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Chapter 12 THERMODYNAMIC PROPERTY RELATIONS

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Partial Derivatives and Associated Relations

12-1C For functions that depend on one variable, they are identical. For functions that depend on two or more variable, 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.

12-2C (a) $(\partial x)_{\mathbf{y}} = dx$; (b) $(\partial z)_{\mathbf{y}} \le dz$; and (c) $dz = (\partial z)_x + (\partial z)_{\mathbf{y}}$

12-3C Yes.

12-4C Yes.

12-5 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 kPa·m³/kg·K (Table A-1).

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

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

(a) The change in T can be expressed as $dT \cong \Delta T = 300 \times 0.01 = 3.0$ K. At v = constant,

$$(dP)_{\nu} = \frac{RdT}{\nu} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(3.0 \text{ K})}{1.2 \text{ m}^3/\text{kg}} = 0.7175 \text{ kPa}$$

(b) The change in \boldsymbol{v} can be expressed as $d\boldsymbol{v} \cong \Delta \boldsymbol{v} = 1.2 \times 0.01 = 0.012 \text{ m}^3/\text{kg}$. At T = constant,

$$(dP)_T = -\frac{RTdv}{v^2} = -\frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(300 \text{ K})(0.012 \text{ m}^3/\text{kg})}{(1.2 \text{ m}^3/\text{kg})^2} = -0.7175 \text{ kPa}$$

(c) When both \boldsymbol{v} and T increases by 1%, the change in P becomes

$$dP = (dP)_{\mu} + (dP)_{\tau} = 0.7175 + (-0.7175) = 0$$

Thus the changes in T and \boldsymbol{v} balance each other.

12-6 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/v. Noting that R is a constant and P = P(T, v),

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

(a) The change in T can be expressed as $dT \cong \Delta T = 300 \times 0.01 = 3.0$ K. At \boldsymbol{v} = constant,

$$(dP)_{v} = \frac{RdT}{v} = \frac{(2.0769 \text{ kPa} \cdot \text{m}^{3}/\text{kg} \cdot \text{K})(3.0 \text{ K})}{1.2 \text{ m}^{3}/\text{kg}} = 5.192 \text{ kPa}$$

(b) The change in \boldsymbol{v} can be expressed as $d\boldsymbol{v} \cong \Delta \boldsymbol{v} = 1.2 \times 0.01 = 0.012 \text{ m}^3/\text{kg}$. At T = constant,

$$(dP)_T = -\frac{RTd\boldsymbol{v}}{\boldsymbol{v}^2} = \frac{(2.0769 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(300 \text{ K})(0.012 \text{ m}^3)}{(1.2 \text{ m}^3/\text{kg})^2} = -5.192 \text{ kPa}$$

(c) When both \boldsymbol{v} and T increases by 1%, the change in P becomes

$$dP = (dP)_{v} + (dP)_{T} = 5.192 + (-5.192) = 0$$

Thus the changes in T and v balance each other.

12-7 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-2*b*.

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

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

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

$$c_{v}(400\text{K}) = \left(\frac{du(T)}{dT}\right)_{T=400\text{ K}} \cong \left(\frac{\Delta u(T)}{\Delta T}\right)_{T\cong400\text{ K}}$$
$$= \frac{u(410\text{ K}) - u(390\text{ K})}{(410 - 390)\text{K}}$$
$$= \frac{(8,523 - 8,104)/28.0 \text{ kJ/kg}}{(410 - 390)\text{K}} = 0.748 \text{ kJ/kg} \cdot \text{K}$$

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



12-8E 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

$$c_{p} (800 \text{ R}) = \left(\frac{dh(T)}{dT}\right)_{T=800 \text{ R}} \cong \left(\frac{\Delta h(T)}{\Delta T}\right)_{T\equiv800 \text{ R}}$$
$$= \frac{h(820 \text{ R}) - h(780 \text{ R})}{(820 - 780)\text{R}}$$
$$= \frac{(5704.7 - 5424.2)/28.013 \text{ Btu/lbm}}{(820 - 780)\text{R}} = 0.250 \text{ Btu/lbm} \cdot \text{R}$$

(Compare: Table A-2Eb at 800 R = $340^{\circ}F \rightarrow c_p = 0.250 \text{ Btu/lbm} \cdot \text{R}$)

$$c_{v} (800 \text{ R}) = \left(\frac{du(T)}{dT}\right)_{T=800 \text{ R}} \cong \left(\frac{\Delta u(T)}{\Delta T}\right)_{T\equiv800 \text{ R}}$$
$$= \frac{u(820 \text{ R}) - u(780 \text{ R})}{(820 - 780)\text{R}}$$
$$= \frac{(4076.3 - 3875.2)/28.013 \text{ Btu/lbm}}{(820 - 780)\text{R}} = 0.179 \text{ Btu/lbm} \cdot \text{R}$$

(Compare: Table A-2Eb at 800 R = $340^{\circ}F \rightarrow c_v = 0.179 \text{ Btu/lbm} \cdot \text{R}$)

12-9 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 $P \boldsymbol{v} = RT$ can be expressed as $\boldsymbol{v} = RT/P$. Note that *R* is a constant and $\boldsymbol{v} = \boldsymbol{v}(T, P)$. Applying the total differential relation and using average values for *T* and *P*,

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

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

$$\boldsymbol{v}_1 = \frac{RT_1}{P_1} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(400 \text{ K})}{100 \text{ kPa}} = 1.1480 \text{ m}^3/\text{kg}$$
$$\boldsymbol{v}_2 = \frac{RT_2}{P_2} = \frac{(0.287 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(404 \text{ K})}{96 \text{ kPa}} = 1.2078 \text{ m}^3/\text{kg}$$

Thus,

$$\Delta v = v_2 - v_1 = 1.2078 - 1.1480 = 0.0598 \text{ m}^3/\text{kg}$$

The two results are identical.

12-5

12-10 Using the equation of state P(v-a) = RT, the cyclic relation, and the reciprocity relation at constant v are to be verified.

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

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

where

$$P = \frac{RT}{\boldsymbol{v} - a} \longrightarrow \left(\frac{\partial P}{\partial \boldsymbol{v}}\right)_T = \frac{-RT}{(\boldsymbol{v} - a)^2} = -\frac{P}{\boldsymbol{v} - a}$$
$$\boldsymbol{v} = \frac{RT}{P} + a \longrightarrow \left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_P = \frac{R}{P}$$
$$T = \frac{P(\boldsymbol{v} - a)}{R} \longrightarrow \left(\frac{\partial T}{\partial P}\right)_{\boldsymbol{v}} = \frac{\boldsymbol{v} - a}{R}$$

Substituting,

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

which is the desired result.

(b) The reciprocity rule for this gas at v = constant can be expressed as

$$\left(\frac{\partial P}{\partial T}\right)_{\boldsymbol{v}} = \frac{1}{(\partial T / \partial P)_{\boldsymbol{v}}}$$
$$T = \frac{P(\boldsymbol{v} - a)}{R} \longrightarrow \left(\frac{\partial T}{\partial P}\right)_{\boldsymbol{v}} = \frac{\boldsymbol{v} - a}{R}$$
$$P = \frac{RT}{\boldsymbol{v} - a} \longrightarrow \left(\frac{\partial P}{\partial T}\right)_{\boldsymbol{v}} = \frac{R}{\boldsymbol{v} - a}$$

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

12-11 It is to be proven for an ideal gas that the P = 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

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

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

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



12-12 A relation is to be derived for the slope of the v = 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 \boldsymbol{v} constant,

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

which is the slope of the v = constant lines on a *T*-*P* diagram.

The Maxwell Relations

12-13 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,

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

$$\left(\frac{\Delta s}{\Delta P}\right)_{T=50^{\circ}\text{C}} \stackrel{?}{\cong} - \left(\frac{\Delta v}{\Delta T}\right)_{P=700\text{kPa}}$$

$$\left(\frac{s_{900 \text{ kPa}} - s_{500 \text{ kPa}}}{(900 - 500)\text{kPa}}\right)_{T=50^{\circ}\text{C}} \stackrel{?}{\cong} - \left(\frac{v_{70^{\circ}\text{C}} - v_{30^{\circ}\text{C}}}{(70 - 30)^{\circ}\text{C}}\right)_{P=700\text{kPa}}$$

$$\frac{(0.9660 - 1.0309)\text{kJ/kg} \cdot \text{K}}{(900 - 500)\text{kPa}} \stackrel{?}{\cong} - \frac{(0.036373 - 0.029966)\text{m}^{3}/\text{kg}}{(70 - 30)^{\circ}\text{C}}$$

$$- 1.621 \times 10^{-4} \text{ m}^{3}/\text{kg} \cdot \text{K} \cong - 1.602 \times 10^{-4} \text{ m}^{3}/\text{kg} \cdot \text{K}$$

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

12-14 Problem 12-13 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=50 [C] P=700 [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. 12-19) 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] DELTAs=-0.06484 [kJ/kg-K] DELTAT=40 [C] DELTAv=0.006407 [m^3/kg] LeftSide=-0.0001621 [m^3/kg-K] P=700 [kPa] P[1]=500 [kPa] P[2]=900 [kPa] P_increment=200 [kPa] RightSide=-0.0001602 [m^3/kg-K] s[1]=1.0309 [kJ/kg-K] s[2]=0.9660 [kJ/kg-K] T=50 [C] T[1]=30 [C] T[2]=70 [C] T_increment=20 [C] v[1]=0.02997 [m^3/kg] v[2]=0.03637 [m^3/kg]

12-15E 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,

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

$$\left(\frac{\Delta s}{\Delta P}\right)_{T=800^{\circ}\text{F}} \stackrel{?}{\cong} - \left(\frac{\Delta \boldsymbol{v}}{\Delta T}\right)_{P=400\text{psia}}$$

$$\left(\frac{s_{450 \text{ psia}} - s_{350 \text{ psia}}}{(450 - 350)\text{psia}}\right)_{T=800^{\circ}\text{F}} \stackrel{?}{\cong} - \left(\frac{\boldsymbol{v}_{900^{\circ}\text{F}} - \boldsymbol{v}_{700^{\circ}\text{F}}}{(900 - 700)^{\circ}\text{F}}\right)_{P=400\text{psia}}$$

$$\frac{(1.6706 - 1.7009)\text{Btu/lbm} \cdot \text{R}}{(450 - 350)\text{psia}} \stackrel{?}{\cong} - \frac{(1.9777 - 1.6507)\text{ft}^3/\text{lbm}}{(900 - 700)^{\circ}\text{F}}$$

$$- 1.639 \times 10^{-3} \text{ ft}^3/\text{lbm} \cdot \text{R} \cong - 1.635 \times 10^{-3} \text{ ft}^3/\text{lbm} \cdot \text{R}$$

since 1 Btu = 5.4039 psia t^3 , and R = °F for temperature differences. Thus the fourth Maxwell relation is satisfied.

12-16 Using the Maxwell relations, a relation for $(\partial s/\partial P)_T$ for a gas whose equation of state is $P(\boldsymbol{\nu} \cdot b) = RT$ is to be obtained.

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

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

From the fourth Maxwell relation,

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

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

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

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

From the third Maxwell relation,

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

12-18 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,

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

From the third Maxwell relation,

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

12-19 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 $\left(\frac{\partial s}{\partial P}\right)_{\boldsymbol{v}} = -\left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{s}$,

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

Using the definition of c_p ,

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

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

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

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,

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

Substituting this into the original equation in the problem statement produces

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

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

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

12-20 It is to be shown how *T*, *v*, *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

$$dh = Tds + vdP$$

Comparing the coefficient of these two expressions

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

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

From the definition of the enthalpy,

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

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

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

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

The Clapeyron Equation

12-21C It enables us to determine the enthalpy of vaporization from h_{fg} at a given temperature from the P, v, T data alone.

12-22C It is assumed that $v_{fg} \cong v_g \cong RT/P$, and $h_{fg} \cong$ constant for small temperature intervals.

12-23 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,

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

$$\cong T (\mathbf{v}_g - \mathbf{v}_f)_{@300 \text{ kPa}} \left(\frac{\Delta P}{\Delta T} \right)_{\text{sat, 300 kPa}}$$

$$= T_{\text{sat}@300 \text{ kPa}} (\mathbf{v}_g - \mathbf{v}_f)_{@300 \text{ kPa}} \left(\frac{(325 - 275) \text{ kPa}}{T_{\text{sat}@325 \text{ kPa}} - T_{\text{sat}@275 \text{ kPa}}} \right)$$

$$= (133.52 + 273.15 \text{ K})(0.60582 - 0.001073 \text{ m}^3/\text{kg}) \left(\frac{50 \text{ kPa}}{(136.27 - 130.58)^{\circ}\text{C}} \right)$$

$$= 2159.9 \text{ kJ/kg}$$

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

12-24 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,

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

$$\approx T (\mathbf{v}_g - \mathbf{v}_f)_{@120^{\circ}\text{C}} \left(\frac{\Delta P}{\Delta T} \right)_{\text{sat,120^{\circ}\text{C}}}$$

$$= T (\mathbf{v}_g - \mathbf{v}_f)_{@120^{\circ}\text{C}} \left(\frac{P_{\text{sat}@125^{\circ}\text{C}} - P_{\text{sat}@115^{\circ}\text{C}}}{125^{\circ}\text{C} - 115^{\circ}\text{C}} \right)$$

$$= (120 + 273.15 \text{ K})(0.89133 - 0.001060 \text{ m}^3/\text{kg}) \left(\frac{(232.23 - 169.18)\text{kPa}}{10 \text{ K}} \right)$$

$$= 2206.8 \text{ kJ/kg}$$

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

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

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Analysis (a) From the Clapeyron equation,

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

$$\cong T (\boldsymbol{v}_g - \boldsymbol{v}_f)_{@\ 10^\circ F} \left(\frac{\Delta P}{\Delta T} \right)_{sat,\ 10^\circ F}$$

$$= T (\boldsymbol{v}_g - \boldsymbol{v}_f)_{@\ 10^\circ F} \left(\frac{P_{sat@\ 15^\circ F} - P_{sat@\ 5^\circ F}}{15^\circ F - 5^\circ F} \right)$$

$$= (10 + 459.67 \text{ R})(1.7345 - 0.01201 \text{ ft}^3/\text{lbm}) \left(\frac{(29.759 - 23.793) \text{ psia}}{10 \text{ R}} \right)$$

$$= 482.6 \text{ psia} \cdot \text{ft}^3/\text{lbm} = 89.31 \text{ Btu/lbm} \quad (0.1\% \text{ error})$$

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

(b) From the Clapeyron-Clausius equation,

$$\ln\left(\frac{P_2}{P_1}\right)_{\text{sat}} \approx \frac{h_{fg}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)_{\text{sat}}$$
$$\ln\left(\frac{23.793 \text{ psia}}{29.759 \text{ psia}}\right) \approx \frac{h_{fg}}{0.01946 \text{ Btu/lbm} \cdot \text{R}} \left(\frac{1}{15 + 459.67 \text{ R}} - \frac{1}{5 + 459.67 \text{ R}}\right)$$
$$h_{fg} = 96.04 \text{ Btu/lbm} \quad (7.6\% \text{ error})$$

The tabulated value of h_{fg} at 10°F is **89.23 Btu/lbm**.

