
Example 1

The fundamental relation for the entropy of an electron gas can be approximated as

$$S(U, V, N) = B N^{1/6} V^{1/3} U^{1/2}, \text{ where} \quad (\text{A})$$

$$B = 2^{3/2} \pi^{4/3} k_B m^{1/2} N_{\text{avag}}^{1/6} / (3^{1/3} h_P). \quad (\text{B})$$

Here, k_B denotes the Boltzmann constant that has a value of $\bar{R}/N_{\text{Avag}} = 1.3804 \times 10^{-26} \text{ kJ K}^{-1}$, h_P is the Planck constant that has a value of $6.62517 \times 10^{-37} \text{ kJ s}$, m denotes the electron mass of $9.1086 \times 10^{-31} \text{ kg}$, N the number of $\kappa\mu\omicron\lambda\epsilon$ of the gas, V its volume in m^3 , and U its energy in kJ . Determine \bar{s} , T , and P when $\bar{u} = 4000 \text{ kJ k mole}^{-1}$, and $\bar{v} = 1.2 \text{ m}^3 \text{ kmole}^{-1}$.

Solution

The value of $B = 5.21442 \text{ kg}^{1/2} \text{ k mole}^{1/6} \text{ s K}^{-1}$. From Eq. (A),

$$\bar{s} = S/N = (B/N) N^{1/6} (\bar{v}N)^{1/3} (\bar{u}N)^{1/2} = B \bar{v}^{1/3} \bar{u}^{1/2}, \text{ i.e.,} \quad (\text{C})$$

$$\bar{s} = 5.21442 (\text{kg}^{1/2} \text{ K}^{-1} \text{ Kmole}^{1/6} \text{ s})(1.2 \text{ m}^3 \text{ k mole}^{-1})^{1/3} (4000 \text{ kJ kmole}^{-1})^{1/2}.$$

Recalling that the units $\text{kg (m/s}^2) \text{ m} \equiv \text{J}$.

$$\bar{s} = 350 \text{ kg}^{1/2} \text{ m kJ}^{1/2} \text{ kmole}^{-1} \text{ K}^{-1} = 350.45 \text{ kJ kmole}^{-1} \text{ K}^{-1}.$$

From the entropy fundamental equation

$$1/T = (\partial \bar{s} / \partial \bar{u})_{\bar{v}}.$$

Differentiating Eq. (C) with respect to \bar{u} and using this relation,

$$1/T = (1/2) B \bar{v}^{1/3} / \bar{u}^{1/2} = 0.04381 \text{ or } T = 22.8 \text{ K}. \quad (\text{D})$$

Similarly, since

$$P/T = (\partial \bar{s} / \partial \bar{v})_{\bar{u}},$$

Upon differentiating Eq. (C) and using the above relation,

$$P/T = (1/3) B \bar{u}^{1/2} / \bar{v}^{2/3} = 94.35 \text{ kPa K}^{-1}. \quad (\text{E})$$

Using the value for $T = 22.83 \text{ K}$, the pressure $P = 2222.4 \text{ kPa}$. The enthalpy

$$\bar{h} = \bar{u} + P \bar{v} = 4000 + 2222.4 \times 1.2 = 6666.9 \text{ kJ kmole}^{-1}.$$

Remarks

Eq. (C) can be expressed in the form

$$\bar{u}(\bar{s}, \bar{v}) = \bar{s}^2 / (B^2 \bar{v}^{2/3}). \quad (\text{F})$$

Equation (F) is referred to as the energy representation of the fundamental equation (cf. Chapter 5).

Rewriting Eq. (D)

$$\bar{u}(T, \bar{v}) = 1/4 B^2 \bar{v}^{2/3} T^2. \quad (\text{G})$$

Differentiating this relation with respect to T we obtain the result

$$c_v = (\partial \bar{u} / \partial T)_v = (1/2) B^2 \bar{v}^{2/3} T. \quad (\text{H})$$

Dividing Eq. (E) by Eq. (D) we obtain the expression

$$\bar{u}(P, \bar{v}) = (3/2) P \bar{v}. \quad (\text{I})$$

Likewise, using the entropy fundamental state equation (Eq. (A)), we can also tabulate other nonmeasurable thermodynamic properties such as $\bar{a} (= \bar{u} - T \bar{s})$ and $\bar{g} (= \bar{h} - T \bar{s})$.

