)_P \left( \frac{\partial P}{\partial \nu} \right)_T = (-\beta \nu) \left( \frac{1}{-\alpha \nu} \right) = \frac{\beta}{\alpha} \quad (c)$$

where we used the definitions of  $\alpha$  and  $\beta$ . Substituting (b) and (c) into (a),

$$\left( \frac{\partial h}{\partial s} \right)_\nu = T + \nu \left( \frac{\partial P}{\partial s} \right)_\nu = T + \frac{T\beta\nu}{c_\nu\alpha} > T$$

Here  $\alpha$  is positive for all phases of all substances.  $T$  is the absolute temperature that is also positive, so is  $c_\nu$ . Therefore, the second term on the right is always a positive quantity since  $\beta$  is given to be positive. Then we conclude that the slope of  $P = \text{constant}$  lines is **less** than the slope of  $\nu = \text{constant}$  lines.

**12-88** Using the cyclic relation and the first Maxwell relation, the other three Maxwell relations are to be obtained.

**Analysis** (1) Using the properties  $P$ ,  $s$ ,  $\mathbf{v}$ , the cyclic relation can be expressed as

$$\left(\frac{\partial P}{\partial s}\right)_{\mathbf{v}} \left(\frac{\partial s}{\partial \mathbf{v}}\right)_P \left(\frac{\partial \mathbf{v}}{\partial P}\right)_s = -1$$

Substituting the first Maxwell relation,  $\left(\frac{\partial T}{\partial \mathbf{v}}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_{\mathbf{v}}$ ,

$$-\left(\frac{\partial T}{\partial \mathbf{v}}\right)_s \left(\frac{\partial s}{\partial \mathbf{v}}\right)_P \left(\frac{\partial \mathbf{v}}{\partial P}\right)_s = -1 \longrightarrow \left(\frac{\partial T}{\partial P}\right)_s \left(\frac{\partial s}{\partial \mathbf{v}}\right)_P = 1 \longrightarrow \left(\frac{\partial T}{\partial P}\right)_s = \left(\frac{\partial \mathbf{v}}{\partial s}\right)_P$$

(2) Using the properties  $T$ ,  $\mathbf{v}$ ,  $s$ , the cyclic relation can be expressed as

$$\left(\frac{\partial T}{\partial \mathbf{v}}\right)_s \left(\frac{\partial \mathbf{v}}{\partial s}\right)_T \left(\frac{\partial s}{\partial T}\right)_{\mathbf{v}} = -1$$

Substituting the first Maxwell relation,  $\left(\frac{\partial T}{\partial \mathbf{v}}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_{\mathbf{v}}$ ,

$$-\left(\frac{\partial P}{\partial s}\right)_{\mathbf{v}} \left(\frac{\partial \mathbf{v}}{\partial s}\right)_T \left(\frac{\partial s}{\partial T}\right)_{\mathbf{v}} = -1 \longrightarrow \left(\frac{\partial P}{\partial T}\right)_{\mathbf{v}} \left(\frac{\partial \mathbf{v}}{\partial s}\right)_T = 1 \longrightarrow \left(\frac{\partial s}{\partial \mathbf{v}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\mathbf{v}}$$

(3) Using the properties  $P$ ,  $T$ ,  $\mathbf{v}$ , the cyclic relation can be expressed as

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

Substituting the third Maxwell relation,  $\left(\frac{\partial s}{\partial \mathbf{v}}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{\mathbf{v}}$ ,

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

**12-89** It is to be shown that the slope of a constant-pressure line on an  $h$ - $s$  diagram is constant in the saturation region and increases with temperature in the superheated region.

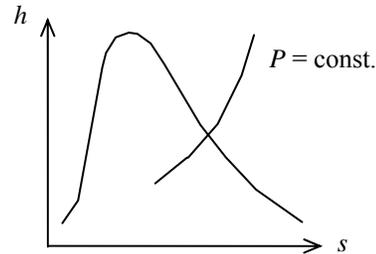
**Analysis** For  $P = \text{constant}$ ,  $dP = 0$  and the given relation reduces to  $dh = Tds$ , which can also be expressed as

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

Thus the slope of the  $P = \text{constant}$  lines on an  $h$ - $s$  diagram is equal to the temperature.

(a) In the saturation region,  $T = \text{constant}$  for  $P = \text{constant}$  lines, and the slope remains constant.

(b) In the superheat region, the slope increases with increasing temperature since the slope is equal temperature.



**12-90** It is to be shown that

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

**Analysis** Using the definition of  $c_v$ ,

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

Substituting the first Maxwell relation  $\left(\frac{\partial s}{\partial P}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_s$ ,

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

Using the definition of  $c_p$ ,

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

Substituting the second Maxwell relation  $\left(\frac{\partial s}{\partial v}\right)_P = \left(\frac{\partial P}{\partial T}\right)_s$ ,

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

**12-91** It is to be proven that for a simple compressible substance  $\left(\frac{\partial s}{\partial \nu}\right)_u = \frac{P}{T}$ .

**Analysis** The proof is simply obtained as

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

**12-92** It is to be proven by using the definitions of pressure and temperature,  $T = \left(\frac{\partial u}{\partial s}\right)_\nu$  and  $P = -\left(\frac{\partial u}{\partial \nu}\right)_s$ ,

that for ideal gases, the development of the constant-pressure specific heat yields  $\left(\frac{\partial h}{\partial P}\right)_T = 0$

**Analysis** The definition for enthalpy is

$$h = u + P\nu$$

Then,

$$\left(\frac{\partial h}{\partial P}\right)_T = \left(\frac{\partial u}{\partial P}\right)_T + P\left(\frac{\partial \nu}{\partial P}\right)_T + \nu\left(\frac{\partial P}{\partial P}\right)_T$$

Assume  $u = u(s, \nu)$

Then,

$$\begin{aligned} du &= \left(\frac{\partial u}{\partial s}\right)_\nu ds + \left(\frac{\partial u}{\partial \nu}\right)_s d\nu \\ \left(\frac{\partial u}{\partial P}\right)_T &= \left(\frac{\partial u}{\partial s}\right)_\nu \left(\frac{\partial s}{\partial P}\right)_T + \left(\frac{\partial u}{\partial \nu}\right)_s \left(\frac{\partial \nu}{\partial P}\right)_T \\ \left(\frac{\partial u}{\partial P}\right)_T &= T \left[ -\left(\frac{\partial \nu}{\partial T}\right)_P \right] - P \left(\frac{\partial \nu}{\partial P}\right)_T = -(T + P) \left(\frac{\partial \nu}{\partial P}\right)_T \\ \left(\frac{\partial h}{\partial P}\right)_T &= -(T + P) \left(\frac{\partial \nu}{\partial P}\right)_T + P \left(\frac{\partial \nu}{\partial P}\right)_T + \nu = -T \left(\frac{\partial \nu}{\partial P}\right)_T + \nu \end{aligned}$$

For ideal gases

$$\nu = \frac{RT}{P} \quad \text{and} \quad \left(\frac{\partial \nu}{\partial P}\right)_T = -\frac{\nu}{P}$$

Then,

$$\left(\frac{\partial h}{\partial P}\right)_T = -\frac{TR}{P} + \nu = -\nu + \nu = 0$$

**12-93** It is to be proven by using the definitions of pressure and temperature,  $T = \left(\frac{\partial u}{\partial s}\right)_v$  and  $P = -\left(\frac{\partial u}{\partial v}\right)_s$  that for ideal gases, the development of the constant-volume specific heat yields  $\left(\frac{\partial u}{\partial v}\right)_T = 0$ .