12-26 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

$$h_{fg,Clapeyron} = T \boldsymbol{v}_{fg} \frac{\Delta P}{\Delta T}$$

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

$$T_{1} = T - T_{\text{increment}} = 100 - 5 = 95^{\circ}\text{C}$$

$$T_{2} = T + T_{\text{increment}} = 100 + 5 = 105^{\circ}\text{C}$$

$$P_{1} = P_{\text{sat}@~95^{\circ}\text{C}} = 84.61 \text{ kPa}$$

$$P_{2} = P_{\text{sat}@~105^{\circ}\text{C}} = 120.90 \text{ kPa}$$

$$\Delta T = T_{2} - T_{1} = 105 - 95 = 10^{\circ}\text{C}$$

$$\Delta P = P_{2} - P_{1} = 120.90 - 84.61 = 36.29 \text{ kPa}$$

$$\boldsymbol{v}_{f@~100^{\circ}\text{C}} = 0.001043 \text{ m}^{3}/\text{kg}$$

$$\boldsymbol{v}_{g@~100^{\circ}\text{C}} = 1.6720 \text{ m}^{3}/\text{kg}$$

$$\boldsymbol{v}_{fg} = \boldsymbol{v}_{g} - \boldsymbol{v}_{f} = 1.6720 - 0.001043 = 1.6710 \text{ m}^{3}/\text{kg}$$

Substituting,

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

The enthalpy of vaporization from steam table is

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

The percent error in using Clapeyron equation is

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

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 satruated vapor at the temperature."

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h_fg_Clapeyron=(T+273.15)*v_fg*DELTAP/DELTAT*Convert(m^3-kPa,kJ)"[kJ/kg]"
PercentError=ABS(h_fg_Clapeyron-h_fg)/h_fg*100"[%]"

h _{fq}	h _{fg,Clapeyron}	PercentError	Т
[kJ/ǩg]	[kJ/kg]	[%]	[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



12-27E A substance is cooled in a piston-cylinder device until it turns from saturated vapor to saturated liquid 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,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T\boldsymbol{v}_{fg}} = \frac{(250 \text{ Btu})\left(\frac{5.404 \text{ psia} \cdot \text{ft}^3}{1 \text{ Btu}}\right) / (0.5 \text{ lbm})}{(475 \text{ R})(1.5 \text{ ft}^3) / (0.5 \text{ lbm})} = 1.896 \text{ psia/R}$$

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 ,

$$T_2 = T_1 + \frac{P_2 - P_1}{dP / dT} = 475 \text{ R} + \frac{(60 - 50)\text{psia}}{1.896 \text{ psia/R}} = 480.3 \text{ R}$$



12-28E A substance is cooled in a piston-cylinder device until it turns from saturated vapor to saturated liquid 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,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T\boldsymbol{v}_{fg}} = \frac{(250 \text{ Btu}) \left(\frac{5.404 \text{ psia} \cdot \text{ft}^3}{1 \text{ Btu}}\right) / (0.5 \text{ lbm})}{(475 \text{ R})(1.5 \text{ ft}^3) / (0.5 \text{ lbm})} = 1.896 \text{ psia/R}$$

Using the finite difference approximation,

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

Solving for P_2 ,

$$P_2 = P_1 + \frac{dP}{dT}(T_2 - T_1) = 50 \text{ psia} + (1.896 \text{ psia/R})(470 - 475)\text{R} = 40.52 \text{ psia}$$



12-29E A substance is cooled in a piston-cylinder device until it turns from saturated vapor to saturated liquid at a constant pressure and temperature. The s_{fg} of this substance at the given temperature is to be estimated.

Analysis From the Clapeyron equation,

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

Solving for *s*_{fg},

$$s_{fg} = \frac{h_{fg}}{T} = \frac{(250 \text{ Btu})/(0.5 \text{ lbm})}{475 \text{ R}} = 1.053 \text{ Btu/lbm} \cdot \text{R}$$

Alternatively,

$$s_{fg} = \left(\frac{dP}{dT}\right)_{\text{sat}} \boldsymbol{\nu}_{fg} = (1.896 \text{ psia/R}) \frac{1.5 \text{ ft}^3}{0.5 \text{ lbm}} \left(\frac{1 \text{ Btu}}{5.404 \text{ psia} \cdot \text{ft}^3}\right) = 1.053 \text{ Btu/lbm} \cdot \text{R}$$



12-30E 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,

$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T\boldsymbol{v}_{fg}} = \frac{90.886 \text{ Btu/lbm}}{(460 \text{ R})(2.1446 \text{ ft}^3/\text{lbm})} \left(\frac{5.404 \text{ psia} \cdot \text{ft}^3}{1 \text{ Btu}}\right) = 0.4979 \text{ psia/R}$$

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 -15° F

$$P_2 = P_1 + \frac{dP}{dT}(T_2 - T_1) = 21.185 \text{ psia} + (0.4979 \text{ psia/R})(445 - 460)\text{R} = 13.72 \text{ psia}$$

Solving for P_2 at -30° F

$$P_2 = P_1 + \frac{dP}{dT}(T_2 - T_1) = 21.185 \text{ psia} + (0.4979 \text{ psia/R})(430 - 460)\text{R} = 6.25 \text{ psia}$$

12-31E 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

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

Using the finite difference approximation,

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

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

$$P_{2} = P_{1} + \frac{h_{fg}}{T v_{fg}} (T_{2} - T_{1})$$

= 116.7 psia + $\frac{154.85 \text{ Btu/lbm}}{(560 \text{ R})(0.86332 \text{ ft}^{3}/\text{lbm})} \left(\frac{5.404 \text{ psia} \cdot \text{ft}^{3}}{1 \text{ Btu}}\right) (110 - 100) \text{R}$
= **134.0 psia**

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

$$P_{2} = P_{1} + \frac{h_{fg}}{T v_{fg}} (T_{2} - T_{1})$$

= 116.7 psia + $\frac{154.85 \text{ Btu/lbm}}{(560 \text{ R})(0.86332 \text{ ft}^{3}/\text{lbm})} \left(\frac{5.404 \text{ psia} \cdot \text{ft}^{3}}{1 \text{ Btu}}\right) (90 - 100) \text{R}$
= **99.4 psia**

12-32 It is to be shown that
$$c_{p,g} - c_{p,f} = T \left(\frac{\partial (h_{fg} / T)}{\partial T} \right)_P + \boldsymbol{v}_{fg} \left(\frac{\partial P}{\partial T} \right)_{\text{sat}}$$

Analysis The definition of specific heat and Clapeyron equation are

$$c_{p} = \left(\frac{\partial h}{\partial T}\right)_{p}$$
$$\left(\frac{dP}{dT}\right)_{\text{sat}} = \frac{h_{fg}}{T\boldsymbol{v}_{fg}}$$

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

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

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

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

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

12-33C Yes, through the relation

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

12-34E The specific heat difference $c_p - c_v$ for liquid water at 1000 psia and 300°F is to be estimated. *Analysis* The specific heat difference $c_p - c_v$ is given as

$$c_{p} - c_{v} = -T \left(\frac{\partial v}{\partial T}\right)_{P}^{2} \left(\frac{\partial P}{\partial v}\right)_{T}$$

Approximating differentials by differences about the specified state,

$$c_{p} - c_{v} \cong -T \left(\frac{\Delta v}{\Delta T}\right)_{P=1000\text{psia}}^{2} \left(\frac{\Delta P}{\Delta v}\right)_{T=300^{\circ}\text{F}}$$

= -(300 + 459.67 R) $\left(\frac{v_{325^{\circ}\text{F}} - v_{275^{\circ}\text{F}}}{(325 - 275)^{\circ}\text{F}}\right)_{P=1000\text{psia}}^{2} \left(\frac{(1500 - 500)\text{psia}}{v_{1500\text{psia}} - v_{500\text{psia}}}\right)_{T=300^{\circ}\text{F}}$
= -(609.67 R) $\left(\frac{(0.017633 - 0.017151)\text{ft}^{3}/\text{lbm}}{50 \text{ R}}\right)^{2} \left(\frac{1000 \text{ psia}}{(0.017345 - 0.017417)\text{ft}^{3}/\text{lbm}}\right)$
= 0.986 psia \cdot ft³/lbm \cdot R
= **0.183 Btu/lbm** \cdot R (1 Btu = 5.4039 psia \cdot ft³)

Properties are obtained from Table A-7E.

12-35 The volume expansivity β and the isothermal compressibility α of refrigerant-134a at 200 kPa and 30°C are to be estimated.

Analysis The volume expansivity and isothermal compressibility are expressed as

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

Approximating differentials by differences about the specified state,

$$\beta \approx \frac{1}{\nu} \left(\frac{\Delta \nu}{\Delta T} \right)_{P=200 \text{kPa}} = \frac{1}{\nu} \left(\frac{\nu_{40^{\circ}\text{C}} - \nu_{20^{\circ}\text{C}}}{(40 - 20)^{\circ}\text{C}} \right)_{P=200 \text{kPa}}$$
$$= \frac{1}{0.11874 \text{ m}^3/\text{kg}} \left(\frac{(0.12322 - 0.11418)\text{m}^3/\text{kg}}{20 \text{ K}} \right)$$
$$= 0.00381 \text{ K}^{-1}$$

and

$$\alpha \approx -\frac{1}{\upsilon} \left(\frac{\Delta \upsilon}{\Delta P} \right)_{T=30^{\circ}\text{C}} = -\frac{1}{\upsilon} \left(\frac{\upsilon_{240\text{kPa}} - \upsilon_{180\text{kPa}}}{(240 - 180)\text{kPa}} \right)_{T=30^{\circ}\text{C}}$$
$$= -\frac{1}{0.11874 \text{ m}^3/\text{kg}} \left(\frac{(0.09812 - 0.13248)\text{m}^3/\text{kg}}{60 \text{ kPa}} \right)$$
$$= 0.00482 \text{ kPa}^{-1}$$

Assumptions Constant specific heats for air can be used.

Properties For air at the average temperature $(20+300)/2=160^{\circ}C=433$ K, $c_v = 0.731$ kJ/kg·K (Table A-2*b*). **Analysis** Solving the equation of state for *P* gives

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

Then,

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

Using equation 12-29,

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

Substituting,

$$du = c_{\mathbf{v}} dT + \left(\frac{RT}{\mathbf{v} - a} - \frac{RT}{\mathbf{v} - a}\right) d\mathbf{v}$$
$$= c_{\mathbf{v}} dT$$

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

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

The ideal gas model for the air gives

$$du = c_v dT$$

which gives the same answer.

Assumptions Constant specific heats for air can be used.

Properties For air at the average temperature (20+300)/2=160°C=433 K, $c_p = 1.018$ kJ/kg·K (Table A-2*b*). **Analysis** Solving the equation of state for v gives

$$\boldsymbol{v} = \frac{RT}{P} + a$$

Then,

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

Using equation 12-35,

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

Substituting,

$$dh = c_p dT + \left(\frac{RT}{P} + a - \frac{RT}{P}\right) dP$$
$$= c_p dT + adP$$

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

$$h_2 - h_1 = c_p (T_2 - T_1) + a(P_2 - P_1)$$

= (1.018 kJ/kg · K)(300 - 20)K + (0.01 m³/kg)(600 - 100)kPa
= **290.0 kJ/kg**

For an ideal gas,

 $dh = c_p dT$

which when integrated gives

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

Assumptions Constant specific heats for air can be used.

Properties For air at the average temperature (20+300)/2=160°C=433 K, $c_p = 1.018$ kJ/kg·K (Table A-2*b*) and R = 0.287 kJ/kg·K (Table A-1).

Analysis Solving the equation of state for v gives

$$\boldsymbol{v} = \frac{RT}{P} + a$$

Then,

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

The entropy differential is

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

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

$$s_{2} - s_{1} = c_{p} \ln \frac{T_{2}}{T_{1}} - R \ln \frac{P_{2}}{P_{1}}$$

= (1.018 kJ/kg·K)ln $\frac{573 \text{ K}}{293 \text{ K}} - (0.287 \text{ kJ/kg·K}) \ln \frac{600 \text{ kPa}}{100 \text{ kPa}}$
= **0.1686 kJ/kg·K**

12-39 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

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

Then,

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

Using equation 12-29,

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

Substituting,

$$du = c_{v} dT + \left(\frac{RT}{v-a} - \frac{RT}{v-a}\right) dv$$
$$= c_{v} dT$$

Integrating this result between the two states gives

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

The ideal gas model for the helium gives

$$du = c_v dT$$

which gives the same answer.

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

Analysis Solving the equation of state for \boldsymbol{v} gives

$$\boldsymbol{v} = \frac{RT}{P} + a$$

Then,

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

Using equation 12-35,

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

Substituting,

$$dh = c_p dT + \left(\frac{RT}{P} + a - \frac{RT}{P}\right) dP$$
$$= c_p dT + adP$$

Integrating this result between the two states gives

$$h_2 - h_1 = c_p (T_2 - T_1) + a(P_2 - P_1)$$

= (5.1926 kJ/kg · K)(300 - 20)K + (0.01 m³/kg)(600 - 100)kPa
= **1459 kJ/kg**

For an ideal gas,

$$dh = c_n dT$$

which when integrated gives

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

12-41 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-2*a*).

