11-1-1 [OQU] Using the Maxwell's relation and the equation of state, determine a relation for the partial of s with respect to v at constant T for the IG model. Verify the relation using TEST at 100 kPa and 300 K.

SOLUTION:

The ideal gas equation of state can be expressed as $p = \dfrac{RT}{v}$. Then,

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

From the third Maxwell relation,

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

TEST Solution:

Launch the IG system-state TESTcalc and select Air. Evaluate State-1 from the given conditions and State-2 as a neighboring state with p2=p1*1.01 (1 percent change) and T2=T1 (holding T constant). In the I/O panel, calculate the LHS, (s2-s1)/(v2-v1), as 0.335 unit. Using the average value of specific volume, the RHS is calculated as 2*R1/(v1+v2) = 0.335 unit. The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-2 [OQX] Derive the relation for the slope of the n = constant lines on a T-p diagram for a gas that obeys the van der Waals equation of state.

SOLUTION:

The **van der Waals equation** of state:

$\left(p + \dfrac{a}{v^2}\right)(v - b) = RT \left[\dfrac{kJ}{kg}\right]$, where, $a = \dfrac{27R^2 T_{cr}^2}{64 p_{cr}} \left[m^6\right]$; and $b = \dfrac{RT}{8 p_{cr}} \left[m^3\right]$ are material constants.

$T = \left(p + \dfrac{a}{v^2}\right)\dfrac{(v - b)}{R}$

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

Therefore,

$\left(\dfrac{\partial p}{\partial T}\right)_v = \dfrac{1}{\left(\dfrac{\partial T}{\partial p}\right)_v} = \dfrac{R}{(v - b)}$

11-1-3 [OQC] Derive the relation for the volume expansivity (β) and the isothermal compressibility (κ_T) for (a) an ideal gas and (b) a gas whose equation of state is $p(v - b) = RT$.

SOLUTION:

The volume expansivity and isothermal compressibility are expressed as

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

(a) For ideal gas, $v = \dfrac{RT}{p}$

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{p}; \quad \Rightarrow \beta = \frac{1}{v}\left(\frac{R}{p}\right); \quad \Rightarrow \beta = \frac{1}{T}$$

$$\left(\frac{\partial v}{\partial p}\right)_T = -\frac{RT}{p^2}; \quad \Rightarrow \kappa_T = -\frac{1}{v}\left(-\frac{RT}{p^2}\right); \quad \Rightarrow \kappa_T = \frac{1}{p}$$

(b) For gas whose equation of state is $v = \dfrac{RT}{p} + b$,

$$\left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{p}; \quad \Rightarrow \beta = \frac{1}{v}\left(\frac{R}{p}\right); \quad \Rightarrow \beta = \frac{R}{RT + bp}$$

$$\left(\frac{\partial v}{\partial p}\right)_T = -\frac{RT}{p^2}; \quad \Rightarrow \kappa_T = -\frac{1}{v}\left(-\frac{RT}{p^2}\right); \quad \Rightarrow \kappa_T = \frac{v-b}{pv}$$

11-1-4 [OQV] Estimate the volume expansivity (β) and the isothermal compressibility (κ_T) of refrigerant-134a at 200 kPa and 30°C.

SOLUTION:

The volume expansivity and isothermal compressibility are expressed as

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

Approximating differentials by differences about specific state (properties obtained using the manual approach discussed in Chapter 3 or the PC system-state TESTcalc),

$$\beta \cong \frac{1}{v}\left(\frac{\Delta v}{\Delta T}\right)_{p=200\text{kPa}}$$

$$\Rightarrow \beta = \frac{1}{v}\left(\frac{v_{40^\circ C} - v_{20^\circ C}}{(40-20)^\circ C}\right)_{p=200\text{kPa}} ; \quad \Rightarrow \beta = \frac{1}{0.11856}\left(\frac{0.12311 - 0.11394}{20}\right)_{p=200\text{kPa}}$$

$$\Rightarrow \beta = 0.00387 \text{ K}^{-1}$$

$$\kappa_T \cong -\frac{1}{v}\left(\frac{\Delta v}{\Delta p}\right)_T$$

$$\kappa_T = -\frac{1}{v}\left(\frac{v_{240\text{kPa}} - v_{180\text{kPa}}}{240-180}\right)_{T=30^\circ C} ; \quad \Rightarrow \kappa_T = -\frac{1}{0.11856}\left(\frac{0.09794 - 0.13230}{60}\right) ;$$

$$\Rightarrow \kappa_T = 0.00483 \text{ kPa}^{-1}$$

TEST Solution:

Launch the PC system-state TESTcalc and select R-134a. Evaluate State-1 at the given conditions, State-2 as a neighboring state with p2 = p1 and T2=T1+1, and State-3 as another neighboring state with T2=T1, p2 = 1.01*p1. In the I/O panel, evaluate = (1/v1)*(v2-v1)/(T2-T1) as 0.0037 and (-1/v1)*(v3-v1)/(p3-p1) as 0.0051. The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-5 [OQQ] Estimate the Joule-Thomson coefficient (μ_J) of nitrogen at (a) 200 psia, 500°R and (b) 2000 psia, 400°R.

SOLUTION:

(a) Use the manual approach or PC system-state TESTcalc to obtain nitrogen properties.

State-1 (given $p_1 = 200$ psia $= 1379$ kPa; $T_1 = 500$ R $= 277.77$ K)

$h_1 = -24.8 \dfrac{\text{kJ}}{\text{kg}}$

State-2 (given $p_2 = (1.01) p_1$; $h_2 = h_1$)

$T_2 = 277.81$ K

Using forward differencing to approximate the partial derivative,

$$\mu = \left(\frac{\partial T}{\partial p} \right)_h \cong \left(\frac{\Delta T}{\Delta p} \right)_h = \left(\frac{277.81 - 277.77}{1392.8 - 1379} \right) = 0.00258 \ \frac{\text{K}}{\text{kPa}} = 0.032 \ \frac{\text{R}}{\text{psia}}$$

(b)

State-1 (given $p_1 = 2000$ psia $= 13790$ kPa; $T_1 = 400$ R $= 222.22$ K Ÿ)

$h_1 = -129.25 \dfrac{\text{kJ}}{\text{kg}}$

State-2 (given $p_2 = (1.01) p_1$; $h_2 = h_1$)

$T_2 = 222.42$ K

Using forward differencing to approximate the partial derivative,

$$\mu = \left(\frac{\partial T}{\partial p} \right)_h \cong \left(\frac{\Delta T}{\Delta p} \right)_h = \left(\frac{222.42 - 222.22}{13928 - 13790} \right) = 0.00143 \ \frac{\text{K}}{\text{kPa}} = 0.0178 \ \frac{\text{R}}{\text{psia}}$$

TEST Solution:

Launch the PC flow-state TESTcalc and select N2. Evaluate State-1 at the given conditions, State-2 as a neighboring state with p2 = 1.01*p1 and h2=h1. In the I/O panel, evaluate = (T2-T1)/(p2-p1). The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-6 [OQT] For $\beta >= 0$, prove that at every point of a single-phase region of an *h-s* diagram, the slope of a constant-pressure (p = constant) line is greater than the slope of a constant temperature (T = constant) line, but less than the slope of a constant-volume (β = constant) line.