**Analysis** Assume  $u = u(s, v)$

Then,

$$\begin{aligned} du &= \left(\frac{\partial u}{\partial s}\right)_v ds + \left(\frac{\partial u}{\partial v}\right)_s dv \\ \left(\frac{\partial u}{\partial v}\right)_T &= \left(\frac{\partial u}{\partial s}\right)_v \left(\frac{\partial s}{\partial v}\right)_T + \left(\frac{\partial u}{\partial v}\right)_s \left(\frac{\partial v}{\partial v}\right)_T \\ &= T \left(\frac{\partial s}{\partial v}\right)_T + P \end{aligned}$$

From Maxwell equation,

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

For ideal gases

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

Then,

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

**12-94** Expressions for  $h$ ,  $u$ ,  $s^\circ$ ,  $P_r$ , and  $\nu_r$  for an ideal gas whose  $c_p^\circ$  is given by

$$c_p^\circ = \sum a_i T^{i-n} + a_0 e^{\beta/T} \left( \frac{\beta/T}{e^{\beta/T} - 1} \right) \text{ are to be developed.}$$

**Analysis** The enthalpy of this substance relative to a reference state is given by

$$h = \int_{T_{\text{ref}}}^T c_p dT = \sum \frac{a_1}{i-n+1} (T^{i-n+1} - T_{\text{ref}}^{i-n+1}) + a_0 \left[ e^{\beta/T} - e^{\beta/T_{\text{ref}}} - eE_1\left(1 - \frac{\beta}{T}\right) - eE_1\left(1 - \frac{\beta}{T_{\text{ref}}}\right) \right]$$

where  $E_1(x)$  is the exponential integral function of order 1. Similarly,  $s^\circ$  is given by

$$s^\circ = \int_{T_{\text{ref}}}^T \frac{c_p}{T} dT = \sum \frac{a_1}{i-n} (T^{i-n} - T_{\text{ref}}^{i-n}) - a_0 \left[ e^{\beta/T} - e^{\beta/T_{\text{ref}}} - eE_1\left(1 - \frac{\beta}{T}\right) - eE_1\left(1 - \frac{\beta}{T_{\text{ref}}}\right) \right]$$

With these two results,

$$u = h - P\nu$$

$$P_r = e^{s^\circ/R}$$

According to the  $du$  form of Gibbs equations,

$$\frac{du}{T} = -R \frac{d\nu}{\nu}$$

Noting that for ideal gases,  $c_\nu = c_p - R$  and  $du = c_\nu dT$ , this expression reduces to

$$(c_p - R) \frac{dT}{T} = -R \frac{d\nu}{\nu}$$

When this is integrated between the reference and actual states, the result is

$$\int c_p \frac{dT}{T} - R \ln \frac{T}{T_{\text{ref}}} = -R \ln \frac{\nu}{\nu_{\text{ref}}}$$

Solving this for the specific volume ratio gives

$$\frac{\nu}{\nu_{\text{ref}}} = - \frac{\left( e^{s^\circ} - e^R \frac{T}{T_{\text{ref}}} \right)}{e^R} = - \frac{e^{s^\circ}}{e^R} + \frac{e^R \frac{T}{T_{\text{ref}}}}{e^R} = - \frac{e^{s^\circ}}{e^R} + \frac{T}{T_{\text{ref}}} = - \exp(s^\circ - R) + \frac{T}{T_{\text{ref}}}$$

The ratio of the specific volumes at two states which have the same entropy is then

$$\frac{\nu_2}{\nu_1} = \frac{\nu_{r,2}}{\nu_{r,1}} = - \exp(s_2^\circ - s_1^\circ - R) + \frac{T_2}{T_1}$$

Inspection of this result gives

$$\nu_r = - \exp(s^\circ - R) + T$$

**12-95** The  $c_p$  of nitrogen at 300 kPa and 400 K is to be estimated using the relation given and its definition, and the results are to be compared to the value listed in Table A-2b.

**Analysis** (a) We treat nitrogen as an ideal gas with  $R = 0.297 \text{ kJ/kg}\cdot\text{K}$  and  $k = 1.397$ . Note that  $PT^{-k/(k-1)} = C = \text{constant}$  for the isentropic processes of ideal gases. The  $c_p$  relation is given as

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

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

$$P = CT^{k/(k-1)} \longrightarrow \left( \frac{\partial P}{\partial T} \right)_s = \frac{k}{k-1} CT^{k/(k-1)-1} = \frac{k}{k-1} (PT^{-k/(k-1)}) T^{k/(k-1)-1} = \frac{kP}{T(k-1)}$$

Substituting,

$$c_p = T \left( \frac{kP}{T(k-1)} \right) \left( \frac{R}{P} \right) = \frac{kR}{k-1} = \frac{1.397(0.297 \text{ kJ/kg}\cdot\text{K})}{1.397-1} = 1.045 \text{ kJ/kg}\cdot\text{K}$$

(b) The  $c_p$  is defined as  $c_p = \left( \frac{\partial h}{\partial T} \right)_P$ . Replacing the differentials by differences,

$$c_p \cong \left( \frac{\Delta h}{\Delta T} \right)_{P=300\text{kPa}} = \frac{h(410 \text{ K}) - h(390 \text{ K})}{(410 - 390)\text{K}} = \frac{(11,932 - 11,347)/28.0 \text{ kJ/kg}}{(410 - 390)\text{K}} = \mathbf{1.045 \text{ kJ/kg}\cdot\text{K}}$$

(Compare: Table A-2b at 400 K  $\rightarrow c_p = 1.044 \text{ kJ/kg}\cdot\text{K}$ )

**12-96** The temperature change of steam and the average Joule-Thompson coefficient during a throttling process are to be estimated.

**Analysis** The enthalpy of steam at 4.5 MPa and  $T = 300^\circ\text{C}$  is  $h = 2944.2 \text{ kJ/kg}$ . Now consider a throttling process from this state to 2.5 MPa. The temperature of the steam at the end of this throttling process will be

$$\left. \begin{array}{l} P = 2.5 \text{ MPa} \\ h = 2944.2 \text{ kJ/kg} \end{array} \right\} T_2 = 273.72^\circ\text{C}$$

Thus the temperature drop during this throttling process is

$$\Delta T = T_2 - T_1 = 273.72 - 300 = \mathbf{-26.28^\circ\text{C}}$$

The average Joule-Thomson coefficient for this process is determined from

$$\mu = \left( \frac{\partial T}{\partial P} \right)_h \cong \left( \frac{\Delta T}{\Delta P} \right)_{h=3204.7\text{kJ/kg}} = \frac{(273.72 - 300)^\circ\text{C}}{(2.5 - 4.5)\text{MPa}} = \mathbf{13.14^\circ\text{C/MPa}}$$

**12-97** Argon enters a turbine at a specified state and leaves at another specified state. Power output of the turbine and exergy destruction during this process are to be determined using the generalized charts.

**Properties** The gas constant and critical properties of Argon are  $R = 0.2081 \text{ kJ/kg}\cdot\text{K}$ ,  $T_{cr} = 151 \text{ K}$ , and  $P_{cr} = 4.86 \text{ MPa}$  (Table A-1).

**Analysis (a)** The enthalpy and entropy departures of argon at the specified states are determined from the generalized charts to be

$$\left. \begin{aligned} T_{R_1} &= \frac{T_1}{T_{cr}} = \frac{600}{151} = 3.97 \\ P_{R_1} &= \frac{P_1}{P_{cr}} = \frac{7}{4.86} = 1.44 \end{aligned} \right\} Z_{h_1} \cong 0 \text{ and } Z_{s_1} \cong 0$$

Thus argon behaves as an ideal gas at turbine inlet. Also,

$$\left. \begin{aligned} T_{R_2} &= \frac{T_2}{T_{cr}} = \frac{280}{151} = 1.85 \\ P_{R_2} &= \frac{P_2}{P_{cr}} = \frac{1}{4.86} = 0.206 \end{aligned} \right\} Z_{h_2} = 0.04 \text{ and } Z_{s_2} = 0.02$$

Thus,

$$h_2 - h_1 = RT_{cr}(Z_{h_1} - Z_{h_2}) + (h_2 - h_1)_{\text{ideal}} \\ = (0.2081)(151)(0 - 0.04) + 0.5203(280 - 600) = -167.8 \text{ kJ/kg}$$

The power output of the turbine is to be determined from the energy balance equation,

$$\dot{E}_{\text{in}} - \dot{E}_{\text{out}} = \Delta \dot{E}_{\text{system}} = 0 \text{ (steady)} \rightarrow \dot{E}_{\text{in}} = \dot{E}_{\text{out}} \\ \dot{m}(h_1 + V_1^2 / 2) = \dot{m}(h_2 + V_2^2 / 2) + \dot{Q}_{\text{out}} + \dot{W}_{\text{out}} \\ \dot{W}_{\text{out}} = -\dot{m} \left[ (h_2 - h_1) + \frac{V_2^2 - V_1^2}{2} \right] - \dot{Q}_{\text{out}}$$

Substituting,

$$\dot{W}_{\text{out}} = -(5 \text{ kg/s}) \left( -167.8 + \frac{(150 \text{ m/s})^2 - (100 \text{ m/s})^2}{2} \left( \frac{1 \text{ kJ/kg}}{1000 \text{ m}^2/\text{s}^2} \right) \right) - 60 \text{ kJ/s} = 747.8 \text{ kW}$$

(b) Under steady conditions, the rate form of the entropy balance for the turbine simplifies to

$$\dot{S}_{\text{in}} - \dot{S}_{\text{out}} + \dot{S}_{\text{gen}} = \Delta \dot{S}_{\text{system}} \stackrel{\circ}{=} 0 \\ \dot{m}s_1 - \dot{m}s_2 - \frac{\dot{Q}_{\text{out}}}{T_{b,\text{out}}} + \dot{S}_{\text{gen}} = 0 \rightarrow \dot{S}_{\text{gen}} = \dot{m}(s_2 - s_1) + \frac{\dot{Q}_{\text{out}}}{T_0}$$