Analysis Solving the equation of state for v gives

$$\boldsymbol{v} = \frac{RT}{P} + a$$

Then,

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

The entropy differential is

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

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

$$s_{2} - s_{1} = c_{p} \ln \frac{T_{2}}{T_{1}} - R \ln \frac{P_{2}}{P_{1}}$$

= (5.1926 kJ/kg·K)ln $\frac{573 \text{ K}}{293 \text{ K}}$ - (2.0769 kJ/kg·K)ln $\frac{600 \text{ kPa}}{100 \text{ kPa}}$
= -**0.2386 kJ/kg·K**

12-42 General expressions for Δu , Δh , and Δs 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 Δu is obtained from the general relation

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

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

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

Thus,

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

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

(b) A relation for Δh is obtained from the general relation

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

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

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

Thus,

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

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 Δs is obtained from the general relation

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

Substituting $(\partial \mathbf{v}/\partial T)_P = R/T$,

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

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

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

Analysis The general relation for du is

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

Differentiating each term in this equation with respect to P at T = constant yields

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

Using the properties P, T, v, the cyclic relation can be expressed as

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

Substituting, we get

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

The general relation for dh is

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

Differentiating each term in this equation with respect to v at T = constant yields

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

Using the properties \boldsymbol{v}, T, P , the cyclic relation can be expressed as

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

Substituting, we get

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

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

$$ds = \left(\frac{\partial s}{\partial T}\right)_{\boldsymbol{v}} dT + \left(\frac{\partial s}{\partial \boldsymbol{v}}\right)_{T} d\boldsymbol{v}$$

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

$$ds = \frac{c_{\boldsymbol{v}}}{T} dT + \left(\frac{\partial P}{\partial T}\right)_{\boldsymbol{v}} d\boldsymbol{v}$$

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

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

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,

$$dP = \left(\frac{\partial P}{\partial T}\right)_{\boldsymbol{v}} dT + \left(\frac{\partial P}{\partial \boldsymbol{v}}\right)_{T} d\boldsymbol{v}$$

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

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

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

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

12-45 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

$$dS_{\text{tot}} = dS_{\text{A}} + dS_{\text{B}} \ge 0$$

Assume
$$S = S(u, v)$$

Then,

$$ds = \left(\frac{\partial s}{\partial u}\right)_{\boldsymbol{v}} du + \left(\frac{\partial s}{\partial \boldsymbol{v}}\right)_{u} d\boldsymbol{v}$$

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

$$ds = \left(\frac{\partial s}{\partial u}\right)_{\mathbf{v}} du$$

and from the definition of temperature from the problem statement,

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

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

$$E_{in} - E_{out} = dU$$

$$0 = dU \longrightarrow m_A du_A + m_B du_B = 0 \longrightarrow m_B du_B = -m_A du_A$$

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,

$$\lim dS_{\text{tot}} = 0$$
$$T_A \to T_B$$



Analysis Solving the equation of state for v gives

$$\boldsymbol{v} = \frac{RT}{P} + a$$

The specific volume derivative is then

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

The definition for volume expansivity is

Р

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

Combining these two equations gives

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

12-47 An expression for the specific heat difference of a substance whose equation of state is P(v - a) = RT is to be derived.

Analysis The specific heat difference is expressed by

$$c_{p} - c_{v} = -T \left(\frac{\partial v}{\partial T}\right)_{P}^{2} \left(\frac{\partial P}{\partial v}\right)_{T}$$

Solving the equation of state for specific volume,

$$\boldsymbol{v} = \frac{RT}{P} + a$$

The specific volume derivatives are then

$$\begin{pmatrix} \frac{\partial \boldsymbol{v}}{\partial P} \end{pmatrix}_T = -\frac{RT}{P^2} \longrightarrow \left(\frac{\partial P}{\partial \boldsymbol{v}} \right)_T = -\frac{P^2}{RT}$$
$$\begin{pmatrix} \frac{\partial \boldsymbol{v}}{\partial T} \end{pmatrix}_P = \frac{R}{P}$$

Substituting,

$$c_p - c_v = -T\left(\frac{R}{P}\right)^2 \left(-\frac{P^2}{RT}\right) = -T\left(\frac{R^2}{P^2}\right) \left(-\frac{P^2}{RT}\right) = R$$

12-48 An expression for the isothermal compressibility of a substance whose equation of state is P(v - a) = RT is to be derived.

Analysis The definition for the isothermal compressibility is

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

Solving the equation of state for specific volume,

$$\boldsymbol{v} = \frac{RT}{P} + a$$

The specific volume derivative is then

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

Substituting these into the isothermal compressibility equation gives

$$\alpha = \frac{RT}{P^2} \left(\frac{P}{RT + aP} \right) = \frac{RT}{P(RT + aP)}$$

12-49 An expression for the isothermal compressibility 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 definition for the isothermal compressibility is

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

The derivative is

$$\left(\frac{\partial P}{\partial \boldsymbol{v}}\right)_{T} = -\frac{RT}{\left(\boldsymbol{v}-b\right)^{2}} + \frac{a}{T^{1/2}}\frac{2\boldsymbol{v}+b}{\boldsymbol{v}^{2}\left(\boldsymbol{v}+b\right)^{2}}$$

Substituting,

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

12-50 An expression for the volume expansivity 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 definition for volume expansivity is

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

According to the cyclic relation,

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

which on rearrangement becomes

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

Proceeding to perform the differentiations gives

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

and

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

Substituting these results into the definition of the volume expansivity produces

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

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

Analysis The definition for volume expansivity is

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

According to the cyclic relation,

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

which on rearrangement becomes

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

Proceeding to perform the differentiations gives

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

and

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

Substituting these results into the definition of the volume expansivity produces

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

Analysis The definition for the volume expansivity is

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

The definition for the isothermal compressibility is

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

According to the cyclic relation,

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

which on rearrangement becomes

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

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

$$\beta = -\frac{1}{\upsilon} \left(\frac{\partial \upsilon}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_{\upsilon}$$
$$= -\alpha \left(\frac{\partial P}{\partial T} \right)_{\upsilon}$$

12-53 It is to be demonstrated that
$$k = \frac{c_p}{c_v} = -\frac{v\alpha}{(\partial v / \partial P)_s}$$

Analysis The relations for entropy differential are

$$ds = c_{\boldsymbol{v}} \frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_{\boldsymbol{v}} d\boldsymbol{v}$$
$$ds = c_{p} \frac{dT}{T} - \left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{p} dP$$

For fixed s, these basic equations reduce to

$$c_{v} \frac{dT}{T} = -\left(\frac{\partial P}{\partial T}\right)_{v} dv$$
$$c_{p} \frac{dT}{T} = \left(\frac{\partial v}{\partial T}\right)_{p} dP$$

Also, when *s* is fixed,

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

Forming the specific heat ratio from these expressions gives

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

The cyclic relation is

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

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

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

12-54 The Helmholtz function of a substance has the form $a = -RT \ln \frac{v}{v_0} - cT_0 \left(1 - \frac{T}{T_0} + \frac{T}{T_0} \ln \frac{T}{T_0}\right)$. It is to be shown how

to obtain *P*, *h*, *s*, c_{u} and c_{p} from this expression.

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

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

while the applicable Helmholtz equation is

$$da = -Pd\mathbf{v} - sdT$$

Equating the coefficients of the two results produces

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

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

$$P = \frac{RT}{v}$$
$$s = R \ln \frac{v}{v_0} + c \ln \frac{T}{T_0}$$

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

$$h = u + P\mathbf{v}$$

$$= a + Ts + P\mathbf{v}$$

$$= a - T\left(\frac{\partial a}{\partial T}\right)_{\mathbf{v}} - \mathbf{v}\left(\frac{\partial a}{\partial \mathbf{v}}\right)_{T}$$

$$= -RT \ln \frac{\mathbf{v}}{\mathbf{v}_{0}} - cT_{0}\left(1 - \frac{T}{T_{0}} + \frac{T}{T_{0}}\ln \frac{T}{T_{0}}\right) + RT \ln \frac{\mathbf{v}}{\mathbf{v}_{0}} - cT \ln \frac{T}{T_{0}} + RT$$

$$= cT_{0} + cT + RT$$

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

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

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,

$$c_p = R + c_v = R + c$$

The Joule-Thomson Coefficient

12-55C It represents the variation of temperature with pressure during a throttling process.

12-56C 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.

12-57C No. The temperature may even increase as a result of throttling.

12-58C Yes.

12-59C 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 = constant) process.

12-60E The Joule-Thompson coefficient of nitrogen at two states is to be estimated.

Analysis (*a*) The enthalpy of nitrogen at 120 psia and 350 R is, from EES, h = 84.88 Btu/lbm. Approximating differentials by differences about the specified state, the Joule-Thomson coefficient is expressed as

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \cong \left(\frac{\Delta T}{\Delta P}\right)_{h=84.88 \text{ Btu/lbm}}$$

Considering a throttling process from 130 psia to 110 psia at h = 84.88 Btu/lbm, the Joule-Thomson coefficient is determined to be

$$\mu = \left(\frac{T_{110 \text{ psia}} - T_{130 \text{ psia}}}{(110 - 130) \text{ psia}}\right)_{h=84.88 \text{ Btu/lbm}} = \frac{(349.40 - 350.60) \text{ R}}{(110 - 130) \text{ psia}} = 0.0599 \text{ R/psia}$$

(b) The enthalpy of nitrogen at 1200 psia and 700 R is, from EES, h = 170.14 Btu/lbm. Approximating differentials by differences about the specified state, the Joule-Thomson coefficient is expressed as

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \cong \left(\frac{\Delta T}{\Delta P}\right)_{h=170.14 \text{Btu/lbm}}$$

Considering a throttling process from 1210 psia to 1190 psia at h = 170.14 Btu/lbm, the Joule-Thomson coefficient is determined to be

$$\mu = \left(\frac{T_{1190 \text{ psia}} - T_{1210 \text{ psia}}}{(1190 - 1210) \text{ psia}}\right)_{h=170.14 \text{ Btu/lbm}} = \frac{(699.91 - 700.09) \text{ R}}{(1190 - 1210) \text{ psia}} = 0.00929 \text{ R/psia}$$

12-61E Problem 12-60E 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' $\{P_ref=120 [psia]$ $T_ref=350 [R]$ $P=P_ref\}$ h=100 [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]



12-62 Steam is throttled slightly from 1 MPa and 300°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 $T = 300^{\circ}$ 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

$$P = 0.8 \text{ MPa} \\ h = 3051.6 \text{ kJ/kg}$$

Therefore, the temperature will decrease.

12-63E 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

$$P_1 = 40 \text{ psia}$$

 $T_1 = 60^{\circ}\text{F}$ $h_1 = 113.79 \text{ Btu/lbm}$ (Table A - 13E)

The second state will be selected for a pressure of 30 psia. At this pressure and the same enthalpy, we have

$$P_2 = 30 \text{ psia} h_2 = h_1 = 113.79 \text{ kJ/kg}$$
 $T_2 = 56.78^{\circ}\text{F} \text{ (Table A - 13E)}$

Substituting,

$$\mu \cong \frac{T_2 - T_1}{P_2 - P_1} = \frac{(56.78 - 60)R}{(30 - 40)psia} = 0.322 \text{ R/psia}$$

12-64 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

$$P_1 = 200 \text{ kPa}$$

 $T_1 = 90^{\circ}\text{C}$ $h_1 = 333.93 \text{ kJ/kg}$ (Table A - 13)

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

$$P_{2} = 180 \text{ kPa} h_{2} = h_{1} = 333.93 \text{ kJ/kg}$$
 $T_{2} = 89.78^{\circ}\text{C} \text{ (Table A - 13)}$

Substituting,

$$\mu \cong \frac{T_2 - T_1}{P_2 - P_1} = \frac{(89.78 - 90)\text{K}}{(180 - 200)\text{kPa}} = \textbf{0.0110 K/kPa}$$

12-65 The equation of state of a gas is given by $v = \frac{RT}{P} - \frac{bP}{T^2}$. An equation for the Joule-Thomson coefficient inversion

line using this equation is to be derived.

Analysis From Eq. 12-52 of the text,

$$c_{p} = \frac{1}{\mu} \left[T \left(\frac{\partial \boldsymbol{v}}{\partial T} \right)_{P} - \boldsymbol{v} \right]$$

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

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

Using the equation of state to evaluate the partial derivative,

$$\left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_P = \frac{R}{P} + 2\frac{bP}{T^3}$$

Substituting this result into the previous expression produces

$$\frac{RT}{P} + 2\frac{bP}{T^2} = \frac{RT}{P} - \frac{bP}{T^2} \longrightarrow 3\frac{bP}{T^2} = 0$$

The condition along the inversion line is then

$$P = 0$$

12-66 It is to be demonstrated that the Joule-Thomson coefficient is given by $\mu = \frac{T^2}{c_p} \left(\frac{\partial(\boldsymbol{v}/T)}{\partial T}\right)_P$.

Analysis From Eq. 12-52 of the text,

$$c_{p} = \frac{1}{\mu} \left[T \left(\frac{\partial \boldsymbol{v}}{\partial T} \right)_{P} - \boldsymbol{v} \right]$$

Expanding the partial derivative of v/T produces

$$\left(\frac{\partial \boldsymbol{v}/T}{\partial T}\right)_{P} = \frac{1}{T} \left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{P} - \frac{\boldsymbol{v}}{T^{2}}$$

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

$$\mu = \frac{T^2}{c_p} \left(\frac{\partial (\boldsymbol{v} / T)}{\partial T} \right)_p$$

12-67 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,

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

When $\mu = 0$, this equation becomes

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

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

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

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

The dh, du, and ds of Real Gases

12-68C It is the variation of enthalpy with pressure at a fixed temperature.

12-69C As P_R approaches zero, the gas approaches ideal gas behavior. As a result, the deviation from ideal gas behavior diminishes.

12-70C So that a single chart can be used for all gases instead of a single particular gas.

12-71 The errors involved in the enthalpy and internal energy of 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 CO₂ at the specified state is determined from the generalized chart to be (Fig. A-29)

and

 $T_{R} = \frac{T}{T_{cr}} = \frac{350}{304.2} = 1.151$ $P_{R} = \frac{P}{P_{cr}} = \frac{10}{7.39} = 1.353$ $\longrightarrow Z_{h} = \frac{(\overline{h}_{ideal} - \overline{h})_{T,P}}{R_{u}T_{cr}} = 1.5$

Thus,

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

and,

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

(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

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

and,

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



12-72 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),

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

and

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

(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)

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{225}{126.2} = 1.783$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{6}{3.39} = 1.770$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{320}{126.2} = 2.536$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{12}{3.39} = 2.540$$

$$Z_{h2} = 0.4 \text{ and } Z_{s2} = 0.15$$

Substituting,

$$h_{2} - h_{1} = R_{u}T_{cr}(Z_{h1} - Z_{h2}) + (h_{2} - h_{1})_{ideal}$$

= (8.314)(126.2)(0.6 - 0.4) + 2769
= **2979 kJ/kmol**
$$\bar{s}_{2} - \bar{s}_{1} = R_{u}(Z_{s1} - Z_{s2}) + (\bar{s}_{2} - \bar{s}_{1})_{ideal}$$

= (8.314)(0.25 - 0.15) + 4.510

$$= 5.341 \text{ kJ/kmol} \cdot \text{K}$$

12-73E 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 lbm/lbmol, $T_{cr} = 1164.8$ R, $P_{cr} = 3200$ psia

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

$$P_1 = P_2 = P_{\text{sat}(\underline{a}) 500^\circ\text{F}} = 680.56 \text{ psia}$$

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

$$(\overline{h}_2 - \overline{h}_1)_{\text{ideal}} = \overline{h}_{2,\text{ideal}} - \overline{h}_{1,\text{ideal}} = 12,178.8 - 7738.0 = 4440.8 \text{ Btu/lbmol}$$

and

$$(\bar{s}_2 - \bar{s}_1)_{\text{ideal}} = s_2^\circ - s_1^\circ - R_u \ln \frac{P_2}{P_1} = 53.556 - 49.843 - 0 = 3.713 \text{ Btu/lbmol} \cdot \text{R}$$

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)