SOLUTION:

Using Tds relation: $dh = Tds + vdp$; $\Rightarrow \dfrac{dh}{ds} = T + \dfrac{dp}{ds}$

$p = c$ line: $\left(\dfrac{\partial h}{\partial s} \right)_P = T$

$T = c$ line: $\left(\dfrac{\partial h}{\partial s} \right)_T = T + v\left(\dfrac{\partial p}{\partial s} \right)_T$

The 4th Maxwell relation: $\left(\dfrac{\partial p}{\partial s} \right)_T = -\left(\dfrac{\partial T}{\partial v} \right)_P$

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

Since $\beta > 0$, the slope of $p = c$ line is greater than the slope of $T = c$ line.

$v = c$ line: $\left(\dfrac{\partial h}{\partial s} \right)_v = T + v\left(\dfrac{\partial p}{\partial s} \right)_v$ $\qquad (1)$

From the first *Tds* relation: $ds = \dfrac{c_v}{T} dT + \left(\dfrac{p}{T} \right) dv$;

Divide by dp holding v constant: $\left(\dfrac{\partial s}{\partial p} \right)_v = \dfrac{c_v}{T} \left(\dfrac{\partial T}{\partial p} \right)_v$; $\Rightarrow \left(\dfrac{\partial p}{\partial s} \right)_v = \dfrac{T}{c_v} \left(\dfrac{\partial p}{\partial T} \right)_v$ $\qquad (2)$

Using properties p, T, and v in the cyclic relation,

$\left(\dfrac{\partial p}{\partial T} \right)_v \left(\dfrac{\partial T}{\partial v} \right)_p \left(\dfrac{\partial v}{\partial p} \right)_T = -1$; $\Rightarrow \left(\dfrac{\partial p}{\partial T} \right)_v = -\left(\dfrac{\partial v}{\partial T} \right)_p \left(\dfrac{\partial p}{\partial v} \right)_T$;

$\Rightarrow \left(\dfrac{\partial p}{\partial T} \right)_v = (-\beta v)\left(\dfrac{1}{-\alpha v} \right)$; $\Rightarrow \left(\dfrac{\partial p}{\partial T} \right)_v = \dfrac{\beta}{\alpha}$ $\qquad (3)$

Substituting (2) and (3) in (1)

$\left(\dfrac{\partial h}{\partial s} \right)_v = T + v\left(\dfrac{\partial p}{\partial s} \right)_v$; $\Rightarrow \left(\dfrac{\partial h}{\partial s} \right)_v = T + \dfrac{T\beta v}{C_v \alpha} > T$

   The second term on right is always positive quantity since β is given to be positive. Therefore, the slope of $p = c$ line is less than the slope of $v = c$ line line.

11-1-7 [OQY] Starting with the relation $dh = Tds + vdp$, show that the slope of a constant-pressure line a *h-s* diagram (a) is constant in the saturation region, and (b) increases with temperature in the superheated region.

SOLUTION:

For $p = $ c line, $dp = 0$ and the above 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 = $ c line on an *h-s* diagram is equal to the temperature.

(a) In the saturation region, $T = T_{\text{sat}@p}$ is a constant for a given pressure. Therefore, the slope is constant..

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

11-1-8 [OQF] Derive relation for (a) *Δu*, (b) *Δh* and (c) *Δs* of a gas that obeys the equation of state $(p + a/v^2)v = RT$ for an isothermal process.

SOLUTION:

(a)

$$\Delta u = u_2 - u_1 = \int_{T_1}^{T_2} c_v dT + \int_{v_1}^{v_2} \left(T \left(\frac{\partial p}{\partial T} \right)_v - p \right) dv$$

For isothermal ($T = c$) process:

$$\Delta u = \int_{v_1}^{v_2} \left(T \left(\frac{\partial p}{\partial T} \right)_v - p \right) dv$$

From the given equation of state,

$$p = \frac{RT}{v} - \frac{a}{v^2}; \quad \Rightarrow \quad \left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v}$$

Thus,

$$T \left(\frac{\partial p}{\partial T} \right)_v - p = \frac{RT}{v} - \frac{RT}{v} + \frac{a}{v^2}; \quad \Rightarrow \quad T \left(\frac{\partial p}{\partial T} \right)_v - p = \frac{a}{v^2}$$

Substituting, $\quad \Delta u = \int_{v_1}^{v_2} \frac{a}{v^2} dv; \quad \Rightarrow \quad \Delta u = a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$

(b) The enthalpy change Δh is related to Δu through the relation

$$\Delta h = \Delta u + p_2 v_2 - p_1 v_1;$$

Thus,

$$p_2 v_2 - p_1 v_1 = \left(RT - \frac{a}{v_2} \right) - \left(RT - \frac{a}{v_1} \right); \quad \Rightarrow \quad p_2 v_2 - p_1 v_1 = a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$$

Substituting,

$$\Delta h = 2a \left(\frac{1}{v_1} - \frac{1}{v_2} \right)$$

(c)

$$\Delta s = s_2 - s_1;$$

$$\Delta s = \int_{T_1}^{T_2} \frac{c_v}{T} dT + \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial T} \right)_v dv; \quad \Rightarrow \quad \Delta s = \int_{v_1}^{v_2} \left(\frac{\partial p}{\partial T} \right)_v dv$$

Substituting $\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{v}$, (derived in part (a))

$$\Delta s = \int_{v_1}^{v_2} \frac{R}{v}\,dv; \quad \Rightarrow \quad \Delta s = R \ln \frac{v_2}{v_1}$$

11-1-9 [OQD] Show that $c_v = -T(\partial v/\partial T)_s(\partial p/\partial T)_v$, and $c_p = T(\partial p/\partial T)_s(\partial v/\partial T)_P$.

SOLUTION:

From Eq. (11.38)

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

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

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

Using the definition of c_p from Eq. (11.46)

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

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

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

11-1-10 [OQM] Steam is throttled from 4.5 MPa and 400°C to 3.5 MPa. Estimate the temperature change (ΔT) of the steam during this process and the average Joule-Thomson coefficient (μ_J).

Using the manual approach or the PC system-state TESTcalc, evaluate the states.

State-1 (given $p_1 = 4.5$ MPa; $T_1 = 400°C$)
$h_1 = 3204.7$ kJ/kg.