The exergy destroyed during a process can be determined from an exergy balance or directly from its definition  $X_{\text{destroyed}} = T_0 \dot{S}_{\text{gen}}$ ,

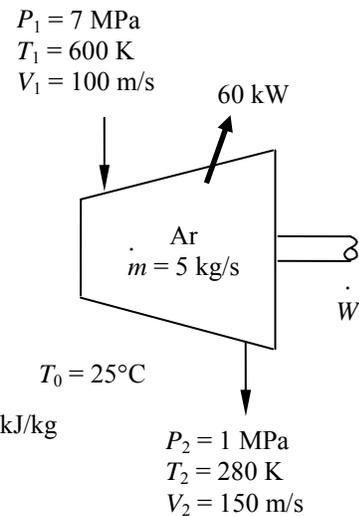
$$\dot{X}_{\text{destroyed}} = T_0 \dot{S}_{\text{gen}} = T_0 \left( \dot{m}(s_2 - s_1) + \frac{\dot{Q}_{\text{out}}}{T_0} \right)$$

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

and  $(s_2 - s_1)_{\text{ideal}} = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} = 0.5203 \ln \frac{280}{600} - 0.2081 \ln \frac{1}{7} = 0.0084 \text{ kJ/kg}\cdot\text{K}$

Thus,  $s_2 - s_1 = R(Z_{s_1} - Z_{s_2}) + (s_2 - s_1)_{\text{ideal}} = (0.2081)[0 - (0.02)] + 0.0084 = 0.0042 \text{ kJ/kg}\cdot\text{K}$

Substituting,  $\dot{X}_{\text{destroyed}} = (298 \text{ K}) \left( (5 \text{ kg/s})(0.0042 \text{ kJ/kg}\cdot\text{K}) + \frac{60 \text{ kW}}{298 \text{ K}} \right) = \mathbf{66.3 \text{ kW}}$



**12-98 EES** Problem 12-97 is reconsidered. The problem is to be solved assuming steam is the working fluid by using the generalized chart method and EES data for steam. The power output and the exergy destruction rate for these two calculation methods against the turbine exit pressure are to be plotted.

*Analysis* The problem is solved using EES, and the results are tabulated and plotted below.

" Input Data "

```
T[1]=600 [K]
P[1]=7000 [kPa]
Vel[1]=100 [m/s]
T[2]=455 [K]
P[2]=1000 [kPa]
Vel[2]=150 [m/s]
Q_dot_out=60 [kW]
T_o=25+273 "[K]"
m_dot=5 [kg/s]
Name$='Steam_iapws'
T_critical=647.3 [K]
P_critical=22090 [kPa]
Fluid$='H2O'
```

```
R_u=8.314
M=molarmass(Fluid$)
R=R_u/M
```

\*\*\*\*\* IDEAL GAS SOLUTION \*\*\*\*\*

"State 1"

```
h_ideal[1]=enthalpy(Fluid$,T=T[1]) "Enthalpy of ideal gas"
s_ideal[1]=entropy(Fluid$, T=T[1], P=P[1]) "Entropy of ideal gas"
```

"State 2"

```
h_ideal[2]=enthalpy(Fluid$,T=T[2]) "Enthalpy of ideal gas"
s_ideal[2]=entropy(Fluid$, T=T[2], P=P[2]) "Entropy of ideal gas"
```

"Conservation of Energy, Steady-flow: "

"E\_dot\_in=E\_dot\_out"

$$m_{\dot{}}(h_{\text{ideal}[1]} + \text{Vel}[1]^2/2 * \text{convert}(m^2/s^2, kJ/kg)) = m_{\dot{}}(h_{\text{ideal}[2]} + \text{Vel}[2]^2/2 * \text{convert}(m^2/s^2, kJ/kg)) + Q_{\dot{}}_{\text{out}} + W_{\dot{}}_{\text{out\_ideal}}$$

"Second Law analysis:"

"S\_dot\_in-S\_dot\_out+S\_dot\_gen = 0"

$$m_{\dot{}}s_{\text{ideal}[1]} - m_{\dot{}}s_{\text{ideal}[2]} - Q_{\dot{}}_{\text{out}}/T_o + S_{\dot{}}_{\text{gen\_ideal}} = 0$$

"Exergy Destroyed:"

$$X_{\dot{}}_{\text{destroyed\_ideal}} = T_o * S_{\dot{}}_{\text{gen\_ideal}}$$

\*\*\*\*\* COMPRESSIBILITY CHART SOLUTION \*\*\*\*\*

"State 1"

```
Tr[1]=T[1]/T_critical
Pr[1]=P[1]/P_critical
Z[1]=COMPRESS(Tr[1], Pr[1])
DELTAh[1]=ENTHDEP(Tr[1], Pr[1])*R*T_critical "Enthalpy departure"
h_chart[1]=h_ideal[1]-DELTAh[1] "Enthalpy of real gas using charts"
DELTAAs[1]=ENTRDEP(Tr[1], Pr[1])*R "Entropy departure"
s_chart[1]=s_ideal[1]-DELTAAs[1] "Entropy of real gas using charts"
```

"State 2"

```

Tr[2]=T[2]/T_critical
Pr[2]=P[2]/P_critical
Z[2]=COMPRESS(Tr[2], Pr[2])
DELTAh[2]=ENTHDEP(Tr[2], Pr[2])*R*T_critical "Enthalpy departure"
DELTAAs[2]=ENTRDEP(Tr[2], Pr[2])*R "Entropy departure"
h_chart[2]=h_ideal[2]-DELTAh[2] "Enthalpy of real gas using charts"
s_chart[2]=s_ideal[2]-DELTAAs[2] "Entropy of real gas using charts"

```

```

"Conservation of Energy, Steady-flow: "
"E_dot_in=E_dot_out"

```

```

m_dot*(h_chart[1]+Vel[1]^2/2*convert(m^2/s^2,kJ/kg))=m_dot*(h_chart[2]+Vel[2]^2/2*convert(m^
2/s^2,kJ/kg))+Q_dot_out+W_dot_out_chart

```

```

"Second Law analysis:"
"S_dot_in-S_dot_out+S_dot_gen = 0"
m_dot*s_chart[1] - m_dot*s_chart[2] - Q_dot_out/T_o + S_dot_gen_chart = 0

```

```

"Exergy Destroyed:"

```

```

X_dot_destroyed_chart = T_o*S_dot_gen_chart"[kW]"

```

```

***** SOLUTION USING EES BUILT-IN PROPERTY DATA *****

```

```

"At state 1"
h_ees[1]=enthalpy(Name$,T=T[1],P=P[1])
s_ees[1]=entropy(Name$,T=T[1],P=P[1])
"At state 2"
h_ees[2]=enthalpy(Name$,T=T[2],P=P[2])
s_ees[2]=entropy(Name$,T=T[2],P=P[2])

```

```

"Conservation of Energy, Steady-flow: "
"E_dot_in=E_dot_out"

```

```

m_dot*(h_ees[1]+Vel[1]^2/2*convert(m^2/s^2,kJ/kg))=m_dot*(h_ees[2]+Vel[2]^2/2*convert(m^2/s
^2,kJ/kg))+Q_dot_out+W_dot_out_ees