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{960}{1164.8} = 0.824$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{680.56}{3200} = 0.213$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{1460}{1164.8} = 1.253$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{680.56}{3200} = 0.213$$

$$\longrightarrow Z_{h2} = 0.157 \text{ and } Z_{s2} = 0.0903$$

The enthalpy and entropy changes per mole basis are

$$\overline{h}_2 - \overline{h}_1 = (\overline{h}_2 - \overline{h}_1)_{ideal} - R_u T_{cr} (Z_{h2} - Z_{h1})$$

= 4440.8 - (1.9858)(1164.8)(0.157 - 0.340) = 4864 kJ/kmol
$$\overline{s}_2 - \overline{s}_1 = (\overline{s}_2 - \overline{s}_1)_{ideal} - R_u (Z_{s2} - Z_{s1})$$

= 3.713 - (1.9858)(0.0903 - 0.277) = 4.084 Btu/lbmol · R

The enthalpy and entropy changes per mass basis are

$$h_{2} - h_{1} = \frac{\overline{h}_{2} - \overline{h}_{1}}{M} = \frac{4864 \text{ Btu/lbmol}}{18.015 \text{ lbm/lbmol}} = 270.0 \text{ Btu/lbm}$$
$$s_{2} - s_{1} = \frac{\overline{s}_{2} - \overline{s}_{1}}{M} = \frac{4.084 \text{ Btu/lbmol} \cdot \text{K}}{18.015 \text{ lbm/lbmol}} = 0.2267 \text{ Btu/lbm} \cdot \text{R}$$

(b) The inlet and exit state properties of water are

$$T_{1} = 500^{\circ} \text{F} \begin{cases} h_{1} = 1202.3 \text{ Btu/lbm} \\ s_{1} = 1.4334 \text{ Btu/lbm} \cdot \text{R} \end{cases}$$
(Table A-4E)

$$P_{2} = 680.56 \text{ psia} \{ h_{2} = 1515.7 \text{ Btu/lbm} \\ T_{2} = 1000^{\circ}\text{F} \{ s_{2} = 1.7008 \text{ Btu/lbm} \cdot \text{R} \}$$
(from EES)

The enthalpy and entropy changes are

$$h_2 - h_1 = 1515.7 - 1202.3 =$$
 313.4 Btu/lbm
 $s_2 - s_1 = 1.7008 - 1.4334 =$ **0.2674 Btu/lbm** · **R**

12-74E 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)

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

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

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

and

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

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)

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{1960}{1164.8} = 1.683$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{3000}{3200} = 0.9375$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{1460}{1164.8} = 1.253$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{1000}{3200} = 0.3125$$

$$\longrightarrow Z_{h2} = 0.233 \text{ and } Z_{s2} = 0.134$$

The enthalpy and entropy changes per mole basis are

$$\begin{aligned} \overline{h}_2 &- \overline{h}_1 = (\overline{h}_2 - \overline{h}_1)_{ideal} - R_u T_{cr} (Z_{h2} - Z_{h1}) \\ &= -4853.7 - (1.9858)(1164.8)(0.233 - 0.387) = -4497.5 \text{ Btu/lbmol} \\ \overline{s}_2 &- \overline{s}_1 = (\overline{s}_2 - \overline{s}_1)_{ideal} - R_u (Z_{s2} - Z_{s1}) \\ &= -0.6734 - (1.9858)(0.134 - 0.188) = -0.5662 \text{ Btu/lbmol} \cdot \text{R} \end{aligned}$$

The enthalpy and entropy changes per mass basis are

$$h_2 - h_1 = \frac{h_2 - h_1}{M} = \frac{-4497.5 \text{ Btu/lbmol}}{18.015 \text{ lbm/lbmol}} = -249.7 \text{ Btu/lbm}$$
$$s_2 - s_1 = \frac{\overline{s}_2 - \overline{s}_1}{M} = \frac{-0.5662 \text{ Btu/lbmol} \cdot \text{R}}{18.015 \text{ lbm/lbmol}} = -0.0314 \text{ Btu/lbm} \cdot \text{R}$$

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

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$$P_{1} = 3000 \text{ psia} \quad h_{1} = 1764.6 \text{ Btu/lbm}$$

$$T_{1} = 1500^{\circ}\text{F} \quad s_{1} = 1.6883 \text{ Btu/lbm} \cdot \text{R}$$

$$P_{2} = 1000 \text{ psia} \quad h_{2} = 1506.2 \text{ Btu/lbm}$$

$$T_{2} = 1000^{\circ}\text{F} \quad s_{2} = 1.6535 \text{ Btu/lbm} \cdot \text{R}$$

The enthalpy and entropy changes are

$$h_2 - h_1 = 1506.2 - 1764.6 = -258.4$$
 Btu/lbm
 $s_2 - s_1 = 1.6535 - 1.6883 = -0.0348$ Btu/lbm·R

12-75 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)

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

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

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

and

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

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)

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{873}{647.1} = 1.349$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{1}{22.06} = 0.0453$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{673}{647.1} = 1.040$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{0.5}{22.06} = 0.0227$$

The enthalpy and entropy changes per mole basis are

$$\overline{h}_{2} - \overline{h}_{1} = (\overline{h}_{2} - \overline{h}_{1})_{ideal} - R_{u}T_{cr}(Z_{h2} - Z_{h1})$$

$$= -7672 - (8.314)(647.1)(0.0223 - 0.0288) = -7637 \text{ kJ/kmol}$$

$$\overline{s}_{2} - \overline{s}_{1} = (\overline{s}_{2} - \overline{s}_{1})_{ideal} - R_{u}(Z_{s2} - Z_{s1})$$

$$= -4.2052 - (8.314)(0.0146 - 0.0157) = -4.1961 \text{ kJ/kmol} \cdot \text{K}$$

The enthalpy and entropy changes per mass basis are

$$h_2 - h_1 = \frac{h_2 - h_1}{M} = \frac{-7637 \text{ kJ/kmol}}{18.015 \text{ kg/kmol}} = -423.9 \text{ kJ/kg}$$
$$s_2 - s_1 = \frac{\overline{s}_2 - \overline{s}_1}{M} = \frac{-4.1961 \text{ kJ/kmol} \cdot \text{K}}{18.015 \text{ kg/kmol}} = -0.2329 \text{ kJ/kg} \cdot \text{K}$$

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

$$P_{1} = 1000 \text{ kPa} \quad h_{1} = 3698.6 \text{ kJ/kg}$$

$$T_{1} = 600^{\circ}\text{C} \quad s_{1} = 8.0311 \text{ kJ/kg} \cdot \text{K}$$

$$P_{2} = 500 \text{ kPa} \quad h_{2} = 3272.4 \text{ kJ/kg}$$

$$T_{2} = 400^{\circ}\text{C} \quad s_{2} = 7.7956 \text{ kJ/kg} \cdot \text{K}$$

The enthalpy and entropy changes are

$$h_2 - h_1 = 3272.4 - 3698.6 = -426.2 \text{ kJ/kg}$$

 $s_2 - s_1 = 7.7956 - 8.0311 = -0.2355 \text{ kJ/kg} \cdot \text{K}$

12-76 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

$$\dot{E}_{in} - \dot{E}_{out} = \Delta \dot{E}_{system}^{(d)(steady)} = 0$$
$$\dot{E}_{in} = \dot{E}_{out}$$
$$\dot{W}_{C,in} + \dot{m}h_1 = \dot{m}h_2$$
$$\dot{W}_{C,in} = \dot{m}(h_2 - h_1)$$

The enthalpy departures of CH_4 at the specified states are determined from the generalized charts to be (Fig. A-29)

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{263}{191.1} = 1.376$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{0.8}{4.64} = 0.172$$



and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{448}{191.1} = 2.34$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{6}{4.64} = 1.29$$

Thus,

$$h_2 - h_1 = RT_{\rm cr}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{\rm ideal}$$

= (0.5182)(191.1)(0.075 - 0.25) + 2.2537(175 - (-10))
= 399.6 kJ/kg

Substituting,

$$\dot{W}_{\rm C,in} = (0.2 \text{ kg/s})(399.6 \text{ kJ/kg}) = 79.9 \text{ kW}$$

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

$$(\bar{s}_2 - \bar{s}_1)_{ideal} = \int_{1}^{2} \frac{c_p}{T} dT - R_u \ln \frac{P_2}{P_1} = \int_{1}^{2} \left(\frac{a}{T} + b + cT + dT^2\right) dT - R_u \ln \frac{P_2}{P_1}$$

= $a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) + \frac{d}{3}(T_2^3 - T_1^3) - R_u \ln \frac{P_2}{P_1}$
0 = $-4.04 \ln \frac{T_2}{450} + 30.48 \left(\frac{T_2}{100} - 4.50\right) - 0.786 \left[\left(\frac{T_2}{100}\right)^2 - 4.50^2\right] + 0.01058 \left[\left(\frac{T_2}{100}\right)^3 - 4.50^3\right]$
- $(8.314) \ln \frac{7000}{750}$

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

 $T_2 = 532 \,\mathrm{K}$

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

$$\overline{w}_{in} = (\overline{h}_2 - \overline{h}_1)_{ideal} = \int_1^2 c_p dT = \int_1^2 (a + bT + cT^2 + dT^3) dT$$
$$= a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4)$$
$$= -4.04(532 - 450) + 0.1524(532^2 - 450^2) - 52.4(5.32^3 - 4.50^3) + 0.7935(5.32^4 - 4.50^4)$$

= 9111 kJ/kmol

The work input per unit mass basis is

$$w_{\rm in} = \frac{\overline{w}_{\rm in}}{M} = \frac{9111 \,\text{kJ/kmol}}{44.097 \,\text{kg/kmol}} = 207 \,\text{kJ/kg}$$

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

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{450}{370} = 1.22$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{0.5}{4.26} = 0.176$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{532}{370} = 1.44$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{7}{4.26} = 1.64$$

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

$$w_{\text{in}} = h_2 - h_1 = (h_2 - h_1)_{\text{ideal}} - RT_{\text{cr}}(Z_{h2} - Z_{h1})$$

= 207 - (0.1885)(370)(0.971 - 0.136)
= **148 kJ/kg**

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Propane

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

M = 31.999 lbm/lbmol, R = 0.06206 Btu/lbm · R, $T_{cr} = 278.6$ R, $P_{cr} = 736$ 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,

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

 $s_2^\circ = s_1^\circ - 2.085 = 53.921 - 2.085 = 51.836 \text{ Btu/lbmol} \cdot \text{R}$
 $s_2^\circ = 51.836 \text{ Btu/lbmol} \cdot \text{R} \longrightarrow T_2 = 802 \text{ R}, \ \overline{h}_{2,\text{ideal}} = 5614.1 \text{ Btu/lbmol}$

The enthalpy change per mole basis is

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

The enthalpy change per mass basis is

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

An energy balance on the nozzle gives

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

Solving for the exit velocity,

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

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

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{1060}{278.6} = 3.805 \\ P_{R1} = \frac{P_1}{P_{cr}} = \frac{200}{736} = 0.272 \end{cases} \qquad T_{R2} = \frac{T_2}{T_{cr}} = \frac{802}{278.6} = 2.879 \\ P_{R2} = \frac{P_2}{P_{cr}} = \frac{70}{736} = 0.0951 \end{cases} \qquad Z_{h2} = 0.00894 \\ P_{R2} = \frac{P_2}{P_{cr}} = \frac{70}{736} = 0.0951 \end{cases}$$

The enthalpy change is

$$h_2 - h_1 = (h_2 - h_1)_{ideal} - RT_{cr}(Z_{h2} - Z_{h1})$$

= -60.30 Btu/lbm - (0.06206 Btu/lbm · R)(278.6 R)(0.00894 - 0.000759)
= -60.44 Btu/lbm

The exit velocity is

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



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)

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{373}{370} = 1.008$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{1}{4.26} = 0.235$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{373}{370} = 1.008$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{4}{4.26} = 0.939$$

$$\longrightarrow Z_{h2} = 1.8 \text{ and } Z_2 = 0.50$$



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

$$P\mathbf{v} = ZRT \cong Z_{avg}RT = C = constant$$

Then the boundary work becomes

$$w_{b,\text{in}} = -\int_{1}^{2} P d\boldsymbol{v} = -\int_{1}^{2} \frac{C}{\boldsymbol{v}} d\boldsymbol{v} = -C \ln \frac{\boldsymbol{v}_{2}}{\boldsymbol{v}_{1}} = Z_{\text{avg}} RT \ln \frac{Z_{2}RT/P_{2}}{Z_{1}RT/P_{1}} = -Z_{\text{ave}} RT \ln \frac{Z_{2}P_{1}}{Z_{1}P_{2}}$$
$$= -(0.71)(0.1885 \text{ kJ/kg} \cdot \text{K})(373 \text{ K}) \ln \frac{(0.50)(1)}{(0.92)(4)} = 99.6 \text{ kJ/kg}$$

Also,

$$h_2 - h_1 = RT_{cr}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{ideal} = (0.1885)(370)(0.28 - 1.8) + 0 = -106 \text{ kJ/kg}$$

$$u_2 - u_1 = (h_2 - h_1) - R(Z_2T_2 - Z_1T_1) = -106 - (0.1885)[(0.5)(373) - (0.92)(373)] = -76.5 \text{ kJ/kg}$$

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

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

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

$$q_{\text{in}} = (u_2 - u_1) - w_{b,\text{in}} = -76.5 - 99.6 = -176.1 \text{ kJ/kg} \rightarrow q_{\text{out}} = 176.1 \text{ kJ/kg}$$

12-55

12-80 Problem 12-79 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_ideal=R*T[1]*Ln(p[1]/p[2])
```

"First Law - note that u_ideal[2] is equal to u_ideal[1]" q_ideal-w_ideal=u_ideal[2]-u_ideal[1]

"Entropy change" DELTAs_ideal=s_ideal[2]-s_ideal[1]