State-2 (given $p_2 = 3.5$ MPa; $h_2 = h_1$)
$T_2 = 392.56°C$
Thus the temperature drop during this throttling process is

$$\Delta T = T_2 - T_1 = 392.56 - 400 = -7.44°C$$

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

$$\mu = \left(\frac{\partial T}{\partial p}\right)_h; \quad \Rightarrow \mu \cong \left(\frac{\Delta T}{\Delta p}\right)_{h=3204.7 \text{ kJ/kg}}$$

$$\Rightarrow \mu = \frac{(392.56 - 400) \ °C}{(3.5 - 4.5) \ MPa}; \quad \Rightarrow \mu = 7.44 \ °C/MPa$$

TEST Solution:

Launch the PC flow-state TESTcalc and select H2O. Evaluate State-1 and State-2 from the given conditions and using the fact that throttling is isenthalpic (h2 = h1). In the I/O panel, evaluate = (T2-T1)/(p2-p1). The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-11 [OQJ] Consider an infinitesimal reversible adiabatic compression or expansion process. By taking $s = s(P,v)$ and using the Maxwell relations, show that for this process $Pv^k =$ constant, where k is isentropic expansion exponent defined as $k = (v/P)(\partial P/\partial v)_s$. Also, show that the isentropic expansion exponent k reduces to the specific heat ratio (C_P/C_v) for an ideal gas.

SOLUTION:

Using Taylor's theorem, the total differential ds of $s = s(p,v)$ can be expressed as

$$ds = \left(\frac{\partial s}{\partial p}\right)_v dp + \left(\frac{\partial s}{\partial v}\right)_p dv; \qquad (1)$$

Now substituting following Maxwell relations

$$\left(\frac{\partial s}{\partial p}\right)_v = -\left(\frac{\partial v}{\partial T}\right)_s \quad \text{and} \quad \left(\frac{\partial s}{\partial v}\right)_p = \left(\frac{\partial p}{\partial T}\right)_s$$

into Eq. (1) and setting $ds = 0$ (isentropic condition), we get

$$-\left(\frac{\partial v}{\partial T}\right)_s dp + \left(\frac{\partial p}{\partial T}\right)_s dv = 0;$$

$$\Rightarrow dp - \left(\frac{\partial T}{\partial v}\right)_s \left(\frac{\partial p}{\partial T}\right)_s dv = 0; \quad \Rightarrow dp - \left(\frac{\partial p}{\partial v}\right)_s dv = 0;$$

$$\Rightarrow \frac{dp}{p} - \frac{1}{p}\left(\frac{\partial p}{\partial v}\right)_s dv = 0; \qquad (2)$$

By definition, the isentropic expansion exponent k is:

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

Substituting in equation (2)

$$\frac{dp}{p} + k\frac{dv}{v} = 0$$

Taking k constant and integrating,

$$\ln p + k \ln v = c; \quad \Rightarrow \ln pv^k = c$$

Thus, $\qquad pv^k = c$

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

$$(s,T,v) \rightarrow \left(\frac{\partial s}{\partial T}\right)_v \left(\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial T}{\partial v}\right)_s = -1; \quad \Rightarrow \quad \frac{c_v}{T}\left(\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial T}{\partial v}\right)_s = -1 \qquad (3)$$

$$(s,T,p) \rightarrow \left(\frac{\partial s}{\partial T}\right)_p \left(\frac{\partial p}{\partial s}\right)_T \left(\frac{\partial T}{\partial p}\right)_s = -1; \quad \Rightarrow \quad \frac{c_p}{T}\left(\frac{\partial p}{\partial s}\right)_T \left(\frac{\partial T}{\partial p}\right)_s = -1 \qquad (4)$$

where we use Eqs. (11.38) and (11.46):

$$c_v = T\left(\frac{\partial s}{\partial T}\right)_v \quad \text{and} \quad c_p = T\left(\frac{\partial s}{\partial T}\right)_p$$

Equating the left hand sides of Eqs (3) and (4), we obtain:

$$\frac{c_p}{c_v} = \left(\frac{\partial s}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_s \left(\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial T}{\partial v}\right)_s = \left(\frac{\partial s}{\partial p}\frac{\partial v}{\partial s}\right)_T \left(\frac{\partial p}{\partial T}\frac{\partial T}{\partial v}\right)_s = \left(\frac{\partial v}{\partial p}\right)_T \left(\frac{\partial p}{\partial v}\right)_s;$$

For an ideal gas

$$\left(\frac{\partial v}{\partial p}\right)_T = \left(\frac{\partial\left(RT/p\right)}{\partial p}\right)_T; \quad \Rightarrow \quad \left(\frac{\partial v}{\partial p}\right)_T = -\frac{v}{p}$$

Substituting,

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

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

11-1-12 [OQW] Consider a mixture of two gases A and B. Show that when the mass fraction x_A and x_B are known, the mole-fraction can be determined from $y_A = M_B/[M_A(1/x_A-1) + M_B]$ and $y_B = 1 - y_A$ where M_A and M_B are the molar masses of A and B.

SOLUTION:

Starting from the definition of mole fraction:

$$y_A = \frac{n_A}{n} = \frac{n_A}{n_A + n_B} = \frac{\left(\dfrac{m_A}{\bar{M}_A}\right)}{\left(\dfrac{m_A}{\bar{M}_A}\right)+\left(\dfrac{m_B}{\bar{M}_B}\right)} = \frac{\left(\dfrac{m_A}{m}\dfrac{1}{\bar{M}_A}\right)}{\left(\dfrac{m_A}{m}\dfrac{1}{\bar{M}_A}\right)+\left(\dfrac{m_B}{m}\dfrac{1}{\bar{M}_B}\right)}$$

$$\Rightarrow y_A = \frac{\left(x_A\dfrac{1}{\bar{M}_A}\right)}{\left(x_A\dfrac{1}{\bar{M}_A}\right)+\left(x_B\dfrac{1}{\bar{M}_B}\right)} = \frac{\left(\dfrac{x_A}{\bar{M}_A}\right)}{\left(\dfrac{x_A}{\bar{M}_A}\right)+\left(\dfrac{1-x_A}{\bar{M}_B}\right)} = \frac{\left(\bar{M}_A\bar{M}_B\right)\left(\dfrac{x_A}{\bar{M}_A}\right)}{\left(\bar{M}_A\bar{M}_B\right)\left[\left(\dfrac{x_A}{\bar{M}_A}\right)+\left(\dfrac{1-x_A}{\bar{M}_B}\right)\right]}$$

$$\Rightarrow y_A = \frac{\bar{M}_B x_A}{\bar{M}_B x_A + \bar{M}_A\left(1-x_A\right)} = \frac{\bar{M}_B}{\bar{M}_B + \bar{M}_A\left(\dfrac{1}{x_A}-1\right)}$$

$n = n_A + n_B;$

$\Rightarrow \quad 1 = \dfrac{n_A}{n}+\dfrac{n_B}{n};$

$\Rightarrow \quad 1 = y_A + y_B;$

$\Rightarrow \quad y_B = 1 - y_A$

11-1-13 [OTN] Nitrogen gas at 400 K and 300 kPa behaves as an ideal gas. Estimate the c_p and c_v of nitrogen at this state.