```

```

"Second Law analysis:"
"S_dot_in-S_dot_out+S_dot_gen = 0"
m_dot*s_ees[1] - m_dot*s_ees[2] - Q_dot_out/T_o + S_dot_gen_ees= 0

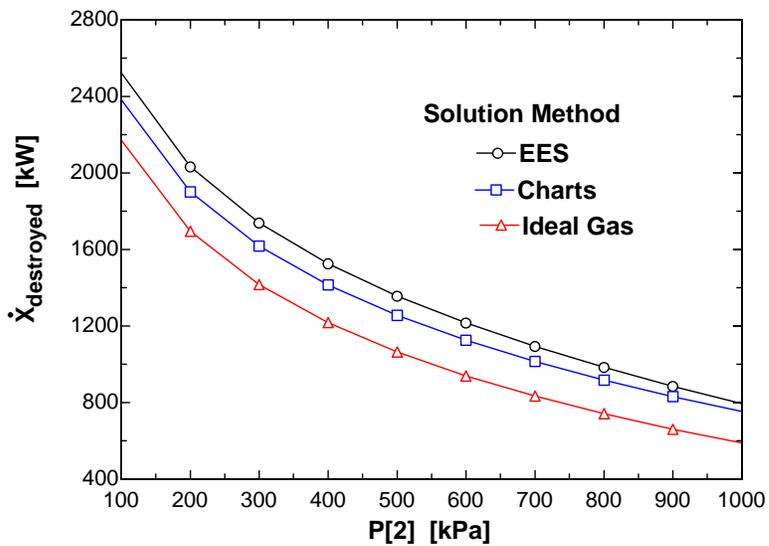
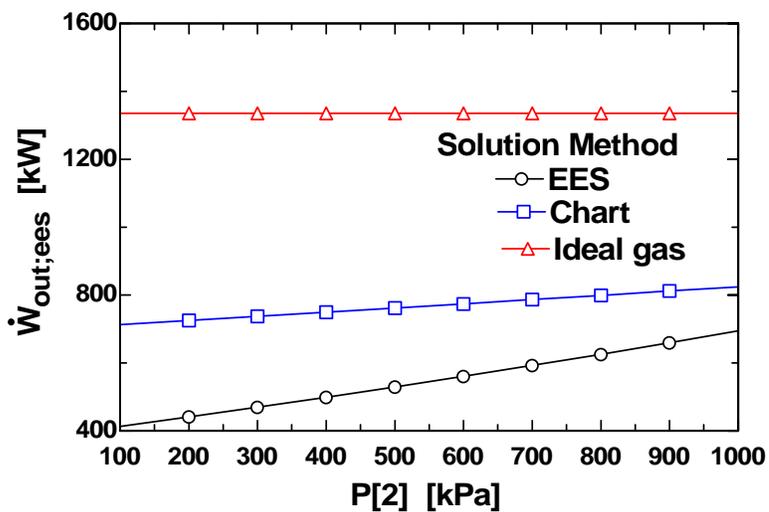
```

```

"Exergy Destroyed:"
X_dot_destroyed_ees = T_o*S_dot_gen_ees

```

$P_2$ [kPa]	$T_2$ [K]	$W_{outchart}$ [kW]	$W_{outees}$ [kW]	$W_{outideal}$ [kW]	$X_{destroyedchart}$ [kW]	$X_{destroyeees}$ [kW]	$X_{destroyideal}$ [kW]
100	455	713.3	420.6	1336	2383	2519	2171
200	455	725.2	448.1	1336	1901	2029	1694
300	455	737.3	476.5	1336	1617	1736	1416
400	455	749.5	505.8	1336	1415	1523	1218
500	455	761.7	536.1	1336	1256	1354	1064
600	455	774.1	567.5	1336	1126	1212	939
700	455	786.5	600	1336	1014	1090	833
800	455	799.1	633.9	1336	917.3	980.1	741.2
900	455	811.8	669.3	1336	831	880.6	660.2
1000	455	824.5	706.6	1336	753.1	788.4	587.7



**12-99** An adiabatic storage tank that is initially evacuated is connected to a supply line that carries nitrogen. A valve is opened, and nitrogen flows into the tank. The final temperature in the tank is to be determined by treating nitrogen as an ideal gas and using the generalized charts, and the results are to be compared to the given actual value.

**Assumptions** 1 Uniform flow conditions exist. 2 Kinetic and potential energies are negligible.

**Analysis** We take the tank as the system, which is a control volume since mass crosses the boundary. Noting that the microscopic energies of flowing and nonflowing fluids are represented by enthalpy  $h$  and internal energy  $u$ , respectively, the mass and energy balances for this uniform-flow system can be expressed as

$$\text{Mass balance: } m_{\text{in}} - m_{\text{out}} = \Delta m_{\text{system}} \rightarrow m_i = m_2 \quad (\text{since } m_{\text{out}} = m_{\text{initial}} = 0)$$

$$\text{Energy balance: } E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}} \rightarrow 0 + m_i h_i = m_2 u_2$$

$$\text{Combining the two balances: } u_2 = h_i$$

(a) From the ideal gas property table of nitrogen, at 225 K we read

$$\bar{u}_2 = \bar{h}_i = \bar{h}_{@225\text{ K}} = 6,537 \text{ kJ/kmol}$$

The temperature that corresponds to this  $\bar{u}_2$  value is

$$T_2 = \mathbf{314.8 \text{ K}} \quad (7.4\% \text{ error})$$

(b) Using the generalized enthalpy departure chart,  $h_i$  is determined to be

$$\left. \begin{aligned} T_{R,i} &= \frac{T_i}{T_{\text{cr}}} = \frac{225}{126.2} = 1.78 \\ P_{R,i} &= \frac{P_i}{P_{\text{cr}}} = \frac{10}{3.39} = 2.95 \end{aligned} \right\} Z_{h,i} = \frac{\bar{h}_{i,\text{ideal}} - \bar{h}_i}{R_u T_{\text{cr}}} = 0.9 \quad (\text{Fig. A-29})$$

Thus,

$$\bar{h}_i = \bar{h}_{i,\text{ideal}} - 0.9 R_u T_{\text{cr}} = 6,537 - (0.9)(8.314)(126.2) = 5,593 \text{ kJ/kmol}$$

and

$$\bar{u}_2 = \bar{h}_i = 5,593 \text{ kJ/kmol}$$

Try  $T_2 = 280 \text{ K}$ . Then at  $P_{R2} = 2.95$  and  $T_{R2} = 2.22$  we read  $Z_2 = 0.98$  and  $(\bar{h}_{2,\text{ideal}} - \bar{h}_2) / R_u T_{\text{cr}} = 0.55$

Thus,

$$\bar{h}_2 = \bar{h}_{2,\text{ideal}} - 0.55 R_u T_{\text{cr}} = 8,141 - (0.55)(8.314)(126.2) = 7,564 \text{ kJ/kmol}$$

$$\bar{u}_2 = \bar{h}_2 - Z R_u T_2 = 7,564 - (0.98)(8.314)(280) = 5,283 \text{ kJ/kmol}$$

Try  $T_2 = 300 \text{ K}$ . Then at  $P_{R2} = 2.95$  and  $T_{R2} = 2.38$  we read  $Z_2 = 1.0$  and  $(\bar{h}_{2,\text{ideal}} - \bar{h}_2) / R_u T_{\text{cr}} = 0.50$

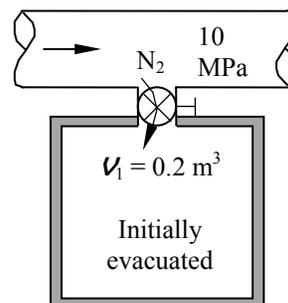
Thus,

$$\bar{h}_2 = \bar{h}_{2,\text{ideal}} - 0.50 R_u T_{\text{cr}} = 8,723 - (0.50)(8.314)(126.2) = 8,198 \text{ kJ/kmol}$$

$$\bar{u}_2 = \bar{h}_2 - Z R_u T_2 = 8,198 - (1.0)(8.314)(300) = 5,704 \text{ kJ/kmol}$$

By linear interpolation,

$$T_2 = \mathbf{294.7 \text{ K}} \quad (0.6\% \text{ error})$$



**12-100** Propane is compressed in a steady-flow device. The entropy change and the specific work required for this compression are to be determined using the departure charts and treating the propane as an ideal gas with temperature variable specific heats.

**Properties** The properties of propane are (Table A-1, A-2a)

$$M = 44.097 \text{ kg/kmol}, R = 0.1885 \text{ kJ/kg} \cdot \text{K}, T_{\text{cr}} = 370 \text{ K}, P_{\text{cr}} = 4.26 \text{ MPa}, c_p = 1.6794 \text{ kJ/kg} \cdot \text{K}$$

**Analysis** (a) Using empirical correlation for the  $c_p$  of propane as given in Table A-2c gives

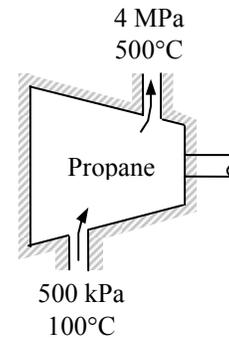
$$\begin{aligned} \bar{w}_{\text{in}} &= (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \int_1^2 c_p dT = \int_1^2 (a + bT + cT^2 + dT^3) dT \\ &= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4) \\ &= -4.04(773 - 373) + \frac{0.3048}{2}(773^2 - 373^2) - \frac{15.72 \times 10^{-5}}{3}(773^3 - 373^3) + \frac{31.74 \times 10^{-9}}{4}(773^4 - 373^4) \\ &= 49,440 \text{ kJ/kmol} \end{aligned}$$

The work input per unit mass is

$$w_{\text{in}} = \frac{\bar{w}_{\text{in}}}{M} = \frac{49,440 \text{ kJ/kmol}}{44.097 \text{ kg/kmol}} = \mathbf{1121 \text{ kJ/kg}}$$