```
"***** COMPRESSABILITY 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[1]=h_ideal[1]-DELTAh[1]
                                    "Enthalpy of real gas using charts"
u[1]=h[1]-Z[1]*R*T[1]
       "Internal energy of gas using charts"
DELTAs[1]=ENTRDEP(Tr[1], Pr[1])*R "Entropy departure"
s[1]=s_ideal[1]-DELTAs[1]
                                   "Entropy of real gas using charts"
"State 2"
T[2]=T[1]
Tr[2]=Tr[1]
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"
DELTAs[2]=ENTRDEP(Tr[2], Pr[2])*R "Entropy departure"
                                    "Enthalpy of real gas using charts"
h[2]=h_ideal[2]-DELTAh[2]
s[2]=s ideal[2]-DELTAs[2]
                                    "Entropy of real gas using charts"
u[2]=h[2]-Z[2]*R*T[2]
                                    "Internal energy of gas using charts"
```

"First Law - note that u[2] is not equal to u[1]" q_chart-w_chart=u[2]-u[1]

"Entropy Change" DELTAs_chart=s[2]-s[1]

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

"At state 1" u_ees[1]=intEnergy(Name\$,T=T[1],p=p[1]) s_ees[1]=entropy(Name\$,T=T[1],p=p[1]) "At state 2" u_ees[2]=IntEnergy(Name\$,T=T[2],p=p[2]) s_ees[2]=entropy(Name\$,T=T[2],p=p[2])

"Work using EES built-in properties- note use of EES Integral funcion to evaluate the integral of pdv." w_ees=integral(p_ees, v_ees, v_ees[1],v_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]

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"Entropy change" DELTAs_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

DELTAh[1]=16.48 [kJ/kg] DELTAh[2]=91.96 [kJ/kg] DELTAs[1]=0.03029 [kJ/kg-K] DELTAs[2]=0.1851 [kJ/kg-K] DELTAs_chart=-0.4162 [kJ/kg-K] DELTAs_ees=-0.4711 [kJ/kg-K] DELTAs_ideal=-0.2614 [kJ/kg-K] Fluid\$='C3H8' h[1]=-2232 [kJ/kg] h[2]=-2308 [kJ/kg] h_ideal[1]=-2216 [kJ/kg] h_ideal[2]=-2216 [kJ/kg] M=44.1 Name\$='Propane' p=4000 p[1]=1000 [kPa] p[2]=4000 [kPa] pr[1]=0.2165 pr[2]=0.8658 p critical=4620 [kPa] p ees=4000 q_chart=-155.3 [kJ/kg] q_ees=-175.8 [kJ/kg] q_ideal=-97.54 [kJ/kg] R=0.1885 [kJ/kg-K] R_u=8.314 [kJ/mole-K] s[1]=6.073 [kJ/kg-K]

s[2]=5.657 [kJ/kg-K] s_ees[1]=2.797 [kJ/kg-K] s_ees[2]=2.326 [kJ/kg-K] s ideal[1]=6.103 [kJ/kg-K] s_ideal[2]=5.842 [kJ/kg-K] T[1]=373.2 [K] T[2]=373.2 [K] Tr[1]=1.009 Tr[2]=1.009 T_critical=370 [K] u[1]=-2298 [kJ/kg] u[2]=-2351 [kJ/kg] u_ees[1]=688.4 [kJ/kg] u ees[2]=617.1 [kJ/kg] u_ideal[1]=-2286 [kJ/kg] u_ideal[2]=-2286 [kJ/kg] v=0.01074 v[1]=0.06506 [m^3/kg] v[2]=0.01074 [m^3/kg] v_ees=0.009426 v ees[1]=0.0646 [m^3/kg] v_ees[2]=0.009426 [m^3/kg] w_chart=-101.9 [kJ/kg] w_ees=-104.5 [kJ/kg] w_ideal=-97.54 [kJ/kg] Z[1]=0.9246 Z[2]=0.6104

12-81 Propane is compressed isothermally by a piston-cylinder device. The exergy destruction associated with this process is to be determined.

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

Properties The gas constant of propane is R = 0.1885 kJ/kg.K (Table A-1).

Analysis The exergy destruction is determined from its definition $x_{destroyed} = T_0 s_{gen}$ 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

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

$$(s_2 - s_1)_{\text{ideal}} = c_p \ln \frac{T_2}{T_1}^{70} - R \ln \frac{P_2}{P_1} = 0 - 0.1885 \ln \frac{4}{1} = -0.261 \text{ kJ/kg} \cdot \text{K}$$

$$T_{R1} = \frac{T_1}{T_{\text{cr}}} = \frac{373}{370} = 1.008$$

$$P_{R1} = \frac{P_1}{P_{\text{cr}}} = \frac{1}{4.26} = 0.235$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{373}{370} = 1.008$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{4}{4.26} = 0.939$$

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

$$x_{\text{destroyed}} = T_0 s_{\text{gen}} = T_0 \left((s_2 - s_1) + \frac{q_{\text{out}}}{T_{\text{surr}}} \right)$$
$$= \left(303 \text{ K} \right) \left(-0.504 + \frac{176.1 \text{ kJ/kg}}{303 \text{ K}} \right) \text{kJ/kg} \cdot \text{K}$$
$$= 23.4 \text{ kJ/kg}$$

12-82 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 1The 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 kJ/kg.K (Table A-1).

Analysis (*a*) For this problem, we use critical properties, compressibility factor, and enthalpy departure factors in EES. The compressibility factor of oxygen at the initial state is determined from EES to be

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{175}{154.6} = 1.13$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{6}{5.043} = 1.19$$

$$\longrightarrow Z_1 = 0.682 \text{ and } Z_{h1} = 1.33$$



Then,

$$P\mathbf{v} = ZRT \longrightarrow \mathbf{v}_{1} = \frac{(0.682)(0.2598 \text{ kPa} \cdot \text{m}^{3}/\text{kg} \cdot \text{K})(175 \text{ K})}{6000 \text{ kPa}} = 0.00516 \text{ m}^{3}/\text{kg}$$
$$m = \frac{\mathbf{v}}{\mathbf{v}_{1}} = \frac{0.05 \text{ m}^{3}}{0.00516 \text{ m}^{3}/\text{kg}} = 9.68 \text{ kg}$$

The specific volume of oxygen remains constant during this process, $v_2 = v_1$. Thus,

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{225}{154.8} = 1.46$$

$$v_{R2} = \frac{v_2}{RT_{cr} / P_{cr}} = \frac{0.00516 \text{ m}^3/\text{kg}}{(0.2598 \text{ kPa} \cdot \text{m}^3/\text{kg} \cdot \text{K})(154.6 \text{ K})/(5043 \text{ kPa})} = 0.649 \begin{cases} Z_2 = 0.853 \\ Z_{h2} = 1.09 \\ P_{R2} = 1.91 \end{cases}$$

$$P_2 = P_{R2}P_{cr} = (1.91)(5043) = 9652 \text{ kPa}$$

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

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

$$W_{in} = \Delta U = m(u_2 - u_1)$$

$$W_{in} = m[h_2 - h_1 - (P_2 v_2 - P_1 v_1)] = m[h_2 - h_1 - R(Z_2 T_2 - Z_1 T_1)]$$

where

$$h_2 - h_1 = RT_{cr}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{ideal}$$

= (0.2598)(154.6)(1.33 - 1.09) + 52.96
= 62.51 kJ/kg

Substituting,

$$W_{\rm in} = (9.68 \text{ kg})[62.51 - (0.2598 \text{ kJ/kg} \cdot \text{K})\{(0.853)(225) - (0.682)(175)\}\text{K}] = 423 \text{ kJ}$$

Discussion The following routine in EES is used to get the solution above. Reading values from Fig. A-15 and A-29 together with properties in the book could yield different results.

"Given"

V=0.05 [m^3] T1=175 [K] P1=6000 [kPa] T2=225 [K]

"Properties"

Fluid\$='O2'

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```
R_u=8.314 [kJ/kmol-K]
T_cr=T_CRIT(Fluid$)
P_cr=P_CRIT(Fluid$)
MM=molarmass(Fluid$)
R=R u/MM
"Analysis"
"(a)"
T_R1=T1/T_cr
P_R1=P1/P_cr
Z_h1=ENTHDEP(T_R1, P_R1) "the function that returns enthalpy departure factor at T_R1 and P_R1"
Z_1=COMPRESS(T_R1, P_R1) "the function that returns compressibility factor at T_R1 and P_R1"
T_R2=T2/T_cr
v_R2=(v2*P_cr)/(R*T_cr)
v1=Z 1*R*T1/P1
m=V/v1
v2=v1
Z_h2=ENTHDEP(T_R2, P_R2) "the function that returns enthalpy departure factor at T_R2 and P_R2"
Z_2=COMPRESS(T_R2, P_R2) "the function that returns compressibility factor at T_R2 and P_R2"
P2=Z 2*R*T2/v2
P2=P_R2*P_cr
"(b)"
h1_ideal=enthalpy(Fluid$, T=T1)
h2_ideal=enthalpy(Fluid$, T=T2)
DELTAh_ideal=(h2_ideal-h1_ideal)
DELTAh=R*T_cr*(Z_h1-Z_h2)+DELTAh_ideal
DELTAu=DELTAh-R*(Z_2*T2-Z_1*T1)
W in=m*DELTAu
```

Solution

DELTAh=62.51 [kJ/kg]	T1=175 [K]
DELTAh_ideal=52.96 [kJ/kg]	T2=225 [K]
DELTAu=43.65 [kJ/kg]	T_cr=154.6 [K]
Fluid\$='O2'	T_R1=1.132
h1_ideal=-121.8 [kJ/kg]	T_R2=1.456
h2_ideal=-68.8 [kJ/kg]	V=0.05 [m^3]
m=9.682 [kg]	v1=0.005164 [m^3/kg]
MM=32 [kg/kmol]	v2=0.005164 [m^3/kg]
P1=6000 [kPa]	v_R2=0.6485
P2=9652 [kPa]	W_in=422.6 [kJ]
P_cr=5043 [kPa]	Z_1=0.6815
P_R1=1.19	Z_2=0.8527
P_R2=1.914	Z_h1=1.331
R=0.2598 [kJ/kg-K]	Z_h2=1.094
R u=8.314 [kJ/kmol-K]	

12-83 The heat transfer and entropy changes of CO_2 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 CO₂ (Table A-20),

$$(h_{2} - h_{1})_{ideal} = h_{2,ideal} - h_{1,ideal} = 161,293 - 12,,269 = 149,024 \text{ kJ/kmol}$$
$$(\bar{s}_{2} - \bar{s}_{1})_{ideal} = s_{2}^{\circ} - s_{1}^{\circ} - R_{u} \ln \frac{P_{2}}{P_{1}} = 333.770 - 222.367 - 8.314 \times \ln \frac{8}{1} = 94.115 \text{ kJ/kmol} \cdot \text{K}$$
$$(h_{2} - h_{1})_{ideal} = \frac{(\bar{h}_{2} - \bar{h}_{1})_{ideal}}{M} = \frac{149,024 \text{ kJ/kmol}}{44 \text{ kg/kmol}} = 3386.9 \text{ kJ/kg}$$

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

$$q_{\text{ideal}} = (u_2 - u_1)_{\text{ideal}} = (h_2 - h_1)_{\text{ideal}} - R(T_2 - T_1) ,$$

= 3386.9 kJ/kg - (0.1889 kJ/kg.K)(2984 - 373) = **2893.7 kJ/kg**

The entropy change is

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

The compressibility factor and the enthalpy and entropy departures of CO_2 at the specified states are determined from the generalized charts to be (we used EES)

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{373}{304.2} = 1.226$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{1}{7.39} = 0.135$$

$$Z_1 = 0.976, Z_{h1} = 0.1028 \text{ and } Z_{s1} = 0.05987$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{2985}{304.2} = 9.813$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{8}{7.39} = 1.083$$

$$\longrightarrow Z_2 = 1.009, \ Z_{h2} = -0.1144 \text{ and } Z_{s2} = -0.002685$$

Thus,

$$q_{\text{chart}} = u_2 - u_1 = (h_2 - h_1)_{\text{ideal}} - RT_{\text{cr}}(Z_{h2} - Z_{h1}) - Z_1R(T_2 - T_1)$$

= 3386.9 - (0.1889)(304.2)(-0.1144 - 0.1028) - (0.976)(0.1889)(2887 - 373) = **2935.9 kJ/kg**

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

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:

$$T_{1} = 373 \text{ K} \begin{cases} \boldsymbol{\nu}_{1} = 0.06885 \text{ m}^{3}/\text{kg} \\ \boldsymbol{\nu}_{1} = -8.614 \text{ kJ/kg} \\ \boldsymbol{\nu}_{1} = -0.2464 \text{ kJ/kg.K} \end{cases} \qquad P_{2} = 8 \text{ MPa} \\ \boldsymbol{\nu}_{2} = \boldsymbol{\nu}_{1} = 0.06885 \text{ m}^{3}/\text{kg} \begin{cases} T_{2} = 2879 \text{ K} \\ \boldsymbol{\nu}_{2} = 2754 \text{ kJ/kg.K} \\ \boldsymbol{\nu}_{2} = 2754 \text{ kJ/kg.K} \end{cases}$$

Then

$$q_{\text{EES}} = u_2 - u_1 = 2754 - (-8.614) =$$
2763 kJ/kg
 $\Delta s_{\text{EES}} = (s_2 - s_1)_{\text{EES}} = s_2 - s_1 = 1.85 - (-0.2464) =$ **2.097 kJ/kg.K**

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Review Problems

12-84 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 = 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 = constant lines on an *h*-s diagram is equal to the temperature.

(a) In the saturation region, T = constant for P = constant lines, and the slope remains constant.

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



12-85 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 , v , the cyclic relation can be expressed as

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

Substituting the first Maxwell relation,

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

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

(2) Using the properties T, v, s, the cyclic relation can be expressed as

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

Substituting the first Maxwell relation,

$$\left(\frac{\partial T}{\partial \boldsymbol{v}}\right)_{s} = -\left(\frac{\partial P}{\partial s}\right)_{\boldsymbol{v}}^{\dagger},$$

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

(3) Using the properties P, T, v, the cyclic relation can be expressed as

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

Substituting the third Maxwell relation,

$$\left(\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{v}}\right)_{T} = \left(\frac{\partial \boldsymbol{T}}{\partial \boldsymbol{T}}\right)_{\boldsymbol{v}},$$

 (\hat{a}) (∂P)

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

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12-86 For $\beta \ge 0$, 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: $dh = Tds + vdP \longrightarrow \frac{dh}{ds} = T + v\frac{dP}{ds}$

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

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

But the 4th Maxwell relation:

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

Therefore, the slope of P = constant lines is **greater** than the slope of T = constant lines.

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

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

From the ds relation:

$$ds = \frac{c_{v}}{T} dT + \left(\frac{\partial P}{\partial T}\right)_{v} dv$$

Divide by dP holding v constant:

 $\left(\frac{\partial s}{\partial P}\right)_{\boldsymbol{v}} = \frac{c_{\boldsymbol{v}}}{T} \left(\frac{\partial T}{\partial P}\right)_{\boldsymbol{v}} \quad \text{or} \quad \left(\frac{\partial P}{\partial s}\right)_{\boldsymbol{v}} = \frac{T}{c_{\boldsymbol{v}}} \left(\frac{\partial P}{\partial T}\right)_{\boldsymbol{v}} (b)$

Using the properties P, T, v, the cyclic relation can be expressed as

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

where we used the definitions of α and β . Substituting (b) and (c) into (a),

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

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

12-87 It is to be shown that

$$c_{\boldsymbol{v}} = -T\left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{s}\left(\frac{\partial P}{\partial T}\right)_{\boldsymbol{v}}$$
 and $c_{p} = T\left(\frac{\partial P}{\partial T}\right)_{s}\left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{F}$

Analysis Using the definition of c_v ,

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

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

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

Using the definition of c_p ,

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

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

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

12-88 It is to be proven that for a simple compressible substance $\left(\frac{\partial s}{\partial \boldsymbol{v}}\right)_u = \frac{P}{T}$.