TEST Solution

Launch the IG system-state TESTcalc and select N2. Evaluate the neighboring states (1 deg-C difference) as described in the TEST-code, which can be found in the problems module of the TEST-pro site at www.thermofluids.net. Note that for State-2, the pressure is held constant (p2=p1) and for State-3 the specific volume is held constant (v3=v1). In the I/O panel, calculate cp from =(h2-h1)/(T2-T1) and cv from =(u2-u1)/(T3-T1) to produce

(a) 1.048 kJ/kg-K, (b) 0.7514 kJ/kg-K

11-1-14 [OTR] A system contains oxygen (ideal gas) at 400 K and 100 kPa. As a result of some disturbance, the conditions of the gas change to 404 K and 98 kPa. (a) Estimate the change in the specific volume (Δv) of the gas using the ideal-gas relation and using Taylor's theorem. (b) Determine the exact answer using the IG equation of state.

Solution

(a) Taylor's theorem for $v = v(p,T)$ can be expressed as:

$$\Delta v \cong dv = \left(\frac{\partial v}{\partial p}\right)_T dp + \left(\frac{\partial v}{\partial T}\right)_p dT;$$

For oxygen: $R = \dfrac{\bar{R}}{\bar{M}_{O2}} = \dfrac{8.314}{32} = 0.260$

The IG relation produces:

$$v = \frac{RT}{p};$$

$$\Rightarrow \left(\frac{\partial v}{\partial p}\right)_T = -\frac{RT}{p^2} = -\frac{(0.260)(402)}{99^2} = -0.01066 \text{ unit}$$

And $\left(\dfrac{\partial v}{\partial T}\right)_p = \dfrac{R}{p} = \dfrac{0.260}{99} = 0.0026263 \text{ unit}$

Therefore, $\Delta v \cong dv = \left(\dfrac{\partial v}{\partial p}\right)_T dp + \left(\dfrac{\partial v}{\partial T}\right)_p dT = (-0.01066)(-2) + (0.0026263)(4) = 0.0318 \ \dfrac{\text{m}^3}{\text{kg}}$

(b) The exact change in v can be calculated from the known IG relation.

$$\Delta v = v_2 - v_1 = R\left(\frac{T_2}{p_2} - \frac{T_1}{p_1}\right) = (0.260)\left(\frac{404}{100} - \frac{400}{98}\right) = 0.0318;$$

$$\Rightarrow \quad \Delta p = \frac{1}{3.488}\left(\frac{355}{1.01} - \frac{350}{1}\right) = 0.0318 \ \frac{\text{m}^3}{\text{kg}}$$

TEST Solution

Launch the IG system-state TESTcalc and select O2. Evaluate the neighboring states from the given conditions as described in the TEST-code, which can be found in the problems module of the TEST-pro site at www.thermofluids.net. Evaluate the derivative in the I/O panel using central or forward differencing.

11-1-15 [OTS] Estimate the specific-heat difference (c_p - c_v) for liquid water at 20 MPa and 60°C.

SOLUTION:

The specific heat difference 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 difference about the specific state and obtaining the properties using the system-state PC TESTcalc,

$$c_p - c_v \cong -T \left(\frac{\Delta v}{\Delta T} \right)_{p=20\text{MPa}}^2 \left(\frac{\Delta p}{\Delta v} \right)_{T=60^o C};$$

$$\Rightarrow c_p - c_v = -(60 + 273.15) \left(\frac{v_{65^o C} - v_{55^o C}}{65 - 55} \right)_{p=20\text{MPa}}^2 \left(\frac{30000 - 10000}{v_{30 \text{ MPa}} - v_{10 \text{ MPa}}} \right)_{T=60^o C};$$

$$\Rightarrow c_p - c_v = -(333.15) \left(5.0 \times 10^{-7} \right)^2 \left(-2.063 \times 10^9 \right);$$

$$\Rightarrow c_p - c_v = 0.172 \text{ kJ/kg} \cdot \text{K}$$

TEST Solution

Launch the PC system-state TESTcalc and select H2O. Evaluate the four neighboring states as described in the TEST-code, which can be found in the problems module of the TEST-pro site at www.thermofluids.net. Calculate the partial derivatives in the I/O panel. Note that evaluating c_v directly is not possible due to high error associated with finding neighboring states at constant volume for a liquid.

11-1-16 [OTO] Estimate the specific-heat difference (c_p - c_v) for liquid water at 1000 psia and 150°F.

SOLUTION:

The specific heat difference 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 difference about the specific state and obtaining the properties using the system-state PC TESTcalc (note that the pressure difference must be huge in order to create any appreciable change in the specific volume),

$$c_p - c_v \cong -T \left(\frac{\Delta v}{\Delta T} \right)_{p=1000 \text{ psia}}^2 \left(\frac{\Delta p}{\Delta v} \right)_{T=150° \text{F}} \cong -T \left(\frac{\Delta v}{\Delta T} \right)_{p=7 \text{ MPa}}^2 \left(\frac{\Delta p}{\Delta v} \right)_{T=65° \text{C}} ;$$

$$\Rightarrow c_p - c_v = -(65 + 273) \left(\frac{v_{70°C} - v_{60°C}}{70 - 60} \right)_{p=7\text{MPa}}^2 \left(\frac{30000 - 1000}{v_{30 \text{ MPa}} - v_{1 \text{ MPa}}} \right)_{T=65°C} ;$$

$$\Rightarrow c_p - c_v = -(338) \left(6.0 \times 10^{-7} \right)^2 \left(-3.13 \times 10^9 \right);$$

$$\Rightarrow c_p - c_v = 0.381 \text{ kJ/kg} \cdot \text{K}$$

TEST Solution

Launch the PC system-state TESTcalc and select H2O. Evaluate the four neighboring states as described in the TEST-code, which can be found in the problems module of the TEST-pro site at www.thermofluids.net. Calculate the partial derivatives in the I/O panel. Note that evaluating c_v directly is not possible due to high error associated with finding neighboring states at constant volume for a liquid.

11-1-17 [OTB] Plot the Joule-Thomson coefficient (μ_J) for nitrogen over the pressure range of 100 psia to 1500 psia at the enthalpy values of 100 Btu/lbm, 175 Btu/lbm and 225 Btu/lbm. Discuss the results.

Analysis

The PC model for nitrogen is used to find the temperature under the given conditions. A one percent drop in pressure can be regarded as a differential change.