Similarly, the entropy change is given by

$$\begin{aligned} (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} &= \int_1^2 \frac{c_p}{T} dT - R_u \ln \frac{P_2}{P_1} = \int_1^2 \left( \frac{a}{T} + b + cT + dT^2 \right) dT - R_u \ln \frac{P_2}{P_1} \\ &= a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) + \frac{d}{3}(T_2^3 - T_1^3) - R_u \ln \frac{P_2}{P_1} \\ &= -4.04 \ln \frac{773}{373} + 0.3048(773 - 373) - \frac{15.72 \times 10^{-5}}{2}(773^2 - 373^2) + \frac{31.74 \times 10^{-9}}{3}(773^3 - 373^3) \\ &\quad - (8.314) \ln \frac{4000}{500} \\ &= 69.995 \text{ kJ/kmol} \cdot \text{K} \end{aligned}$$



The entropy change per unit mass is

$$(s_2 - s_1)_{\text{ideal}} = \frac{(\bar{s}_2 - \bar{s}_1)_{\text{ideal}}}{M} = \frac{69.995 \text{ kJ/kmol} \cdot \text{K}}{44.097 \text{ kg/kmol}} = \mathbf{1.587 \text{ kJ/kg} \cdot \text{K}}$$

(b) The enthalpy and entropy departures of propane at the specified states are determined from the generalized charts to be (Fig. A-29, A-30 or from EES)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{373}{370} = 1.008 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{0.5}{4.26} = 0.117 \end{aligned} \right\} \begin{aligned} Z_{h1} &= 0.124 \\ Z_{s1} &= 0.0837 \end{aligned} \quad \left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{773}{370} = 2.089 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{4}{4.26} = 0.939 \end{aligned} \right\} \begin{aligned} Z_{h2} &= 0.233 \\ Z_{s2} &= 0.105 \end{aligned}$$

The work input is determined from

$$\begin{aligned} w_{\text{in}} &= h_2 - h_1 = (h_2 - h_1)_{\text{ideal}} - RT_{\text{cr}}(Z_{h2} - Z_{h1}) \\ &= 1121 - (0.1885)(370)(0.233 - 0.124) = \mathbf{1113 \text{ kJ/kg}} \end{aligned}$$

and the entropy change is determined to be

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

$$= 1.587 - (0.1885)(0.105 - 0.0837) = \mathbf{1.583 \text{ kJ/kg} \cdot \text{K}}$$

**Discussion** Let us see what happens when constant specific heats for propane at the room temperature are used when calculating enthalpy and entropy changes under ideal gas assumption. The entropy and enthalpy changes are determined from

$$(h_2 - h_1)_{\text{ideal}} = c_p(T_2 - T_1) = (1.6794 \text{ kJ/kg} \cdot \text{K})(500 - 100)\text{K} = 671.8 \text{ kJ/kg}$$

$$(s_2 - s_1)_{\text{ideal}} = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}$$

$$= (1.6794) \ln \frac{773}{373} - (0.1885) \ln \frac{4000}{500} = 0.8318 \text{ kJ/kg} \cdot \text{K}$$

With departure factors,

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

$$= 671.8 - (0.1885)(370)(0.233 - 0.124) = 664.2 \text{ kJ/kg}$$

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

$$= 0.8318 - (0.1885)(0.105 - 0.0837) = \mathbf{0.8278 \text{ kJ/kg} \cdot \text{K}}$$

These are not any close to the results obtained using variable specific heats. This shows that using constant specific heats may yield unacceptable results.

**12-101** Propane is compressed in a steady-flow device. The second-law efficiency of the compression process is to be determined.

**Properties** The properties of propane are (Table A-1, A-2a)

$$M = 44.097 \text{ kg/kmol}, R = 0.1885 \text{ kJ/kg} \cdot \text{K}, T_{\text{cr}} = 370 \text{ K}, P_{\text{cr}} = 4.26 \text{ MPa}, c_p = 1.6794 \text{ kJ/kg} \cdot \text{K}$$

**Analysis** Using the variable specific heat results of the previous problem, the actual and reversible works are

$$\begin{aligned} w_{\text{in}} &= h_2 - h_1 = 1113 \text{ kJ/kg} \\ w_{\text{rev,in}} &= h_2 - h_1 - T_0(s_2 - s_1) = 1113 \text{ kJ/kg} - (298 \text{ K})(1.583 \text{ kJ/kg} \cdot \text{K}) = 641.3 \text{ kJ/kg} \end{aligned}$$

The second-law efficiency is then

$$\eta_{\text{II}} = \frac{w_{\text{rev,in}}}{w_{\text{in}}} = \frac{641.3}{1113} = \mathbf{0.576}$$

**12-102E** Methane is to be adiabatically and reversibly compressed in a steady-flow device. The specific work required for this compression is to be determined using the departure charts and treating the methane as an ideal gas with temperature variable specific heats.

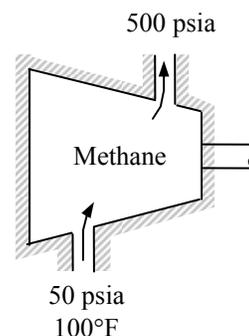
**Properties** The properties of methane are (Table A-1E)

$$M = 16.043 \text{ lbm/lbmol}, R = 0.1238 \text{ Btu/lbm} \cdot \text{R}, T_{\text{cr}} = 343.9 \text{ R}, P_{\text{cr}} = 673 \text{ psia}$$

**Analysis** The temperature at the exit state may be determined by the fact that the process is isentropic and the molar entropy change between the inlet and exit is zero.

When the expression of Table A-2Ec is substituted for  $c_p$  and the integration performed, we obtain

$$\begin{aligned} (\bar{s}_2 - \bar{s}_1)_{\text{ideal}} &= \int_1^2 \frac{c_p}{T} dT - R_u \ln \frac{P_2}{P_1} = \int_1^2 \left( \frac{a}{T} + b + cT + dT^2 \right) dT - R_u \ln \frac{P_2}{P_1} \\ &= a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) + \frac{d}{3}(T_2^3 - T_1^3) - R_u \ln \frac{P_2}{P_1} \end{aligned}$$



Substituting,

$$\begin{aligned} 0 &= 4.75 \ln \frac{T_2}{560} + 0.006666(T_2 - 560) + \frac{0.09352 \times 10^{-5}}{2}(T_2^2 - 560^2) \\ &\quad - \frac{0.4510 \times 10^{-9}}{3}(T_2^3 - 560^3) - (1.9858) \ln \frac{500}{50} \end{aligned}$$

Solving this equation by EES or an iterative solution gives

$$T_2 = 892 \text{ R}$$

When an energy balance is applied to the compressor, it becomes

$$\begin{aligned} \bar{w}_{\text{in}} &= (\bar{h}_2 - \bar{h}_1)_{\text{ideal}} = \int_1^2 c_p dT = \int_1^2 (a + bT + cT^2 + dT^3) dT \\ &= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4) \\ &= 4.75(892 - 560) + \frac{0.006666}{2}(892^2 - 560^2) + \frac{0.09352 \times 10^{-5}}{3}(892^3 - 560^3) \\ &\quad - \frac{0.4510 \times 10^{-9}}{4}(892^4 - 560^4) \\ &= 3290 \text{ Btu/lbmol} \end{aligned}$$

The work input per unit mass basis is

$$w_{\text{in}} = \frac{\bar{w}_{\text{in}}}{M} = \frac{3290 \text{ Btu/lbmol}}{16.043 \text{ lbm/lbmol}} = \mathbf{205.1 \text{ Btu/lbm}}$$

The enthalpy departures of propane at the specified states are determined from the generalized charts to be (Fig. A-29 or from EES)

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{560}{343.9} = 1.628 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{50}{673} = 0.0743 \end{aligned} \right\} \longrightarrow Z_{h1} = 0.0332$$

and

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{cr}} = \frac{892}{343.9} = 2.594 \\ P_{R2} &= \frac{P_2}{P_{cr}} = \frac{500}{673} = 0.743 \end{aligned} \right\} \longrightarrow Z_{h2} = 0.0990$$

The work input is determined to be

$$\begin{aligned} w_{in} &= h_2 - h_1 = (h_2 - h_1)_{ideal} - RT_{cr}(Z_{h2} - Z_{h1}) \\ &= 205.1 \text{ Btu/lbm} - (0.1238 \text{ Btu/lbm} \cdot \text{R})(343.9 \text{ R})(0.0990 - 0.0332) \\ &= \mathbf{202.3 \text{ Btu/lbm}} \end{aligned}$$

**12-103** The volume expansivity of water is given. The change in volume of water when it is heated at constant pressure is to be determined.

**Properties** The volume expansivity of water is given to be  $0.207 \times 10^{-6} \text{ K}^{-1}$  at  $20^\circ\text{C}$ .