Analysis The proof is simply obtained as

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

12-89 It is to be proven by using the definitions of pressure and temperature, $T = \left(\frac{\partial u}{\partial s}\right)_{\mathbf{v}}$ and $P = -\left(\frac{\partial u}{\partial \mathbf{v}}\right)_{s}$ that for ideal gases, the development of the constant-pressure specific heat yields $\left(\frac{\partial}{\partial P}\right)_{T} = 0$

Analysis The definition for enthalpy is

$$h = u + P \boldsymbol{v}$$

Then,

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

Assume u = u(s, v)

Then,

$$du = \left(\frac{\partial u}{\partial s}\right)_{\boldsymbol{v}} ds + \left(\frac{\partial u}{\partial \boldsymbol{v}}\right)_{s} d\boldsymbol{v}$$

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

$$\left(\frac{\partial u}{\partial P}\right)_{T} = T \left[-\left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{P}\right] - P \left(\frac{\partial \boldsymbol{v}}{\partial P}\right)_{T} = -(T+P) \left(\frac{\partial \boldsymbol{v}}{\partial P}\right)_{T}$$

$$\left(\frac{\partial h}{\partial P}\right)_{T} = -(T+P) \left(\frac{\partial \boldsymbol{v}}{\partial P}\right)_{T} + P \left(\frac{\partial \boldsymbol{v}}{\partial P}\right)_{T} + \boldsymbol{v} = -T \left(\frac{\partial \boldsymbol{v}}{\partial P}\right)_{T} + \boldsymbol{v}$$

For ideal gases

$$\boldsymbol{v} = \frac{RT}{P}$$
 and $\left(\frac{\partial \boldsymbol{v}}{\partial P}\right)_T = \frac{R}{P}$

Then,

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

12-90 It is to be proven by using the definitions of pressure and temperature, $T = \left(\frac{\partial u}{\partial s}\right)_{\boldsymbol{v}}$ and $P = -\left(\frac{\partial u}{\partial \boldsymbol{v}}\right)_{s}$ that for ideal gases, the development of the constant-volume specific heat yields $\left(\frac{\partial u}{\partial \boldsymbol{v}}\right)_{T} = 0$.

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

Then,

$$du = \left(\frac{\partial u}{\partial s}\right)_{\boldsymbol{v}} ds + \left(\frac{\partial u}{\partial \boldsymbol{v}}\right)_{s} d\boldsymbol{v}$$
$$\left(\frac{\partial u}{\partial \boldsymbol{v}}\right)_{T} = \left(\frac{\partial u}{\partial s}\right)_{\boldsymbol{v}} \left(\frac{\partial s}{\partial \boldsymbol{v}}\right)_{T} + \left(\frac{\partial u}{\partial \boldsymbol{v}}\right)_{s} \left(\frac{\partial \boldsymbol{v}}{\partial \boldsymbol{v}}\right)_{T}$$
$$= T \left(\frac{\partial s}{\partial \boldsymbol{v}}\right)_{T} + P$$

From Maxwell equation,

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

For ideal gases

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

Then,

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

12-91 Expressions for *h*, *u*, *s^o*, *P_r*, and *v_r* for an ideal gas whose c_p^{o} is given by $c_p^{o} = \sum a_i \left[\ln \left(\frac{T}{T_r} \right) \right]^{i-n}$ are to be

developed.

Analysis By making the change in variable, $x = \ln(T/T_r)$, the enthalpy of this substance relative to a reference state is given by

$$h = \int_{T_{ref}}^{T} c_p dT = \sum a_i \int_{x_{ref}}^{x} x^{i-n} e^x dx$$

= $\sum a_i e^x \left[x^{i-n} - (i-n)x^{i-n-1} + (i-n)(i-n-1)x^{i-n-2} - \dots + (-1)^{i-n}(i-n)! - x^{i-n-1}_{ref} + (i-n)x^{i-n-1}_{ref} - (i-n)(i-n-1)x^{i-n-2}_{ref} + \dots - (-1)^{i-n}(i-n)! \right]$

Similarly, s^0 is given by

$$s^{o} = \int_{T_{ref}}^{T} \left(\frac{c_{p}}{T}\right) dT = \sum a_{i}T_{r} \int_{x_{ref}}^{x} x^{i-n} e^{2x} dx$$

=
$$\sum \frac{a_{i}e^{2x}}{2^{i-n}} \left[(2x)^{i-n} - (i-n)(2x)^{i-n-1} + (i-n)(i-n-1)(2x)^{i-n-2} - \dots + (-1)^{i-n}(i-n)! - (2x)^{i-n-2} - \dots + (-1)^{i-n}(i-n)! \right]$$

With these two results,

$$u = h - P \mathbf{v}$$
$$P_r = e^{s^\circ / R}$$

According to the *du* form of Gibbs equations,

$$\frac{du}{T} = -R \frac{dv}{v}$$

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

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

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

$$\int c_p \frac{dT}{T} - R \ln \frac{T}{T_{\text{ref}}} = -R \ln \frac{\boldsymbol{v}}{\boldsymbol{v}_{\text{ref}}}$$

Solving this for the specific volume ratio gives

$$\frac{\boldsymbol{v}}{\boldsymbol{v}_{\text{ref}}} = \exp\left[-\left(s^o - R(T - T_{ref})\right)R\right]$$

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

$$\frac{\boldsymbol{\nu}}{\boldsymbol{\nu}_{\text{ref}}} = \exp\left[-\left(s_2^{\text{o}} - s_1^{\text{o}} - R(T_2 - T_1)\right)R\right]$$

Inspection of this result gives

$$\boldsymbol{v}_r = \exp\left[-\left(s^o - RT\right) / R\right]$$

12-92 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 μ is zero,

$$\mu = \frac{1}{c_p} \left(T \left(\frac{\partial \boldsymbol{v}}{\partial T} \right)_P - \boldsymbol{v} \right) = 0$$

which can also be written as

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

since it is given that

$$\boldsymbol{v} = \frac{ZRT}{P} \tag{b}$$

Taking the derivative of (b) with respect to T holding P constant gives

$$\left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{P} = \left(\frac{\partial \left(ZRT / P\right)}{\partial T}\right)_{P} = \frac{R}{P} \left(T \left(\frac{\partial Z}{\partial T}\right)_{P} + Z\right)$$

Substituting in (*a*),

$$\frac{TR}{P} \left(T \left(\frac{\partial Z}{\partial T} \right)_P + Z \right) - \frac{ZRT}{P} = 0$$
$$T \left(\frac{\partial Z}{\partial T} \right)_P + Z - Z = 0$$
$$\left(\frac{\partial Z}{\partial T} \right)_P = 0$$

which is the desired relation.

12-93 It is to be shown that for an isentropic expansion or compression process $P \mathbf{v}^k = \text{constant}$. 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 $s = s(\vec{P}, v)$, the total differential ds can be expressed as

$$ds = \left(\frac{\partial s}{\partial P}\right)_{\boldsymbol{v}} dP + \left(\frac{\partial s}{\partial \boldsymbol{v}}\right)_{P} d\boldsymbol{v} = 0$$

We now substitute the Maxwell relations below into (*a*)

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

to get

$$-\left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{s} dP + \left(\frac{\partial P}{\partial T}\right)_{s} d\boldsymbol{v} = 0$$

Rearranging,

Dividing

$$dP - \left(\frac{\partial T}{\partial \boldsymbol{v}}\right)_{s} \left(\frac{\partial P}{\partial T}\right)_{s} d\boldsymbol{v} = 0 \longrightarrow dP - \left(\frac{\partial P}{\partial \boldsymbol{v}}\right)_{s} d\boldsymbol{v} = 0$$

by P , $\frac{dP}{P} - \frac{1}{P} \left(\frac{\partial P}{\partial \boldsymbol{v}}\right)_{s} d\boldsymbol{v} = 0$

We now define isentropic expansion exponent k as

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

Substituting in (*b*),

$$\frac{dP}{P} + k \frac{d\mathbf{v}}{\mathbf{v}} = 0$$

Taking *k* to be a constant and integrating,

 $\ln P + k \ln v = \text{constant} \longrightarrow \ln P v^k = \text{constant}$

Thus,

 $P \boldsymbol{v}^k = \text{constant}$

To show that $k = c_p/c_v$ for an ideal gas, we write the cyclic relations for the following two groups of variables:

$$(s,T,\boldsymbol{v}) \longrightarrow \left(\frac{\partial s}{\partial T}\right)_{\boldsymbol{v}} \left(\frac{\partial \boldsymbol{v}}{\partial s}\right)_{T} \left(\frac{\partial T}{\partial \boldsymbol{v}}\right)_{s} = -1 \longrightarrow \frac{c_{\boldsymbol{v}}}{T} \left(\frac{\partial \boldsymbol{v}}{\partial s}\right)_{T} \left(\frac{\partial T}{\partial \boldsymbol{v}}\right)_{s} = -1 \quad (c)$$

$$(s,T,P) \longrightarrow \left(\frac{\partial s}{\partial T}\right)_{P} \left(\frac{\partial P}{\partial s}\right)_{T} \left(\frac{\partial T}{\partial P}\right)_{s} = -1 \longrightarrow \frac{c_{P}}{T} \left(\frac{\partial P}{\partial s}\right)_{T} \left(\frac{\partial T}{\partial P}\right)_{s} = -1 \quad (d)$$

where we used the relations

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

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

$$\left(\frac{\partial \boldsymbol{\nu}}{\partial P}\right)_T = \left(\frac{\partial (RT / P)}{\partial P}\right)_T = -\frac{\boldsymbol{\nu}}{P}$$

Substituting,

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

which is the desired relation.

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(a)

(b)

Analysis (*a*) We treat nitrogen as an ideal gas with R = 0.297 kJ/kg·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

$$c_{p} = T \left(\frac{\partial P}{\partial T}\right)_{s} \left(\frac{\partial \mathbf{v}}{\partial T}\right)_{p}$$
$$\mathbf{v} = \frac{RT}{P} \longrightarrow \left(\frac{\partial \mathbf{v}}{\partial T}\right)_{p} = \frac{R}{P}$$
$$P = CT^{k/(k-1)} \longrightarrow \left(\frac{\partial P}{\partial T}\right)_{s} = \frac{k}{k-1} CT^{k/(k-1)-1} = \frac{k}{k-1} \left(PT^{-k/(k-1)}\right) T^{k/(k-1)-1} = \frac{kP}{T(k-1)}$$

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,

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

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

12-95 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 $T = 300^{\circ}$ C is h = 2944.2 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

$$P = 2.5 \text{ MPa} \\ h = 2944.2 \text{ kJ/kg} \end{cases} T_2 = 273.72^{\circ}\text{C}$$

Thus the temperature drop during this throttling process is

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

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

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

12-96 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 kJ/kg.K, $T_{cr} = 151$ K, and $P_{cr} = 4.86$ 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

$$T_{R_{1}} = \frac{T_{1}}{T_{cr}} = \frac{800}{151} = 5.30$$

$$P_{R_{1}} = \frac{P_{1}}{P_{cr}} = \frac{9}{4.86} = 1.85$$

$$Z_{h_{1}} \approx 0 \text{ and } Z_{s_{1}} \approx 0$$

$$P_{1} = 9 \text{ MPa}$$

$$T_{1} = 800 \text{ K}$$

$$V_{1} = 100 \text{ m/s}$$

$$20 \text{ kW}$$

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

$$T_{R_2} = \frac{T_2}{T_{cr}} = \frac{450}{151} = 2.98$$

$$P_{R_2} = \frac{P_2}{P_{cr}} = \frac{1.5}{4.86} = 0.309$$

$$Z_{h_2} = 0.024 \text{ and } Z_{s_2} = 0.013$$

Thus,

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

= (0.2081)(151)(0 - 0.024) + 0.5203(450 - 800) = -182.9 kJ/kg

The power output of the turbine is to be determined from the energy balance equation,

$$\dot{E}_{in} - \dot{E}_{out} = \Delta \dot{E}_{system} = 0 \text{ (steady)} \rightarrow \dot{E}_{in} = \dot{E}_{out}$$
$$\dot{m}(h_1 + V_1^2 / 2) = \dot{m}(h_2 + V_2^2 / 2) + \dot{Q}_{out} + \dot{W}_{out}$$
$$\dot{W}_{out} = -\dot{m} \left[(h_2 - h_1) + \frac{V_2^2 - V_1^2}{2} \right] - \dot{Q}_{out}$$

Substituting,

$$\dot{W}_{\text{out}} = -(3 \text{ kg/s}) \left(-182.9 + \frac{(150 \text{ m/s})^2 - (100 \text{ m/s})^2}{2} \left(\frac{1 \text{ kJ/kg}}{1000 \text{ m}^2/\text{s}^2} \right) \right) - 20 \text{ kJ/s} = 510 \text{ kW}$$

(b) Under steady conditions, the rate form of the entropy balance for the turbine simplifies to

$$\dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen} = \Delta \dot{S}_{system}^{70} = 0$$

$$\dot{m}s_1 - \dot{m}s_2 - \frac{\dot{Q}_{out}}{T_{b,out}} + \dot{S}_{gen} = 0 \quad \rightarrow \quad \dot{S}_{gen} = \dot{m}(s_2 - s_2) + \frac{\dot{Q}_{out}}{T_0}$$

The exergy destroyed during a process can be determined from an exergy balance or directly from its definition $X_{\text{destroyed}} = T_0 S_{\text{gen}}$,

$$\dot{X}_{\text{destroyed}} = T_0 \dot{S}_{\text{gen}} = T_0 \left(\dot{m}(s_2 - s_2) + \frac{\dot{Q}_{\text{out}}}{T_0} \right)$$

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

and
$$(s_2 - s_1)_{ideal} = c_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} = 0.5203 \ln \frac{450}{800} - 0.2081 \ln \frac{1.5}{9} = 0.0735 \text{ kJ/kg} \cdot \text{K}$$

Thus, $s_2 - s_1 = R(Z_{s_1} - Z_{s_2}) + (s_2 - s_1)_{ideal} = (0.2081)[0 - (0.013)] + 0.0735 = 0.0708 \text{ kJ/kg} \cdot \text{K}$ Substituting,

$$\dot{X}_{\text{destroyed}} = (298 \text{ K}) \left((3 \text{ kg/s}) (0.0708 \text{ kJ/kg} \cdot \text{K}) + \frac{20 \text{ kW}}{298 \text{ K}} \right) = 83.3 \text{ kW}$$

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$$P_2 = 1.5 \text{ MPa}$$

 $T_2 = 450 \text{ K}$
 $V_2 = 150 \text{ m/s}$

12-72

12-97 Problem 12-96 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]=800 [K] P[1]=9000 [kPa] Vel[1]=100 [m/s] T[2]=450 [K] P[2]=1500 [kPa] Vel[2]=1500 [kPa] Vel[2]=150 [m/s] Q_dot_out=20 [kW] T_o=25+273 "[K]" m_dot=3 [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"

```
\label{eq:m_dot} m_dot^*(h_ideal[1]+Vel[1]^2/2^*convert(m^2/s^2,kJ/kg)) = m_dot^*(h_ideal[2]+Vel[2]^2/2^*convert(m^2/s^2,kJ/kg)) + Q_dot_out+W_dot_out_ideal
```

```
"Second Law analysis:"
"S_dot_in-S_dot_out+S_dot_gen = 0"
m_dot*s_ideal[1] - m_dot*s_ideal[2] - Q_dot_out/T_o + S_dot_gen_ideal = 0
```