Approximating differentials by differences at specific state,

$$\mu_J \equiv \left(\frac{\partial T}{\partial p}\right)_h \approx \left[\frac{(T_2 - T_1)}{(p_2 - p_1)}\right]_h ; \qquad \left[\frac{^\circ F}{psia}\right]$$

Using the system-state PC TESTcalc, State-1 is found from the given pressure and enthalpy and a neighboring state at a slightly higher pressure (p2 = 1.01*p1) while holding enthalpy the same as the original state (h2=h1). In the I/O panel, calculate the Joule-Thomson coefficient by evaluating (T2-T1)/(p2-p1). Repeat with a different p1 and h1 as necessary. The results were plotted on the following graph:
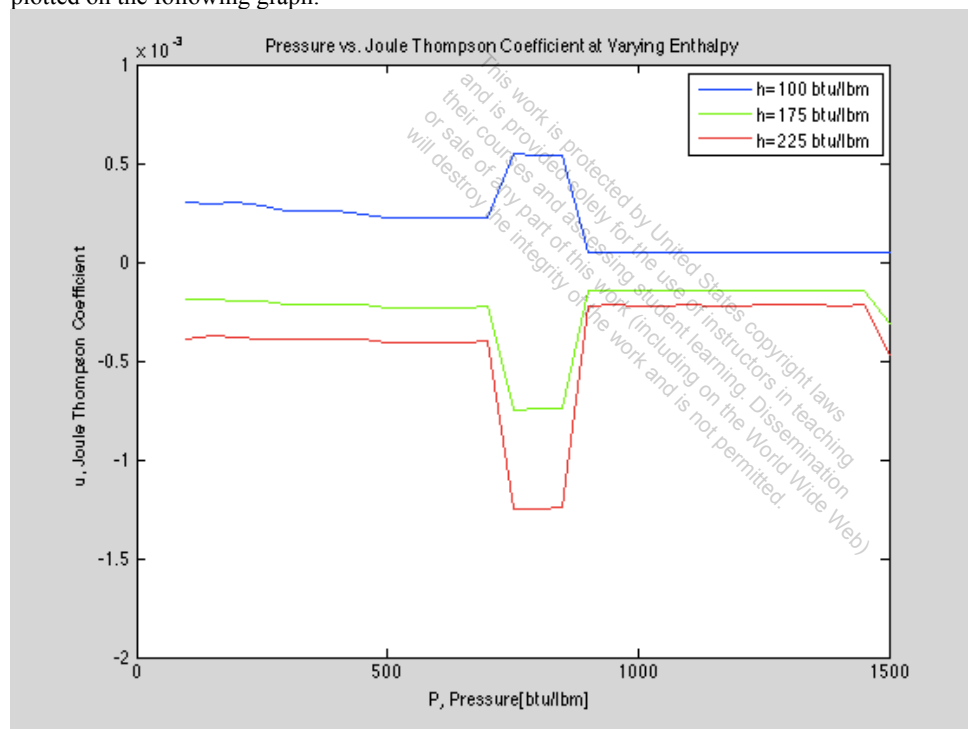
11-1-18 [OTA] Determine the enthalpy change (Δh) and the entropy change (Δs) of nitrogen per unit mole as it undergoes a change of state from 225 K and 6 MPa to 320 K and 12 MPa, (a) by assuming ideal-gas behavior, and (b) by accounting for the deviation from ideal-gas behavior through the use of generalized charts (L-K model).

SOLUTION:

From Table C-1 or the PG system-state TESTcalc, obtain the necessary material properties of

N_2: $c_p = 1.031 \dfrac{\text{kJ}}{\text{kg} \cdot \text{K}}$, $c_v = 0.734 \dfrac{\text{kJ}}{\text{kg} \cdot \text{K}}$, $R = 0.2968 \dfrac{\text{kJ}}{\text{kg} \cdot \text{K}}$

Given: $p_1 = 6$ MPa; $T_1 = 225$ K

Given: $p_2 = 12$ MPa; $T_2 = 320$ K

IG Model:

Using the manual approach described in Chapter 3 or the IG system-state TESTcalc, obtain:

$\Delta h = h_2 - h_1 = 98.0 \dfrac{\text{kJ}}{\text{kg}}$

$\Delta s = s_2 - s_1 = 0.1575 \dfrac{\text{kJ}}{\text{kg} \cdot \text{K}}$

RG Model (L-K):
From Table E-1, or from the RG system-state TESTcacl, obtain the necessary material properties of N_2:

$p_{cr} = 3.39$ MPa, $T_{cr} = 126.2$ K

The reduced pressure and temperature for the given states are

$p_{r1} = \dfrac{p_1}{p_{cr}} = 1.77, \; T_{r1} = \dfrac{T_1}{T_{cr}} = 1.78$

$p_{r2} = \dfrac{p_2}{p_{cr}} = 3.54, \; T_{r2} = \dfrac{T_2}{T_{cr}} = 2.536$

Using the Lee-Kesler compressibility charts, Table E, we obtain the compressibility factors.

$\Delta h = (h_2 - h_1)^{IG} - RT_{cr}(Z_{h,2} - Z_{h,1}) = 103.2 \dfrac{\text{kJ}}{\text{kg}}$

$\Delta s = (s_2 - s_1)^{IG} - R(Z_{s,2} - Z_{s,1}) = 0.180 \dfrac{\text{kJ}}{\text{kg} \cdot \text{K}}$

TEST Solution

Launch the IG system-state TESTcalc and select N2. Evaluate the initial and final states from the known conditions and evaluate the property differences in the I/O panel. Generate the TEST-code using the Super-Calculate button. Launch the RG system-state TESTcalc in a separate tab, paste the TEST-code in the I/O panel, and click the Load button to calculate the states. Evaluate the property differences for the RG model in the I/O panel. The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-19 [OTH] Determine the enthalpy change (Δh) and the entropy change (Δs) of carbon dioxide per unit mass as it undergoes a change of state from 250 K and 7 MPa to 280 K and 12 MPa, (a) by assuming ideal-gas behavior, and (b) by accounting for the deviation from ideal-gas behavior.

SOLUTION:

From Table C-1 or the PG system-state TESTcalc, obtain the necessary material properties of

CO_2: $\quad R = 0.1889 \dfrac{kJ}{kg \cdot K}$

Given: $p_1 = 7$ MPa; $T_1 = 250$ K

Given: $p_2 = 12$ MPa; $T_2 = 280$ K

IG Model:

Using the manual approach described in Chapter 3 or the IG system-state TESTcalc, obtain:

$\Delta h = h_2 - h_1 = 25.3 \dfrac{kJ}{kg}$

$\Delta s = s_2 - s_1 = -0.0062 \dfrac{kJ}{kg \cdot K}$

RG Model (L-K):
From Table E-1, or from the RG system-state TESTcacl, obtain the necessary material properties of CO_2:

$p_{cr} = 7.37$ MPa, $T_{cr} = 304.1$ K

The reduced pressure and temperature for the given states are

$p_{r1} = \dfrac{p_1}{p_{cr}} = 0.95, \ T_{r1} = \dfrac{T_1}{T_{cr}} = 0.822$

$p_{r2} = \dfrac{p_2}{p_{cr}} = 1.63, \ T_{r2} = \dfrac{T_2}{T_{cr}} = 0.921$

Using the Lee-Kesler compressibility charts, Table E, we obtain the compressibility factors.

$\Delta h = (h_2 - h_1)^{IG} - RT_{cr}(Z_{h,2} - Z_{h,1}) = 19.0 \dfrac{kJ}{kg}$

$\Delta s = (s_2 - s_1)^{IG} - R(Z_{s,2} - Z_{s,1}) = 2.28 \dfrac{kJ}{kg \cdot K}$

TEST Solution

Launch the IG system-state TESTcalc and select CO2. Evaluate the initial and final states from the known conditions and evaluate the property differences in the I/O panel. Generate the TEST-code using the Super-Calculate button. Launch the RG system-state TESTcalc in a separate tab, paste the TEST-code in the I/O panel, and click the Load button to calculate the states. Evaluate the property differences for the RG model in the I/O panel. The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-20 [OTE] Methane is compressed adiabatically by a steady-state flow compressor from 2 MPa and -10°C to 10 MPa and 110°C at a rate of 0.8 kg/s. Using the generalized charts, determine the required power input to the compressor.