**Analysis** We take  $\nu = \nu(P, T)$ . Its total differential is

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

which, for a constant pressure process, reduces to

$$d\nu = \left(\frac{\partial \nu}{\partial T}\right)_P dT$$

Dividing by  $\nu$  and using the definition of  $\beta$ ,

$$\frac{d\nu}{\nu} = \frac{1}{\nu} \left(\frac{\partial \nu}{\partial T}\right)_P dT = \beta dT$$

Taking  $\beta$  to be a constant, integration from 1 to 2 yields

$$\ln \frac{\nu_2}{\nu_1} = \beta(T_2 - T_1)$$

or

$$\frac{\nu_2}{\nu_1} = \exp[\beta(T_2 - T_1)]$$

Substituting the given values and noting that for a fixed mass  $\nu_2/\nu_1 = v_2/v_1$ ,

$$\begin{aligned} \nu_2 &= \nu_1 \exp[\beta(T_2 - T_1)] = (1 \text{ m}^3) \exp[(0.207 \times 10^{-6} \text{ K}^{-1})(30 - 10)^\circ\text{C}] \\ &= 1.00000414 \text{ m}^3 \end{aligned}$$

Therefore,

$$\Delta \nu = \nu_2 - \nu_1 = 1.00000414 - 1 = 0.00000414 \text{ m}^3 = \mathbf{4.14 \text{ cm}^3}$$

**12-104** It is to be shown that the position of the Joule-Thompson coefficient inversion curve on the  $T$ - $P$  plane is given by  $(\partial Z/\partial T)_P = 0$ .

**Analysis** The inversion curve is the locus of the points at which the Joule-Thompson coefficient  $\mu$  is zero,

$$\mu = \frac{1}{c_p} \left( T \left( \frac{\partial \nu}{\partial T} \right)_P - \nu \right) = 0$$

which can also be written as

$$T \left( \frac{\partial \nu}{\partial T} \right)_P - \frac{ZRT}{P} = 0 \quad (a)$$

since it is given that

$$\nu = \frac{ZRT}{P} \quad (b)$$

Taking the derivative of (b) with respect to  $T$  holding  $P$  constant gives

$$\left( \frac{\partial \nu}{\partial T} \right)_P = \left( \frac{\partial (ZRT/P)}{\partial T} \right)_P = \frac{R}{P} \left( T \left( \frac{\partial Z}{\partial T} \right)_P + Z \right)$$

Substituting in (a),

$$\begin{aligned} \frac{TR}{P} \left( T \left( \frac{\partial Z}{\partial T} \right)_P + Z \right) - \frac{ZRT}{P} &= 0 \\ T \left( \frac{\partial Z}{\partial T} \right)_P + Z - Z &= 0 \\ \left( \frac{\partial Z}{\partial T} \right)_P &= 0 \end{aligned}$$

which is the desired relation.

**12-105** It is to be shown that for an isentropic expansion or compression process  $P\nu^k = \text{constant}$ . It is also to be shown that the isentropic expansion exponent  $k$  reduces to the specific heat ratio  $c_p/c_v$  for an ideal gas.

**Analysis** We note that  $ds = 0$  for an isentropic process. Taking  $s = s(P, \nu)$ , the total differential  $ds$  can be expressed as

$$ds = \left(\frac{\partial s}{\partial P}\right)_\nu dP + \left(\frac{\partial s}{\partial \nu}\right)_P d\nu = 0 \quad (a)$$

We now substitute the Maxwell relations below into (a)

$$\left(\frac{\partial s}{\partial P}\right)_\nu = -\left(\frac{\partial \nu}{\partial T}\right)_s \quad \text{and} \quad \left(\frac{\partial s}{\partial \nu}\right)_P = \left(\frac{\partial P}{\partial T}\right)_s$$

to get

$$-\left(\frac{\partial \nu}{\partial T}\right)_s dP + \left(\frac{\partial P}{\partial T}\right)_s d\nu = 0$$

Rearranging,

$$dP - \left(\frac{\partial T}{\partial \nu}\right)_s \left(\frac{\partial P}{\partial T}\right)_s d\nu = 0 \longrightarrow dP - \left(\frac{\partial P}{\partial \nu}\right)_s d\nu = 0$$

$$\text{Dividing by } P, \quad \frac{dP}{P} - \frac{1}{P} \left(\frac{\partial P}{\partial \nu}\right)_s d\nu = 0 \quad (b)$$

We now define isentropic expansion exponent  $k$  as

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

Substituting in (b),

$$\frac{dP}{P} + k \frac{d\nu}{\nu} = 0$$

Taking  $k$  to be a constant and integrating,

$$\ln P + k \ln \nu = \text{constant} \longrightarrow \ln P\nu^k = \text{constant}$$

Thus,

$$P\nu^k = \text{constant}$$

To show that  $k = c_p/c_v$  for an ideal gas, we write the cyclic relations for the following two groups of variables:

$$(s, T, \nu) \longrightarrow \left(\frac{\partial s}{\partial T}\right)_\nu \left(\frac{\partial \nu}{\partial s}\right)_T \left(\frac{\partial T}{\partial \nu}\right)_s = -1 \longrightarrow \frac{c_v}{T} \left(\frac{\partial \nu}{\partial s}\right)_T \left(\frac{\partial T}{\partial \nu}\right)_s = -1 \quad (c)$$

$$(s, T, P) \longrightarrow \left(\frac{\partial s}{\partial T}\right)_P \left(\frac{\partial P}{\partial s}\right)_T \left(\frac{\partial T}{\partial P}\right)_s = -1 \longrightarrow \frac{c_p}{T} \left(\frac{\partial P}{\partial s}\right)_T \left(\frac{\partial T}{\partial P}\right)_s = -1 \quad (d)$$

where we used the relations

$$c_v = T \left(\frac{\partial s}{\partial T}\right)_\nu \quad \text{and} \quad c_p = T \left(\frac{\partial s}{\partial T}\right)_P$$

Setting Eqs. (c) and (d) equal to each other,

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

or,

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

but

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

Substituting,

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

which is the desired relation.

**12-106 EES** The work done by the refrigerant 134a as it undergoes an isothermal process in a closed system is to be determined using the tabular (EES) data and the generalized charts.

**Analysis** The solution using EES built-in property data is as follows:

$$\left. \begin{aligned} T_1 &= 60^\circ\text{C} \\ P_1 &= 3 \text{ MPa} \end{aligned} \right\} \begin{aligned} u_1 &= 135.65 \text{ kJ/kg} \\ s_1 &= 0.4828 \text{ kJ/kg}\cdot\text{K} \end{aligned}$$

$$\left. \begin{aligned} T_2 &= 60^\circ\text{C} \\ P_2 &= 0.1 \text{ MPa} \end{aligned} \right\} \begin{aligned} u_2 &= 280.35 \text{ kJ/kg} \\ s_2 &= 1.2035 \text{ kJ/kg}\cdot\text{K} \end{aligned}$$

$$\Delta s_{\text{EES}} = s_2 - s_1 = 1.2035 - 0.4828 = 0.7207 \text{ kJ/kg}\cdot\text{K}$$

$$q_{\text{EES}} = T_1 \Delta s_{\text{EES}} = (60 + 273.15 \text{ K})(0.7207 \text{ kJ/kg}\cdot\text{K}) = 240.11 \text{ kJ/kg}$$

$$w_{\text{EES}} = q_{\text{EES}} - (u_2 - u_1) = 240.1 - (280.35 - 135.65) = \mathbf{95.40 \text{ kJ/kg}}$$

For the generalized chart solution we first determine the following factors using EES as

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{cr}} = \frac{333.15}{374.2} = 0.8903 \\ P_{R1} &= \frac{P_1}{P_{cr}} = \frac{3}{4.059} = 0.7391 \end{aligned} \right\} \longrightarrow Z_1 = 0.1292, Z_{h1} = 4.475 \text{ and } Z_{s1} = 4.383$$

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{cr}} = \frac{333.15}{374.2} = 0.8903 \\ P_{R2} &= \frac{P_2}{P_{cr}} = \frac{0.1}{4.059} = 0.02464 \end{aligned} \right\} \longrightarrow Z_2 = 0.988, Z_{h2} = 0.03091 \text{ and } Z_{s2} = 0.02281$$