"Exergy Destroyed:" X_dot_destroyed_ideal = T_o*S_dot_gen_ideal

"***** COMPRESSABILITY 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" DELTAs[1]=ENTRDEP(Tr[1], Pr[1])*R "Entropy departure" s_chart[1]=s_ideal[1]-DELTAs[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])

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DELTAh[2]=ENTHDEP(Tr[2], Pr[2])*R*T_critical "Enthalpy departure" DELTAs[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]-DELTAs[2] "Entropy of real gas using charts"

"Conservation of Energy, Steady-flow: " "E_dot_in=E_dot_out"

 $\label{eq:m_dot} m_dot^*(h_chart[1]+Vel[1]^2/2^*convert(m^2/s^2,kJ/kg)) = m_dot^*(h_chart[2]+Vel[2]^2/2^*convert(m^2/s^2,kJ/kg)) + Q_dot_out+W_dot_out_chart$

"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"

 $\label{eq:m_dot} m_dot^*(h_ees[1]+Vel[1]^2/2^*convert(m^2/s^2,kJ/kg)) = m_dot^*(h_ees[2]+Vel[2]^2/2^*convert(m^2/s^2,kJ/kg)) + Q_dot_out_ees[1]+Vel[1]^2/2^*convert(m^2/s^2,kJ/kg)) = m_dot^*(h_ees[2]+Vel[2]^2/2^*convert(m^2/s^2,kJ/kg)) + Q_dot_out_ees[1]+Vel[1]^2/2^*convert(m^2/s^2,kJ/kg)) = m_dot^*(h_ees[2]+Vel[2]^2/2^*convert(m^2/s^2,kJ/kg)) = m_dot^*(h_ees[2]+Vel[2]^2/2^*convert(m^2/s^2,kJ$

"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}	X _{destroyedees} [kW]	X _{destroyedideal} [kW]
1100	450	1822	1836	2097	909.1	905.7	836
200	450	1829	1853	2097	620	610.9	550.1
300	450	1837	1871	2097	449.7	434.4	382.8
400	450	1844	1890	2097	327.9	306.2	264.1
500	450	1852	1909	2097	232.7	204.2	172
600	450	1859	1929	2097	154.3	118.6	96.79
700	450	1867	1950	2097	87.51	44.06	33.19
800	450	1874	1971	2097	29.18	-22.56	-21.9
900	450	1882	1994	2097	-22.7	-83.47	-70.5



-400

P[2] [kPa]

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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

Mass balance: $m_{\text{in}} - m_{\text{out}} = \Delta m_{\text{system}} \rightarrow m_i = m_2$ (since $m_{\text{out}} = m_{\text{initial}} = 0$)

Energy balance: $E_{in} - E_{out} = \Delta E_{system} \rightarrow 0 + m_i h_i = m_2 u_2$

Combining the two balances: $u_2 = h_i$

(a) From the ideal gas property table of nitrogen, at 225 K we read

$$\overline{u}_2 = \overline{h}_i = \overline{h}_{(a),225 \text{ K}} = 6,537 \text{ kJ/kmol}$$

The temperature that corresponds to this \overline{u}_2 value is

$$T_2 = 314.8 \text{ K}$$
 (7.4% error)

(b) Using the generalized enthalpy departure chart, h_i is determined to be

$$T_{R,i} = \frac{T_i}{T_{cr}} = \frac{225}{126.2} = 1.78$$

$$P_{R,i} = \frac{P_i}{P_{cr}} = \frac{10}{3.39} = 2.95$$

$$Z_{h,i} = \frac{\overline{h_{i,ideal}} - \overline{h_i}}{R_u T_{cr}} = 0.9 \quad \text{(Fig. A-29)}$$

Thus,

$$\overline{h}_i = \overline{h}_{i,\text{ideal}} - 0.9R_u T_{\text{cr}} = 6,537 - (0.9)(8.314)(126.2) = 5,593 \text{ kJ/kmol}$$

and

$$\overline{u}_2 = \overline{h}_i = 5,593 \text{ kJ/kmol}$$

Try $T_2 = 280$ K. Then at $P_{R2} = 2.95$ and $T_{R2} = 2.22$ we read $Z_2 = 0.98$ and $(\overline{h}_{2,ideal} - \overline{h}_2) / R_u T_{cr} = 0.55$

Thus,

$$\overline{h}_2 = \overline{h}_{2,\text{ideal}} - 0.55R_u T_{\text{cr}} = 8,141 - (0.55)(8.314)(126.2) = 7,564 \text{ kJ/kmol}$$

$$\overline{u}_2 = \overline{h}_2 - ZR_u T_2 = 7,564 - (0.98)(8.314)(280) = 5,283 \text{ kJ/kmol}$$

Try $T_2 = 300$ K. Then at $P_{R2} = 2.95$ and $T_{R2} = 2.38$ we read $Z_2 = 1.0$ and $(\overline{h}_{2,ideal} - \overline{h}_2) / R_u T_{cr} = 0.50$

Thus,

$$\overline{h}_2 = \overline{h}_{2,\text{ideal}} - 0.50R_u T_{\text{cr}} = 8,723 - (0.50)(8.314)(126.2) = 8,198 \text{ kJ/kmol}$$

$$\overline{u}_2 = \overline{h}_2 - ZR_u T_2 = 8,198 - (1.0)(8.314)(300) = 5,704 \text{ kJ/kmol}$$

By linear interpolation,

 $T_2 = 294.7 \text{ K}$ (0.6% error)





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

M = 16.043 lbm/lbmol, R = 0.1238 Btu/lbm · R, $T_{cr} = 343.9$ R, $P_{cr} = 673$ 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

$$(\bar{s}_2 - \bar{s}_1)_{ideal} = \int_1^2 \frac{c_p}{T} dT - R_u \ln \frac{P_2}{P_1} = \int_1^2 \left(\frac{a}{T} + b + cT + dT^2\right) dT - R_u \ln \frac{P_2}{P_1}$$
$$= a \ln \frac{T_2}{T_1} + b(T_2 - T_1) + \frac{c}{2}(T_2^2 - T_1^2) + \frac{d}{3}(T_2^3 - T_1^3) - R_u \ln \frac{P_2}{P_1}$$

Substituting,

$$0 = 4.75 \ln \frac{T_2}{560} + 0.006666 (T_2 - 560) + \frac{0.09352 \times 10^{-5}}{2} (T_2^2 - 560^2) - \frac{0.4510 \times 10^{-9}}{3} (T_2^3 - 560^3) - (1.9858) \ln \frac{500}{50}$$

Solving this equation by EES or an iterative solution gives

 $T_2 = 892 \text{ R}$

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

$$\overline{w}_{in} = (\overline{h}_2 - \overline{h}_1)_{ideal} = \int_1^2 c_p dT = \int_1^2 (a + bT + cT^2 + dT^3) dT$$

= $a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) + \frac{c}{3}(T_2^3 - T_1^3) + \frac{d}{4}(T_2^4 - T_1^4)$
= $4.75(892 - 560) + \frac{0.006666}{2}(892^2 - 560^2) + \frac{0.09352 \times 10^{-5}}{3}(892^3 - 560^3)$
 $- \frac{0.4510 \times 10^{-9}}{4}(892^4 - 560^4)$

= 3290 Btu/lbmol

The work input per unit mass basis is

$$w_{\text{in}} = \frac{\overline{w}_{\text{in}}}{M} = \frac{3290 \text{ Btu/lbmol}}{16.043 \text{ lbm/lbmol}} = 205.1 \text{ Btu/lbm}$$

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

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{560}{343.9} = 1.628$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{50}{673} = 0.0743$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{892}{343.9} = 2.594$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{500}{673} = 0.743$$

The work input is determined to be

$$w_{in} = h_2 - h_1 = (h_2 - h_1)_{ideal} - RT_{cr}(Z_{h2} - Z_{h1})$$

= 205.1 Btu/lbm - (0.1238 Btu/lbm · R)(343.9 R)(0.0990 - 0.0332)
= **202.3 Btu/lbm**



12-76



12-100 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 0.207×10^{-6} K⁻¹ at 20°C.

Analysis We take v = v(P, T). Its total differential is

$$d\boldsymbol{v} = \left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{P} dT + \left(\frac{\partial \boldsymbol{v}}{\partial P}\right)_{T} dP$$

which, for a constant pressure process, reduces to

$$d\boldsymbol{v} = \left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_P dT$$

Dividing by \boldsymbol{v} and using the definition of β ,

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

Taking β to be a constant, integration from 1 to 2 yields

$$\ln \frac{\boldsymbol{v}_2}{\boldsymbol{v}_1} = \beta \big(T_2 - T_1 \big)$$

or

$$\frac{\boldsymbol{v}_2}{\boldsymbol{v}_1} = \exp[\beta(T_2 - T_1)]$$

Substituting the given values and noting that for a fixed mass $V_2/V_1 = v_2/v_1$,

$$\boldsymbol{\nu}_2 = \boldsymbol{\nu}_1 \exp[\beta(T_2 - T_1)] = (0.5 \text{ m}^3) \exp[(0.207 \times 10^{-6} \text{ K}^{-1})(50 - 10)^{\circ}\text{C}]$$

= 0.50000414 m³

Therefore,

$$\Delta \boldsymbol{\mathcal{V}} = \boldsymbol{\mathcal{V}}_2 - \boldsymbol{\mathcal{V}}_1 = 0.50000414 - 0.5 = 0.00000414 \text{ m}^3 = 4.14 \text{ cm}^3$$

(C)

12-101 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:

$$T_{1} = 40^{\circ}\text{C} \quad u_{1} = 106.37 \text{ kJ/kg}$$

$$P_{1} = 2 \text{ MPa} \int s_{1} = 0.3916 \text{ kJ/kg.K}$$

$$T_{2} = 40^{\circ}\text{C} \quad u_{2} = 264.25 \text{ kJ/kg}$$

$$P_{2} = 0.1 \text{ MPa} \int s_{2} = 1.1484 \text{ kJ/kg.K}$$

$$\Delta s_{\text{EES}} = s_{2} - s_{1} = 1.1484 - 0.3916 = 0.7568 \text{ kJ/kg.K}$$

$$q_{\text{EES}} = T_{1}\Delta s_{\text{EES}} = (40 + 273.15 \text{ K})(0.7568 \text{ kJ/kg.K}) = 237.00 \text{ kJ/kg}$$

$$w_{\text{EES}} = q_{\text{EES}} - (u_{2} - u_{1}) = 237.00 - (264.25 - 106.37) = 79.1 \text{ kJ/kg}$$

For the generalized chart solution we first determine the following factors using EES as

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{313.2}{374.2} = 0.8369$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{2}{4.059} = 0.4927$$

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{313.2}{374.2} = 0.8369$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{0.1}{4.059} = 0.02464$$

$$\longrightarrow Z_1 = 0.08357, Z_{h1} = 4.82 \text{ and } Z_{s1} = 5.147$$

$$Z_1 = 0.08357, Z_{h1} = 4.82 \text{ and } Z_{s1} = 5.147$$

Then,

$$\begin{split} \Delta h_1 &= Z_{h1} RT_{cr} = (4.82)(0.08148 \text{ kJ/kg.K})(374.2 \text{ K}) = 146.97 \text{ kJ/kg} \\ \Delta s_1 &= Z_{s1} R = (5.147)(0.08148 \text{ kJ/kg.K}) = 0.4194 \text{ kJ/kg.K} \\ \Delta h_2 &= Z_{h2} RT_{cr} = (0.03396)(0.08148 \text{ kJ/kg.K})(374.2 \text{ K}) = 1.04 \text{ kJ/kg} \\ \Delta s_2 &= Z_{s2} R = (0.02635)(0.08148 \text{ kJ/kg.K}) = 0.002147 \text{ kJ/kg.K} \\ \Delta s_{ideal} &= R \ln \frac{P_2}{P_1} = (0.08148 \text{ kJ/kg.K}) \ln \left(\frac{0.1}{2}\right) = 0.2441 \text{ kJ/kg \cdot K} \\ \Delta s_{chart} &= \Delta s_{ideal} - (\Delta s_2 - \Delta s_1) = 0.2441 - (0.002147 - 0.4194) = 0.6613 \text{ kJ/kg \cdot K} \\ q_{chart} &= T_1 \Delta s_{chart} = (40 + 273.15 \text{ K})(0.6613 \text{ kJ/kg.K}) = 207.09 \text{ kJ/kg} \\ \Delta u_{chart} &= \Delta h_{ideal} - (\Delta h_2 - \Delta h_1) - (Z_2 RT_2 - Z_1 RT_1) \\ &= 0 - (1.04 - 146.97) - [(0.9857)(0.08148)(313.2) - (0.08357)(0.08148)(313.2)] = 122.92 \text{ kJ/kg} \\ w_{chart} &= q_{chart} - \Delta u_{chart} = 207.09 - 122.92 = 84.2 \text{ kJ/kg} \end{split}$$

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]=40+273.15"[K]" T[2]=T[1]"[K]" P[1]=2000"[kPa]"

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

"For the isothermal process, the heat transfer is T*(s[2] - s[1]):" DELTAs_EES=(entropy(R134a,T=T[2],P=P[2])-entropy(R134a,T=T[1],P=P[1])) q_EES=T[1]*DELTAs_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:"

 $\begin{array}{l} \mathsf{DELTAu_EES=intEnergy}(\mathsf{R134a},\mathsf{T=T[2]},\mathsf{p=P[2]})\text{-}intEnergy}(\mathsf{R134a},\mathsf{T=T[1]},\mathsf{P=P[1]})\\ \mathsf{q_EES-w_EES=DELTAu_EES}\\ \mathsf{u_1=intEnergy}(\mathsf{R134a},\mathsf{T=T[1]},\mathsf{P=P[1]})\\ \mathsf{u_2=intEnergy}(\mathsf{R134a},\mathsf{T=T[2]},\mathsf{p=P[2]}) \end{array}$

"***** COMPRESSABILITY 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" Z_h1=ENTHDEP(Tr[1], Pr[1]) DELTAs[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]) DELTAh[2]=ENTHDEP(Tr[2], Pr[2])*R*T_critical"Enthalpy departure" Z_h2=ENTHDEP(Tr[2], Pr[2]) DELTAs[2]=ENTRDEP(Tr[2], Pr[2])*R "Entropy departure" Z_s2=ENTRDEP(Tr[2], Pr[2])

"Entropy Change"

DELTAs_ideal= -R*ln(P[2]/P[1]) DELTAs_chart=DELTAs_ideal-(DELTAs[2]-DELTAs[1])