SOLUTION:

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

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

From Table E-1, or from the RG system-state TESTcacl, obtain the necessary material properties of CH_4:

$p_{cr} = 4.6$ MPa, $T_{cr} = 190.4$ K

The enthalpy departures of CH_4 at the specified states are determined from generalized charts to be

$$\left. \begin{array}{l} T_{R1} = \dfrac{T_1}{T_{cr}}; \quad \Rightarrow T_{R1} = \dfrac{263}{191.1}; \quad \Rightarrow T_{R1} = 1.376 \\[2mm] p_{R1} = \dfrac{p_1}{p_{cr}}; \quad \Rightarrow p_{R1} = \dfrac{2}{4.64}; \quad \Rightarrow p_{R1} = 0.431 \end{array} \right\} \rightarrow Z_{h1} = 0.2$$

And

$$\left. \begin{array}{l} T_{R2} = \dfrac{T_2}{T_{cr}}; \quad \Rightarrow T_{R2} = \dfrac{383}{191.1}; \quad \Rightarrow T_{R2} = 2.00 \\[2mm] p_{R2} = \dfrac{p_2}{p_{cr}}; \quad \Rightarrow p_{R2} = \dfrac{10}{4.64}; \quad \Rightarrow p_{R2} = 2.155 \end{array} \right\} \rightarrow Z_{h2} = 0.4$$

Thus,

$$h_2 - h_1 = RT_{cr}(Z_{h1} - Z_{h2}) + (h_2 - h_1)_{ideal};$$
$$\Rightarrow h_2 - h_1 = (0.5182)(191.1)(0.2 - 0.4) + 2.2537(110 - (-10));$$
$$\Rightarrow h_2 - h_1 = 250.6 \text{ kJ/kg}$$

Substituting,

$$\dot{W}_{C,in} = (0.8 \text{ kg/s})(250.6 \text{ kJ/kg});$$
$$\Rightarrow \dot{W}_{C,in} = 201 \text{ kW}$$

TEST Solution

Launch the RG single-flow, open-steady TESTcalc and select CH4. Evaluate the inlet and exit states from the known conditions. In the device panel, load the states, enter Qdot=0, and calculate Wdot_ext. By default, the L-K model is selected, which produces a result of 198 kW. When the N-O model is used, the answer changes to 203 kW. The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-21 [OTI] Methane gas flows through a pipeline with a mass flow rate of 110 lb/s at a pressure of 183 atm and a temperature of 56°F. Determine the volumetric flow rate ($\dot{V}$), in ft³/s, using (a) the ideal gas equation, (b) van der Waals equation and (c) compressibility chart.

SOLUTION:

(a) The mass and volume flow rates are related by:

$$\dot{V} = \frac{\dot{m}}{\rho} = \dot{m}v$$

From Table C-1 or the IG flow-state TESTcalc, obtain the necessary material properties of CH_4:

$$R = 0.518 \ \frac{kJ}{kg \cdot K}$$

Given: $p_1 = 183 \ atm = 18.54 \ MPa$; $T_1 = 56°F = 286.5 \ K$, $\dot{m} = 110 \ \frac{lbm}{s} = 49.9 \ \frac{kg}{s}$

IG Model:

Using the manual approach described in Chapter 3 or the IG system-state TESTcalc, obtain:

$$v = \frac{RT}{p} = 0.0080 \ \frac{m^3}{kg}$$

$$\Rightarrow \dot{V} = \dot{m}v = 0.400 \ \frac{m^3}{s}$$

(b) van der Waals equation:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

where $a = \dfrac{27 R^2 T_{cr}^2}{64 p_{cr}} = 0.892 \ \dfrac{kPa \cdot m^6}{kg^2}$; $b = \dfrac{RT_{cr}}{8 p_{cr}} = 0.00268 \ \dfrac{m^3}{kg}$;

$$\Rightarrow \left(18540 + \frac{0.892}{v^2}\right)(v - 0.00268) = 0.518(286.5)$$

$$\Rightarrow \left(18540 v^2 + 0.892\right)(v - 0.00268) = 148.4 v^2$$

$$\Rightarrow v = 0.0072 \ \frac{m^3}{kg}$$

$$\Rightarrow \dot{V} = \dot{m}v = 0.362 \ \frac{m^3}{s}$$

(c) RG Model (L-K):
From Table E-1, or from the RG system-state TESTcacl, obtain the necessary material properties of CH_4:

$p_{cr} = 4.6$ MPa, $T_{cr} = 190.4$ K

The reduced pressure and temperature for the given states are

$$p_{r1} = \frac{p_1}{p_{cr}} = 4.03, \ T_{r1} = \frac{T_1}{T_{cr}} = 1.50$$

Using the Lee-Kesler compressibility charts, Table E, we obtain the compressibility factor.

$Z = 0.808$

$$v = \frac{ZRT}{p} = 0.0065 \ \frac{m^3}{kg}$$

$$\Rightarrow \ \dot{V} = \dot{m}v = 0.324 \ \frac{m^3}{s}$$

TEST Solution

Launch the RG single-flow, open-steady TESTcalc and select CH4. Evaluate the state from the known conditions. The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-22 [OTL] Determine the specific volume (v) of water vapor at 10 MPa and 360°C, in m³/kg, using (a) the steam tables, (b) compressibility chart and (c) ideal gas equation.

SOLUTION:

From Table C-1 or the IG flow-state TESTcalc, obtain the necessary material properties of H_2O:

$$R = 0.461 \ \frac{kJ}{kg \cdot K}$$

Given: $p_1 = 10$ MPa; $T_1 = 360°C = 633$ K

(a) PC Model:

Using the manual approach described in Chapter 3 or the PC system-state TESTcalc, obtain:

$$v = 0.0232 \ \frac{m^3}{kg}$$

(b) RG Model (L-K):
From Table E-1, or the RG system-state TESTcalc, obtain the necessary material properties of H_2O:

$$p_{cr} = 22.12 \text{ MPa}, \ T_{cr} = 647 \text{ K}$$

The reduced pressure and temperature for the given states are

$$p_{r1} = \frac{p_1}{p_{cr}} = 4.03, \ T_{r1} = \frac{T_1}{T_{cr}} = 1.50$$

Using the Lee-Kesler compressibility charts, Table E, we obtain the compressibility factor.

$$Z = 0.81$$

$$v = \frac{ZRT}{p} = 0.0237 \ \frac{m^3}{kg}$$

(c) IG Model:

Using the manual approach described in Chapter 3 or the IG system-state TESTcalc, obtain:

$$v = \frac{RT}{p} = 0.0292 \ \frac{m^3}{kg}$$

TEST Solution

Launch the PC system-state TESTcalc and select H2O. Evaluate the state from the known conditions. Repeat with the IG and RG model. The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-23 [OTG] Consider refrigerant R-12 vapor at 160°F and 0.5 ft³/lb. Estimate the pressure (*p*) at this state, in atm, using (a) the ideal gas equation, (b) van der Waals equation and (c) compressibility chart.