Then,

$$\Delta h_1 = Z_{h1} RT_{cr} = (4.475)(0.08148 \text{ kJ/kg}\cdot\text{K})(374.2 \text{ K}) = 136.43 \text{ kJ/kg}$$

$$\Delta s_1 = Z_{s1} R = (4.383)(0.08148 \text{ kJ/kg}\cdot\text{K}) = 0.3572 \text{ kJ/kg}\cdot\text{K}$$

$$\Delta h_2 = Z_{h2} RT_{cr} = (0.03091)(0.08148 \text{ kJ/kg}\cdot\text{K})(374.2 \text{ K}) = 0.94 \text{ kJ/kg}$$

$$\Delta s_2 = Z_{s2} R = (0.02281)(0.08148 \text{ kJ/kg}\cdot\text{K}) = 0.001858 \text{ kJ/kg}\cdot\text{K}$$

$$\Delta s_{\text{ideal}} = R \ln \frac{P_2}{P_1} = (0.08148 \text{ kJ/kg}\cdot\text{K}) \ln \left( \frac{0.1}{3} \right) = 0.2771 \text{ kJ/kg}\cdot\text{K}$$

$$\Delta s_{\text{chart}} = \Delta s_{\text{ideal}} - (\Delta s_2 - \Delta s_1) = 0.2771 - (0.001858 - 0.3572) = 0.6324 \text{ kJ/kg}\cdot\text{K}$$

$$q_{\text{chart}} = T_1 \Delta s_{\text{chart}} = (60 + 273.15 \text{ K})(0.6324 \text{ kJ/kg}\cdot\text{K}) = 210.70 \text{ kJ/kg}$$

$$\begin{aligned} \Delta u_{\text{chart}} &= \Delta h_{\text{ideal}} - (\Delta h_2 - \Delta h_1) - (Z_2 RT_2 - Z_1 RT_1) \\ &= 0 - (0.94 - 136.43) - [(0.988)(0.08148)(333) - (0.1292)(0.08148)(333)] = 112.17 \text{ kJ/kg} \end{aligned}$$

$$w_{\text{chart}} = q_{\text{chart}} - \Delta u_{\text{chart}} = 210.70 - 112.17 = \mathbf{98.53 \text{ kJ/kg}}$$

The copy of the EES solution of this problem is given next.

"Input data"

T\_critical=T\_CRIT(R134a) "[K]"

P\_critical=P\_CRIT(R134a) "[kpa]"

T[1]=60+273.15 "[K]"

```

T[2]=T[1]"[K]"
P[1]=3000"[kPa]"
P[2]=100"[kPa]"
R_u=8.314"[kJ/kmol-K]"
M=molarmass(R134a)
R=R_u/M"[kJ/kg-K]"

```

\*\*\*\*\* SOLUTION USING EES BUILT-IN PROPERTY DATA \*\*\*\*\*

```

"For the isothermal process, the heat transfer is T*(s[2] - s[1]):"
DELTA_s_EES=(entropy(R134a,T=T[2],P=P[2])-entropy(R134a,T=T[1],P=P[1]))
q_EES=T[1]*DELTA_s_EES

```

```

s_2=entropy(R134a,T=T[2],P=P[2])
s_1=entropy(R134a,T=T[1],P=P[1])

```

```

"Conservation of energy for the closed system:"
DELTA_u_EES=intEnergy(R134a,T=T[2],p=P[2])-intEnergy(R134a,T=T[1],P=P[1])
q_EES-w_EES=DELTA_u_EES
u_1=intEnergy(R134a,T=T[1],P=P[1])
u_2=intEnergy(R134a,T=T[2],p=P[2])

```

\*\*\*\*\* COMPRESSIBILITY CHART SOLUTION \*\*\*\*\*

```

"State 1"
Tr[1]=T[1]/T_critical
pr[1]=p[1]/p_critical
Z[1]=COMPRESS(Tr[1], Pr[1])
DELTA_h[1]=ENTHDEP(Tr[1], Pr[1])*R*T_critical"Enthalpy departure"
Z_h1=ENTHDEP(Tr[1], Pr[1])
DELTA_s[1]=ENTRDEP(Tr[1], Pr[1])*R "Entropy departure"
Z_s1=ENTRDEP(Tr[1], Pr[1])

```

```

"State 2"
Tr[2]=T[2]/T_critical
Pr[2]=P[2]/P_critical
Z[2]=COMPRESS(Tr[2], Pr[2])
DELTA_h[2]=ENTHDEP(Tr[2], Pr[2])*R*T_critical"Enthalpy departure"
Z_h2=ENTHDEP(Tr[2], Pr[2])
DELTA_s[2]=ENTRDEP(Tr[2], Pr[2])*R "Entropy departure"
Z_s2=ENTRDEP(Tr[2], Pr[2])

```

```

"Entropy Change"
DELTA_s_ideal=-R*ln(P[2]/P[1])
DELTA_s_chart=DELTA_s_ideal-(DELTA_s[2]-DELTA_s[1])

```

```

"For the isothermal process, the heat transfer is T*(s[2] - s[1]):"
q_chart=T[1]*DELTA_s_chart

```

```

"Conservation of energy for the closed system:"
DELTA_h_ideal=0
DELTA_u_chart=DELTA_h_ideal-(DELTA_h[2]-DELTA_h[1])-(Z[2]*R*T[2]-Z[1]*R*T[1])
q_chart-w_chart=DELTA_u_chart

```

## SOLUTION

DELTAh[1]=136.43	R_u=8.314 [kJ/kmol-K]
DELTAh[2]=0.94	s_1=0.4828 [kJ/kg-K]
DELTAh_ideal=0	s_2=1.2035 [kJ/kg-K]
DELTAAs[1]=0.3572	T[1]=333.2 [K]
DELTAAs[2]=0.001858	T[2]=333.2 [K]
DELTAAs_chart=0.6324 [kJ/kg-K]	Tr[1]=0.8903
DELTAAs_EES=0.7207 [kJ/kg-K]	Tr[2]=0.8903
DELTAAs_ideal=0.2771 [kJ/kg-K]	T_critical=374.2 [K]
DELTAu_chart=112.17	u_1=135.65 [kJ/kg]
DELTAu_EES=144.7	u_2=280.35 [kJ/kg]
M=102 [kg/kmol]	w_chart=98.53 [kJ/kg]
P[1]=3000 [kPa]	w_EES=95.42 [kJ/kg]
P[2]=100 [kPa]	Z[1]=0.1292
pr[1]=0.7391	Z[2]=0.988
Pr[2]=0.02464	Z_h1=4.475
P_critical=4059 [kpa]	Z_h2=0.03091
q_chart=210.70 [kJ/kg]	Z_s1=4.383
q_EES=240.11 [kJ/kg]	Z_s2=0.02281
R=0.08148 [kJ/kg-K]	

**12-107** The heat transfer, work, and entropy changes of methane during a process in a piston-cylinder device are to be determined assuming ideal gas behavior, using generalized charts, and real fluid (EES) data.

**Analysis** The ideal gas solution: (Properties are obtained from EES)

State 1:

$$T_1 = 100^\circ\text{C} \longrightarrow h_1 = -4492 \text{ kJ/kg}$$

$$T_1 = 100^\circ\text{C}, P_1 = 4 \text{ MPa} \longrightarrow s_1 = 10.22 \text{ kJ/kg}\cdot\text{K}$$

$$u_1 = h_1 - RT_1 = (-4492) - (0.5182)(100 + 273.15) = -4685 \text{ kJ/kg}$$

$$v_1 = R \frac{T_1}{P_1} = (0.5182 \text{ kJ/kg}\cdot\text{K}) \left( \frac{100 + 273.15 \text{ K}}{4000 \text{ kPa}} \right) = 0.04834 \text{ m}^3/\text{kg}$$

State 2:

$$T_2 = 350^\circ\text{C} \longrightarrow h_2 = -3770 \text{ kJ/kg}$$

$$T_2 = 350^\circ\text{C}, P_2 = 4 \text{ MPa} \longrightarrow s_2 = 11.68 \text{ kJ/kg}\cdot\text{K}$$

$$u_2 = h_2 - RT_2 = (-3770) - (0.5182)(350 + 273.15) = -4093 \text{ kJ/kg}$$

$$v_2 = R \frac{T_2}{P_2} = (0.5182 \text{ kJ/kg}\cdot\text{K}) \left( \frac{350 + 273.15 \text{ K}}{4000 \text{ kPa}} \right) = 0.08073 \text{ m}^3/\text{kg}$$

$$w_{\text{ideal}} = P(v_2 - v_1) = (4000 \text{ kPa})(0.08073 - 0.04834) \text{ m}^3/\text{kg} = \mathbf{129.56 \text{ kJ/kg}}$$

$$q_{\text{ideal}} = w_{\text{ideal}} + (u_2 - u_1) = 129.56 + [(-4093) - (-4685)] = \mathbf{721.70 \text{ kJ/kg}}$$

$$\Delta s_{\text{ideal}} = s_2 - s_1 = 11.68 - 10.22 = \mathbf{1.46 \text{ kJ/kg}}$$