"For the isothermal process, the heat transfer is T*(s[2] - s[1]):" q_chart=T[1]*DELTAs_chart

"Conservation of energy for the closed system:" DELTAh_ideal=0 DELTAu_chart=DELTAh_ideal-(DELTAh[2]-DELTAh[1])-(Z[2]*R*T[2]-Z[1]*R*T[1]) q_chart-w_chart=DELTAu_chart

SOLUTION

DELTAh[1]=146.97 [kJ/kg] DELTAh[2]=1.04 [kJ/kg] DELTAh_ideal=0 [kJ/kg] DELTAs[1]=0.4194 [kJ/kg-K] DELTAs[2]=0.002147 [kJ/kg-K] DELTAs chart=0.6613 [kJ/kg-K] DELTAs_EES=0.7568 [kJ/kg-K] DELTAs_ideal=0.2441 [kJ/kg-K] DELTAu_chart=122.92 [kJ/kg] DELTAu_EES=157.9 [kJ/kg] M=102 P[1]=2000 [kPa] P[2]=100 [kPa] pr[1]=0.4927 Pr[2]=0.02464 P_critical=4059 [kpa] q_chart=207.09 [kJ/kg] q_EES=237.00 [kJ/kg]

R=0.08148 [kJ/kg-K] R_u=8.314 [kJ/kmol-K] s_1=0.3916 s_2=1.1484 [kJ/kg-K] T[1]=313.2 [K] T[2]=313.2 [K] Tr[1]=0.8369 Tr[2]=0.8369 T_critical=374.2 [K] u 1=106.37 u_2=264.25 [kJ/kg] w_chart=84.18 [kJ/kg] w_EES=79.12 [kJ/kg] Z[1]=0.08357 Z[2]=0.9857 Z_h1=4.82 Z_h2=0.03396 Z_s1=5.147 Z s2=0.02635

12-102 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:

$$T_{1} = 100^{\circ}\text{C} \longrightarrow h_{1} = -4492 \text{ kJ/kg}$$

$$T_{1} = 100^{\circ}\text{C}, P_{1} = 4 \text{ MPa} \longrightarrow s_{1} = 10.22 \text{ kJ/kg.K}$$

$$u_{1} = h_{1} - RT_{1} = (-4492) - (0.5182)(100 + 273.15) = -4685 \text{ kJ/kg}$$

$$v_{1} = R \frac{T_{1}}{P_{1}} = (0.5182 \text{ kJ/kg.K}) \left(\frac{100 + 273.15 \text{ K}}{4000 \text{ kPa}}\right) = 0.04834 \text{ m}^{3}/\text{kg}$$

State 2:

$$T_{2} = 350^{\circ}\text{C} \longrightarrow h_{2} = -3770 \text{ kJ/kg}$$

$$T_{2} = 350^{\circ}\text{C}, P_{2} = 4 \text{ MPa} \longrightarrow s_{2} = 11.68 \text{ kJ/kg.K}$$

$$u_{2} = h_{2} - RT_{2} = (-3770) - (0.5182)(350 + 273.15) = -4093 \text{ kJ/kg}$$

$$v_{2} = R \frac{T_{2}}{P_{2}} = (0.5182 \text{ kJ/kg.K}) \left(\frac{350 + 273.15 \text{ K}}{4000 \text{ kPa}}\right) = 0.08073 \text{ m}^{3}/\text{kg}$$

$$w_{\text{ideal}} = P(v_{2} - v_{1}) = (4000 \text{ kPa})(0.08073 - 0.04834)\text{m}^{3}/\text{kg} = 129.56 \text{ kJ/kg}$$

$$q_{\text{ideal}} = w_{\text{ideal}} + (u_{2} - u_{1}) = 129.56 + \left[(-4093) - (-4685)\right] = 721.70 \text{ kJ/kg}$$

$$\Delta s_{\text{ideal}} = s_{2} - s_{1} = 11.68 - 10.22 = 1.46 \text{ kJ/kg}$$

For the generalized chart solution we first determine the following factors using EES as

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{373}{304.2} = 1.227$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{4}{7.39} = 0.5413$$

$$\longrightarrow Z_1 = 0.9023, Z_{h1} = 0.4318 \text{ and } Z_{s1} = 0.2555$$

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{623}{304.2} = 2.048$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{4}{7.39} = 0.5413$$

$$\longrightarrow Z_2 = 0.995, Z_{h2} = 0.1435 \text{ and } Z_{s2} = 0.06446$$

State 1:

$$\begin{split} \Delta h_1 &= Z_{h1} R T_{\rm cr} = (0.4318)(0.5182 \, {\rm kJ/kg.K})(304.2 \, {\rm K}) = 68.07 \, {\rm kJ/kg} \\ h_1 &= h_{1,\rm ideal} - \Delta h_1 = (-4492) - 68.07 = -4560 \, {\rm kJ/kg} \\ u_1 &= h_1 - Z_1 R T_1 = (-4560) - (0.9023)(0.5182)(373.15) = -4734 \, {\rm kJ/kg} \\ \boldsymbol{v}_1 &= Z_1 R \frac{T_1}{P_1} = (0.9023)(0.5182) \frac{373.15}{4000} = 0.04362 \, {\rm m}^3 / {\rm kg} \\ \Delta s_1 &= Z_{s1} R = (0.2555)(0.5182 \, {\rm kJ/kg.K}) = 0.1324 \, {\rm kJ/kg.K} \\ s_1 &= s_{1,\rm ideal} - \Delta s_1 = 10.22 - 0.1324 = 10.09 \, {\rm kJ/kg.K} \end{split}$$

State 2:

$$\Delta h_2 = Z_{h2} R T_{cr} = (0.1435)(0.5182 \text{ kJ/kg.K})(304.2 \text{ K}) = 22.62 \text{ kJ/kg}$$

$$h_2 = h_{2,\text{ideal}} - \Delta h_2 = (-3770) - 22.62 = -3793 \text{ kJ/kg}$$

$$u_2 = h_2 - Z_2 R T_2 = (-3793) - (0.995)(0.5182)(623.15) = -4114 \text{ kJ/kg}$$

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$$v_2 = Z_2 R \frac{T_2}{P_2} = (0.995)(0.5182) \frac{623.15}{4000} = 0.08033 \text{ m}^3/\text{kg}$$

 $\Delta s_2 = Z_{s2} R = (0.06446)(0.5182 \text{ kJ/kg.K}) = 0.03341 \text{ kJ/kg.K}$
 $s_2 = s_{2,\text{ideal}} - \Delta s_2 = 11.68 - 0.03341 = 11.65 \text{ kJ/kg.K}$

Then,

$$w_{\text{chart}} = P(\boldsymbol{v}_2 - \boldsymbol{v}_1) = (4000 \text{ kPa})(0.08033 - 0.04362)\text{m}^3/\text{kg} = \mathbf{146.84 \text{ kJ/kg}}$$
$$q_{\text{chart}} = w_{\text{chart}} + (u_2 - u_1) = 146.84 + [(-4114) - (-4734)] = \mathbf{766.84 \text{ kJ/kg}}$$
$$\Delta s_{\text{chart}} = s_2 - s_1 = 11.65 - 10.09 = \mathbf{1.56 \text{ kJ/kg}}$$

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

$$T_{1} = 100^{\circ}C$$

$$P_{1} = 4 \text{ MPa}$$

$$\begin{cases}
u_{1} = -39.82 \text{ kJ/kg} \\
u_{1} = -39.82 \text{ kJ/kg} \\
s_{1} = -1.439 \text{ kJ/kg.K}
\end{cases}$$

$$T_{2} = 350^{\circ}C$$

$$P_{2} = 4 \text{ MPa}$$

$$\begin{cases}
u_{2} = 0.08141 \text{ m}^{3}/\text{kg} \\
u_{2} = 564.52 \text{ kJ/kg} \\
s_{2} = 0.06329 \text{ kJ/kg.K}
\end{cases}$$

$$w_{\text{EES}} = P(v_2 - v_1) = (4000 \text{ kPa})(0.08141 - 0.04717)\text{m}^3/\text{kg} = 136.96 \text{ kJ/kg}$$

 $q_{\text{EES}} = w_{\text{EES}} + (u_2 - u_1) = 136.97 + [564.52 - (-39.82)] = 741.31 \text{ kJ/kg}$
 $\Delta s_{\text{EES}} = s_2 - s_1 = 0.06329 - (-1.439) = 1.50 \text{ kJ/kg}$

12-103E Methane is compressed steadily. The entropy change and the specific work required are to be determined using the departure charts and the property tables.

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

M = 16.043 lbm/lbmol, $T_{cr} = 343.9$ R, $P_{cr} = 673$ psia, $c_p = 0.532$ Btu/lbm · R, R = 0.1238 Btu/lbm · R

Analysis (a) Using empirical correlation for the c_p of methane as given in Table A-2Ec gives

$$\overline{h}_{2} - \overline{h}_{1} = \int c_{p} dT = \int (a + bT + cT^{2} + dT^{3}) dT$$

$$= a(T_{2} - T_{1}) + \frac{b}{2}(T_{2}^{2} - T_{1}^{2}) + \frac{c}{3}(T_{2}^{3} - T_{1}^{3}) + \frac{d}{4}(T_{2}^{4} - T_{1}^{4})$$

$$= 4.750(1000) + \frac{0.6666 \times 10^{-2}}{2}(1560^{2} - 560^{2}) + \frac{0.09352 \times 10^{-5}}{3}(1560^{3} - 560^{3})$$

$$+ \frac{-0.4510 \times 10^{-9}}{4}(1560^{4} - 560^{4})$$

$$= 12.288 \text{ Btu/lbmol. P}$$

= 12,288Btu/lbmol·R

The work input is equal to the enthalpy change. The enthalpy change per unit mass is

$$w_{in} = h_2 - h_1 = \frac{h_2 - h_1}{M} = \frac{12,288 \text{ Btu/lbmol}}{16.043 \text{ lbm/lbmol}} =$$
765.9 Btu/lbm

Similarly, the entropy change is given by

$$(\bar{s}_{2} - \bar{s}_{1})_{\text{ideal}} = \int_{1}^{2} \frac{c_{p}}{T} dT - R_{u} \ln \frac{P_{2}}{P_{1}} = \int_{1}^{2} \left(\frac{a}{T} + b + cT + dT^{2}\right) dT - R_{u} \ln \frac{P_{2}}{P_{1}}$$

$$= a \ln \frac{T_{2}}{T_{1}} + b(T_{2} - T_{1}) + \frac{c}{2}(T_{2}^{2} - T_{1}^{2}) + \frac{d}{3}(T_{2}^{3} - T_{1}^{3}) - R_{u} \ln \frac{P_{2}}{P_{1}}$$

$$= 4.750 \ln \frac{1560}{560} + 0.6666 \times 10^{-2}(1560 - 560) + \frac{0.09352 \times 10^{-5}}{2}(1560^{2} - 560^{2})$$

$$+ \frac{-0.4510 \times 10^{-9}}{3}(1560^{3} - 560^{3}) - (1.9858) \ln \frac{500}{50}$$

$$= 7.407 \text{ Btu/lbmol} \cdot \text{R}$$

The entropy change per unit mass is

$$(s_2 - s_1)_{ideal} = \frac{(\bar{s}_2 - \bar{s}_1)_{ideal}}{M} = \frac{7.407 \text{ Btu/lbmol} \cdot \text{R}}{16.043 \text{ lbm/lbmol}} = 0.4617 \text{ Btu/lbm} \cdot \text{R}$$

(b) 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. We used EES.)

$$T_{R1} = \frac{T_1}{T_{cr}} = \frac{560}{343.9} = 1.63$$

$$P_{R1} = \frac{P_1}{P_{cr}} = \frac{50}{673} = 0.0743$$

$$\longrightarrow Z_{h1} = 0.03313 \text{ and } Z_{s1} = 0.01617$$

and

$$T_{R2} = \frac{T_2}{T_{cr}} = \frac{1560}{343.9} = 4.54$$

$$P_{R2} = \frac{P_2}{P_{cr}} = \frac{500}{673} = 0.743$$

The work input and entropy changes are

$$w_{in} = h_2 - h_1 = (h_2 - h_1)_{ideal} - RT_{cr}(Z_{h2} - Z_{h1})$$

= 765.9 - (0.1238)(343.9)(0 - 0.03313) = **767.4 Btu/lbm**

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

= 0.4617 - (0.1238)(0.00695 - 0.01617) = **0.4628 Btu/lbm** · **R**

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1100°F

50 psia

100°F

12-104E Methane is compressed in a steady-flow device. The second-law efficiency of the compression process is to be determined.

Analysis The reversible work input to the compressor is determined from

$$w_{\text{rev}} = h_2 - h_1 - T_0(s_2 - s_1) = 767.4 \text{ Btu/lbm} - (537 \text{ R})(0.4628 \text{ Btu/lbm} \cdot \text{R}) = 518.8 \text{ Btu/lbm}$$

The second-law efficiency of the compressor is

$$\eta_{\rm II} = \frac{w_{\rm rev}}{w_{\rm actual}} = \frac{518.8}{767.4} = 0.676 = 67.6\%$$

Fundamentals of Engineering (FE) Exam Problems

12-105 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.

12-106 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,

12-107 Based on the generalized charts, the error involved in the enthalpy of CO_2 at 300 K and 5 MPa if it is assumed to be an ideal gas is

(a) 0	(b) 9%	(c) 16%	(d) 22%	(e) 27%
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Answer (e) 27%

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=300 "K" P=5000 "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(, %) 12-85

12-108 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

12-109 For a gas whose equation of state is $P(\mathbf{v} - \mathbf{b}) = RT$, the specific heat difference $c_p - c_{\mathbf{v}}$ is equal to (b) *R* – *b* (c) R + b(e) R(1 + u/b)(a) *R* (d) 0

Answer (a) R

Solution The general relation for the specific heat difference $c_p - c_v$ is

$$c_{p} - c_{v} = -T \left(\frac{\partial v}{\partial T}\right)_{P}^{2} \left(\frac{\partial P}{\partial v}\right)_{T}$$

For the given gas, P(v - b) = RT. Then,

$$\boldsymbol{v} = \frac{RT}{P} + b \longrightarrow \left(\frac{\partial \boldsymbol{v}}{\partial T}\right)_{P} = \frac{R}{P}$$
$$P = \frac{RT}{\boldsymbol{v} - b} \longrightarrow \left(\frac{\partial P}{\partial \boldsymbol{v}}\right)_{T} = -\frac{RT}{(\boldsymbol{v} - b)^{2}} = -\frac{P}{\boldsymbol{v} - b}$$

Substituting,

$$c_p - c_v = -T\left(\frac{R}{P}\right)^2 \left(-\frac{P}{v-b}\right) = \frac{TR^2}{P(v-b)} = R$$

12-110 --- 12-112 Design and Essay Problems

$$\mathcal{G}$$

12-86