From the PC system-state TESTcalc, obtain (by hovering the pointer over R-12 to display its properties on the message panel after selecting it) the necessary material properties of R −12 :

$$R = \frac{\bar{R}}{\bar{M}} = \frac{8.314}{120.93} = 0.0687 \ \frac{kJ}{kg \cdot K}$$

Given: $v_1 = 0.5 \ \frac{fl^3}{lbm} = 0.0312 \ \frac{fl^3}{lbm}$; $T_1 = 160° F = 344 \ K$

(a) IG Model:

Using the manual approach described in Chapter 3 or the IG system-state TESTcalc, obtain:

$$p = \frac{RT}{v} = 758.2 \ kPa$$

(c) RG Model (L-K):

From Table E-1, or the RG system-state TESTcalc, obtain the necessary material properties of R-12 :

$p_{cr} = 4.135 \ MPa, T_{cr} = 385 \ K$

The reduced pressure and temperature for the given states are

$$p_{r1} = \frac{p_1}{p_{cr}} = 4.03, \ T_{r1} = \frac{T_1}{T_{cr}} = 1.50$$

Using the Lee-Kesler compressibility charts, Table E, we obtain the compressibility factor.

$Z = 0.91$

$$p = \frac{ZRT}{v} = 692 \ \frac{m^3}{kg}$$

TEST Solution

Launch the RG system-state TESTcalc and select H2O. Evaluate the state from the known conditions. Repeat with the PC model. The TEST-code for this problem can be found in the problems module of the TEST-pro site at www.thermofluids.net.

11-1-24 [OTP] For the functions $x = x(y,w)$, $y = y(z,w)$, $z = z(x,w)$, demonstrate that $(\partial x/\partial y)_w(\partial y/\partial z)_w(\partial z/\partial x)_w = 1$.

SOLUTION:

$x = x(y,w)$

$$dx = \left(\frac{\partial x}{\partial w}\right)_y dw + \left(\frac{\partial x}{\partial y}\right)_w dy \qquad (1)$$

Similarly,
$y = y(z,w)$

$$dy = \left(\frac{\partial y}{\partial w}\right)_z dw + \left(\frac{\partial y}{\partial z}\right)_w dz$$

Substituting dy in equation (1)

$$dx = \left(\frac{\partial x}{\partial w}\right)_y dw + \left(\frac{\partial x}{\partial y}\right)_w \left[\left(\frac{\partial y}{\partial w}\right)_z dw + \left(\frac{\partial y}{\partial z}\right)_w dz\right]$$

$$\Rightarrow dx = \left[\left(\frac{\partial x}{\partial w}\right)_y + \left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial w}\right)_z\right] dw + \left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w dz; \qquad (2)$$

Again,

$$dx = \left(\frac{\partial x}{\partial w}\right)_z dw + \left(\frac{\partial x}{\partial z}\right)_w dz \qquad (3)$$

Comparing dz component of equation (2) and (3),

$$\left(\frac{\partial x}{\partial z}\right)_w = \left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w$$

$$\left(\frac{\partial x}{\partial y}\right)_w \left(\frac{\partial y}{\partial z}\right)_w \left(\frac{\partial z}{\partial x}\right)_w = 1$$

11-1-25 [OTZ] The following expressions for the equation of state and the specific heat (c_p) are obeyed by a certain gas: $v = RT/paT^2$ and $c_p = ABTC_p$ where a, A, B, C are constants. Obtain an expression for (a) the Joule-Thomson coefficient (μ_J) and (b) the specific heat (c_v).

SOLUTION:

Given $v = \dfrac{RT}{p} + \alpha T^2$ and $c_p = A + BT + Cp$

From Eq. (11.67), the Joule Thomson coefficient can be written as:

$$\mu_J = -\frac{1}{c_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]; \qquad \left[\frac{K}{kPa}\right],$$

From the given relation: $v = \dfrac{RT}{p} + \alpha T^2$

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} + 2\alpha T$$

$$\mu_J = -\frac{1}{c_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] = -\frac{1}{c_p}\left[\frac{RT}{p} + \alpha T^2 - T\left(\frac{R}{p} + 2\alpha T\right)\right]$$

$$\mu_J = \frac{\alpha T^2}{c_p} = \frac{\alpha T^2}{A + BT + Cp}$$

Using Eq. (11.58)

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

Now, $\left(\dfrac{\partial p}{\partial T}\right)_v = \left(\dfrac{\partial}{\partial T}\left(\dfrac{RT}{v - \alpha T^2}\right)\right)_v = \left(\dfrac{Rv + \alpha RT^2}{\left(v - \alpha T^2\right)^2}\right)$

Therefore, $c_v = c_p - T\left(\dfrac{R}{p} + 2\alpha T\right)\left(\dfrac{Rv + \alpha RT^2}{\left(v - \alpha T^2\right)^2}\right)$

$$\Rightarrow c_v = A + BT + Cp - T\left(\frac{R}{p} + 2\alpha T\right)\left(\frac{Rv + \alpha RT^2}{\left(v - \alpha T^2\right)^2}\right)$$

11-1-26 [OTK] The differential of pressure obtained from a certain equation of state is given by the following expression: $dp = \{2(v - b) / RT\}dv - \{(v - b)^2 / RT^2\}dT$. Determine the equation of state.

SOLUTION:

Expressing the differential in the format of Eq. (11.9),

$$M(v,T) = \frac{2(v-b)}{RT} \text{ and } N(v,T) = \frac{(v-b)^2}{RT^2}$$

For a function $p(v,T)$ to exist, the test of exactness must be satisfied. That is,

$$\left(\frac{\partial M}{\partial T}\right)_v = \left(\frac{\partial N}{\partial v}\right)_T$$

Now, $\left(\dfrac{\partial M}{\partial T}\right)_v = \dfrac{-2(v-b)}{RT^2}$ and $\left(\dfrac{\partial N}{\partial v}\right)_T = \dfrac{2(v-b)}{RT^2}$

The two expressions are not equal. Therefore, the given expression is not the differential of an equation of state.

11-1-27 [OTC] The differential of pressure obtained from a certain equation of state is given by the following expression: $dp = \{-RT/(v - b)^2\}dv + \{R/(v - b)\}dT$. Determine the equation of state.