For the generalized chart solution we first determine the following factors using EES as

$$\left. \begin{aligned} T_{R1} &= \frac{T_1}{T_{\text{cr}}} = \frac{373}{304.2} = 1.227 \\ P_{R1} &= \frac{P_1}{P_{\text{cr}}} = \frac{4}{7.39} = 0.5413 \end{aligned} \right\} \longrightarrow Z_1 = 0.9023, Z_{h1} = 0.4318 \text{ and } Z_{s1} = 0.2555$$

$$\left. \begin{aligned} T_{R2} &= \frac{T_2}{T_{\text{cr}}} = \frac{623}{304.2} = 2.048 \\ P_{R2} &= \frac{P_2}{P_{\text{cr}}} = \frac{4}{7.39} = 0.5413 \end{aligned} \right\} \longrightarrow Z_2 = 0.995, Z_{h2} = 0.1435 \text{ and } Z_{s2} = 0.06446$$

State 1:

$$\Delta h_1 = Z_{h1} RT_{\text{cr}} = (0.4318)(0.5182 \text{ kJ/kg}\cdot\text{K})(304.2 \text{ K}) = 68.07 \text{ kJ/kg}$$

$$h_1 = h_{1,\text{ideal}} - \Delta h_1 = (-4492) - 68.07 = -4560 \text{ kJ/kg}$$

$$u_1 = h_1 - Z_1 RT_1 = (-4560) - (0.9023)(0.5182)(373.15) = -4734 \text{ kJ/kg}$$

$$v_1 = Z_1 R \frac{T_1}{P_1} = (0.9023)(0.5182) \frac{373.15}{4000} = 0.04362 \text{ m}^3/\text{kg}$$

$$\Delta s_1 = Z_{s1} R = (0.2555)(0.5182 \text{ kJ/kg}\cdot\text{K}) = 0.1324 \text{ kJ/kg}\cdot\text{K}$$

$$s_1 = s_{1,\text{ideal}} - \Delta s_1 = 10.22 - 0.1324 = 10.09 \text{ kJ/kg}\cdot\text{K}$$

State 2:

$$\Delta h_2 = Z_{h_2} R T_{cr} = (0.1435)(0.5182 \text{ kJ/kg}\cdot\text{K})(304.2 \text{ K}) = 22.62 \text{ kJ/kg}$$

$$h_2 = h_{2,\text{ideal}} - \Delta h_2 = (-3770) - 22.62 = -3793 \text{ kJ/kg}$$

$$u_2 = h_2 - Z_2 R T_2 = (-3793) - (0.995)(0.5182)(623.15) = -4114 \text{ kJ/kg}$$

$$v_2 = Z_2 R \frac{T_2}{P_2} = (0.995)(0.5182) \frac{623.15}{4000} = 0.08033 \text{ m}^3/\text{kg}$$

$$\Delta s_2 = Z_{s_2} R = (0.06446)(0.5182 \text{ kJ/kg}\cdot\text{K}) = 0.03341 \text{ kJ/kg}\cdot\text{K}$$

$$s_2 = s_{2,\text{ideal}} - \Delta s_2 = 11.68 - 0.03341 = 11.65 \text{ kJ/kg}\cdot\text{K}$$

Then,

$$w_{\text{chart}} = P(v_2 - v_1) = (4000 \text{ kPa})(0.08033 - 0.04362) \text{ m}^3/\text{kg} = \mathbf{146.84 \text{ kJ/kg}}$$

$$q_{\text{chart}} = w_{\text{chart}} + (u_2 - u_1) = 146.84 + [(-4114) - (-4734)] = \mathbf{766.84 \text{ kJ/kg}}$$

$$\Delta s_{\text{chart}} = s_2 - s_1 = 11.65 - 10.09 = \mathbf{1.56 \text{ kJ/kg}}$$

The solution using EES built-in property data is as follows:

$$\left. \begin{array}{l} T_1 = 100^\circ\text{C} \\ P_1 = 4 \text{ MPa} \end{array} \right\} \begin{array}{l} v_1 = 0.04717 \text{ m}^3/\text{kg} \\ u_1 = -39.82 \text{ kJ/kg} \\ s_1 = -1.439 \text{ kJ/kg}\cdot\text{K} \end{array}$$

$$\left. \begin{array}{l} T_2 = 350^\circ\text{C} \\ P_2 = 4 \text{ MPa} \end{array} \right\} \begin{array}{l} v_2 = 0.08141 \text{ m}^3/\text{kg} \\ u_2 = 564.52 \text{ kJ/kg} \\ s_2 = 0.06329 \text{ kJ/kg}\cdot\text{K} \end{array}$$

$$w_{\text{EES}} = P(v_2 - v_1) = (4000 \text{ kPa})(0.08141 - 0.04717) \text{ m}^3/\text{kg} = \mathbf{136.96 \text{ kJ/kg}}$$

$$q_{\text{EES}} = w_{\text{EES}} + (u_2 - u_1) = 136.97 + [564.52 - (-39.82)] = \mathbf{741.31 \text{ kJ/kg}}$$

$$\Delta s_{\text{EES}} = s_2 - s_1 = 0.06329 - (-1.439) = \mathbf{1.50 \text{ kJ/kg}}$$

## Fundamentals of Engineering (FE) Exam Problems

**12-108** A substance whose Joule-Thomson coefficient is negative is throttled to a lower pressure. During this process, (select the correct statement)

- (a) the temperature of the substance will increase.
- (b) the temperature of the substance will decrease.
- (c) the entropy of the substance will remain constant.
- (d) the entropy of the substance will decrease.
- (e) the enthalpy of the substance will decrease.

*Answer* (a) the temperature of the substance will increase.

**12-109** Consider the liquid-vapor saturation curve of a pure substance on the  $P$ - $T$  diagram. The magnitude of the slope of the tangent line to this curve at a temperature  $T$  (in Kelvin) is

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

*Answer* (a) proportional to the enthalpy of vaporization  $h_{fg}$  at that temperature,

**12-110** Based on the generalized charts, the error involved in the enthalpy of  $\text{CO}_2$  at 350 K and 8 MPa if it is assumed to be an ideal gas is

- (a) 0
- (b) 20%
- (c) 33%
- (d) 26%
- (e) 65%

*Answer* (c) 33%

**Solution** Solved by EES Software. Solutions can be verified by copying-and-pasting the following lines on a blank EES screen. (Similar problems and their solutions can be obtained easily by modifying numerical values).

```
T=350 "K"
P=8000 "kPa"
Pcr=P_CRIT(CarbonDioxide)
Tcr=T_CRIT(CarbonDioxide)
Tr=T/Tcr
Pr=P/Pcr
hR=ENTHDEP(Tr, Pr)
h_ideal=11351/Molarmass(CO2) "Table A-20 of the text"
h_chart=h_ideal-R*Tcr*hR
R=0.1889
Error=(h_chart-h_ideal)/h_chart*Convert(, %)
```

**12-111** Based on data from the refrigerant-134a tables, the Joule-Thompson coefficient of refrigerant-134a at 0.8 MPa and 100°C is approximately

- (a) 0                      (b) -5°C/MPa                      (c) 11°C/MPa                      (d) 8°C/MPa                      (e) 26°C/MPa

*Answer* (c) 11°C/MPa

**Solution** Solved by EES Software. Solutions can be verified by copying-and-pasting the following lines on a blank EES screen. (Similar problems and their solutions can be obtained easily by modifying numerical values).

```
T1=100 "C"
P1=800 "kPa"
h1=ENTHALPY(R134a,T=T1,P=P1)
Tlow=TEMPERATURE(R134a,h=h1,P=P1+100)
Thigh=TEMPERATURE(R134a,h=h1,P=P1-100)
JT=(Tlow-Thigh)/200
```

**12-112** For a gas whose equation of state is  $P(\nu - b) = RT$ , the specific heat difference  $c_p - c_\nu$  is equal to

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

*Answer* (a)  $R$

**Solution** The general relation for the specific heat difference  $c_p - c_\nu$  is

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

For the given gas,  $P(\nu - b) = RT$ . Then,

$$\nu = \frac{RT}{P} + b \longrightarrow \left( \frac{\partial \nu}{\partial T} \right)_P = \frac{R}{P}$$

$$P = \frac{RT}{\nu - b} \longrightarrow \left( \frac{\partial P}{\partial \nu} \right)_T = -\frac{RT}{(\nu - b)^2} = -\frac{P}{\nu - b}$$

Substituting,

$$c_p - c_\nu = -T \left( \frac{R}{P} \right)^2 \left( -\frac{P}{\nu - b} \right) = \frac{TR^2}{P(\nu - b)} = R$$

## 12-113 ... 12-115 Design and Essay Problems