SOLUTION:

Expressing the differential in the format of Eq. (11.9),

$$M(v,T) = \frac{-RT}{(v-b)^2} \text{ and } N(v,T) = \frac{R}{(v-b)}$$

For a function $p(v,T)$ to exist, the test of exactness must be satisfied. That is,

$$\left(\frac{\partial M}{\partial T}\right)_v = \left(\frac{\partial N}{\partial v}\right)_T$$

Now, $\left(\dfrac{\partial M}{\partial T}\right)_v = \dfrac{-R}{(v-b)^2}$ and $\left(\dfrac{\partial N}{\partial v}\right)_T = \dfrac{-R}{(v-b)^2}$

Therefore a function $p(v,T)$ exists. Expressing its differential using Taylor's theorem:

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

Comparing with the given differential, we obtain:

$$\left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} \text{ and } \left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{(v-b)}$$

Integrating the second equation, we obtain

$$p = \frac{RT}{(v-b)} + f(v)$$

$$\Rightarrow \left(\frac{\partial p}{\partial v}\right)_T = \frac{-RT}{(v-b)^2} + \frac{df}{dv}$$

Comparing the two expressions for this partial,

$$\frac{df}{dv} = c$$

Therefore, $p = \dfrac{RT}{(v-b)} + c$

xx**11-1-28** [OTU] Derive the relation $c_p = -T(\partial^2 g/\partial T^2)_p$

SOLUTION:

Treating T and p as independent variable

As $c_p = \left(\dfrac{\partial h}{\partial T}\right)_p$,

$$h = h(T, p)$$

$$\Rightarrow dh = \left(\frac{\partial h}{\partial T}\right)_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp;$$

$$\Rightarrow dh = c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp; \qquad (1)$$

Also,

$$s = s(T, p)$$

$$\Rightarrow ds = \left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp; \qquad (2)$$

Substituting Equation (1) and (2) in $dh = Tds + vdp$

$$c_p dT + \left(\frac{\partial h}{\partial p}\right)_T dp = T\left[\left(\frac{\partial s}{\partial T}\right)_p dT + \left(\frac{\partial s}{\partial p}\right)_T dp\right] + vdp$$

Rearranging,

$$\left[c_p - T\left(\frac{\partial s}{\partial T}\right)_p\right] dT = \left[T\left(\frac{\partial s}{\partial p}\right)_T + v - \left(\frac{\partial h}{\partial p}\right)_T\right] dp$$

As T and p are independent, fix p while varying T: $dp = 0$ and $dT \neq 0$
Therefore,

$$\left[c_p - T\left(\frac{\partial s}{\partial T}\right)_p\right] dT = 0;$$

$$\Rightarrow c_p - T\left(\frac{\partial s}{\partial T}\right)_p = 0;$$

$$\Rightarrow c_p = T\left(\frac{\partial s}{\partial T}\right)_p \qquad (3)$$

Now,

$$g = h - Ts$$

$$\Rightarrow \left(\frac{\partial g}{\partial T}\right)_p = \left(\frac{\partial h}{\partial T}\right)_p - T\left(\frac{\partial s}{\partial T}\right)_T - s;$$

$$\Rightarrow \left(\frac{\partial g}{\partial T}\right)_p = c_p - T\left(\frac{\partial s}{\partial T}\right)_T - s; \qquad (4)$$

Substituting Eq. (3) into (4)

$$\Rightarrow \left(\frac{\partial g}{\partial T}\right)_p = -s; \qquad (5)$$

Differentiate Eq. (5), we obtain

$$-\left(\frac{\partial s}{\partial T}\right)_p = \left(\frac{\partial^2 g}{\partial T^2}\right)_p \qquad (5)$$

Combining Equation (3) and (5)

$$c_p = -T\left(\frac{\partial^2 g}{\partial T^2}\right)_p$$

11-1-29 [OTX] Prove that $(\partial\beta/\partial p)_T = -(\partial\kappa_T/\partial T)_p$.

SOLUTION:

Volumetric expansivity:

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

Differentiating equation (1) w.r.t. p at constant T,

$$\left(\frac{\partial\beta}{\partial p}\right)_T = \frac{1}{v}\left(\frac{\partial^2 v}{\partial p\partial T}\right) + \left(\frac{\partial v}{\partial T}\right)_p\left[\frac{\partial}{\partial p}\left(\frac{1}{v}\right)\right]_T$$

$$\Rightarrow \left(\frac{\partial\beta}{\partial p}\right)_T = \frac{1}{v}\left(\frac{\partial^2 v}{\partial p\partial T}\right) + \left(\frac{\partial v}{\partial T}\right)_p\left(\frac{-1}{v^2}\right)\left(\frac{\partial v}{\partial p}\right)_T$$

$$\Rightarrow \left(\frac{\partial\beta}{\partial p}\right)_T = \frac{1}{v}\left(\frac{\partial^2 v}{\partial p\partial T}\right) + \beta k_T \qquad (2)$$

Isothermal compressibility:

$$k_T = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \qquad (3)$$

Differentiating equation (3) w.r.t. T at constant p,

$$\left(\frac{\partial k_T}{\partial T}\right)_p = -\frac{1}{v}\left(\frac{\partial^2 v}{\partial T\partial p}\right) - \left(\frac{\partial v}{\partial p}\right)_T\left[\frac{\partial}{\partial T}\left(\frac{1}{v}\right)\right]_p$$

$$\Rightarrow \left(\frac{\partial k_T}{\partial T}\right)_p = -\frac{1}{v}\left(\frac{\partial^2 v}{\partial T\partial p}\right) - \left(\frac{\partial v}{\partial p}\right)_T\left(\frac{-1}{v^2}\right)\left(\frac{\partial v}{\partial T}\right)_p$$

$$\Rightarrow \left(\frac{\partial k_T}{\partial T}\right)_p = -\frac{1}{v}\left(\frac{\partial^2 v}{\partial T\partial p}\right) - \beta k_T \qquad (4)$$

As $\dfrac{\partial^2 v}{\partial p\partial T} = \dfrac{\partial^2 v}{\partial T\partial p}$, comparing Eqs. (2) and (4) we get

$$\left(\frac{\partial\beta}{\partial p}\right)_T = -\left(\frac{\partial k_T}{\partial T}\right)_p$$

11-1-30 [OTV] At certain states, the *p-v-T* data for a particular gas can be represented as $Z = 1 - Ap/T^4$, where Z is the compressibility factor and A is a constant. Obtain an expression for the difference in specific heats (c_p - c_v).

SOLUTION:

From Eq. (11.59)

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

$$\Rightarrow \quad c_p - c_v = -T\frac{\left(\frac{\partial v}{\partial T}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_T} ; \qquad\qquad (1)$$

the equation of state is:

$$v = Z\left(\frac{RT}{p}\right) = \frac{RT}{p} - \frac{AR}{T^3} ;$$

Thus

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} + \frac{3AR}{T^4} ; \qquad\qquad \left(\frac{\partial v}{\partial p}\right)_T = -\frac{RT}{p^2} ;$$

Substituting in Eq (1),

$$c_p - c_v = \frac{T\left(\frac{R}{p} + \frac{3AR}{T^4}\right)^2}{\frac{RT}{p^2}} ; \quad \Rightarrow \quad C_p - C_v = R\left[1 + \frac{3Ap}{T^4}\right]^2$$

With $\frac{Ap}{T^4} = 1 - Z$

$$c_p - c_v = R\left[1 + 3(1-Z)\right]^2 ;$$

$$\Rightarrow c_p - c_v = R\left(4 - 3Z\right)^2$$