Eliminating \bar{u} in Eqs. (D) and (E) we obtain the state equation $P = P(T, \bar{v})$ for an electron gas in terms of measurable properties, i.e.,

$$P = (B/6) T^2 / \bar{v}^{1/3}. \quad (\text{J})$$

If this state equation (in terms of P , T and \bar{v}) is known, it does not imply that \bar{s} , \bar{u} , \bar{h} , \bar{a} , and \bar{g} can be subsequently determined. This is illustrated by considering the temperature and pressure relations

$$T = \partial \bar{s} / \partial \bar{u}, \text{ and } P/T = \partial \bar{s} / \partial \bar{v} \quad (\text{K})$$

One can use Eq. (J) in (K). These expressions indicate that Eqs. (K) are differential equations in terms of \bar{s} and, in order to integrate and obtain $\bar{s} = \bar{s}(T, \bar{v})$, an integration constant is required which is unknown. Therefore, a fundamental relation is that relation from which all other properties at equilibrium (e.g., T , P , \bar{v} , \bar{s} , \bar{u} , \bar{h} , \bar{a} , \bar{g} , c_p , and c_v) can be directly obtained by differentiation alone. While the Eq. (A) represents a fundamental relation, we can see that the relation Eq. (J) does not.

Example 2

Obtain an expression for the entropy change in an RK gas when the gas is isothermally compressed. Determine the entropy change when superheated R-12 is isothermally compressed at 60°C from 0.0194 m³ kg⁻¹ (state 1) to 0.0126 m³ kg⁻¹ (state 2). Compare the result with the tabulated value of $s_1 = 0.7259$, $s_2 = 0.6881$.

Solution

Consider the RK state equation

$$P = RT/(v-b) - a/(T^{1/2}v(v+b)) \quad (\text{A})$$

From the third Maxwell's relation Eq. (22) and Eq. (A),

$$(\partial s / \partial v)_T = (\partial P / \partial T)_{v,b} = R/(v-b) + (1/2) a/(T^{3/2}v(v+b)). \quad (\text{B})$$

Integrating Eq. (B),

$$\begin{aligned} s_2(T, v_2) - s_1(T, v_1) = \\ R \ln((v_2 - b)/(v_1 - b)) + (1/2)(a/(T^{3/2}b)) \ln(v_2(v_1 + b)/(v_1(v_2 + b))). \end{aligned} \quad (\text{C})$$

The critical conditions for R-12 are $T_c = 385$ K, and $P_c = 41.2$ bar. Therefore $\bar{a} = 208.59$ bar (m³ kmole⁻¹)² K^{1/2}, and $\bar{b} = 0.06731$ m³ kmole⁻¹. The molecular weight $M = 120.92$ kg kmole⁻¹, and $a = \bar{a}/M = 208.59$ bar (m³ kmole⁻¹)² K^{1/2} ÷ 120.92 kg kmole⁻¹ = 1.427 k Pa (m³ kg⁻¹)² K^{1/2}, and

$$b = 0.557 \times 10^{-3} \text{ m}^3 \text{ kg}^{-1}.$$

$$\text{Since, } R = 8.314 \div 120.92 = 0.06876 \text{ kJ kg}^{-1} \text{ K}^{-1},$$

$$\begin{aligned} s_2 - s_1 &= 0.06876 \ln((0.0126 - 0.000557) \div (0.0194 - 0.000557)) \\ &+ (1/2)(1.427 \div (333^{1.5} \cdot 0.000557)) \ln(0.0126(0.0194 + 0.000557) \\ &+ (0.0194 \times (0.0126 + 0.000557))). \\ &= -0.06876 \times 0.448 - 0.211 \times 0.01495 = -0.03396 \text{ kJ kg}^{-1} \text{ K}^{-1}. \end{aligned}$$

Example 3

Show that both the isothermal expansivity $\beta_P = (1/v)(\partial v / \partial T)_P$ and the isobaric compressibility coefficient $\beta_T = - (1/v)(\partial v / \partial P)_T$ tend to zero as $T \rightarrow 0$.

Solution

Example 1 shows that $(\partial s / \partial T)_v \rightarrow 0$ and $(\partial s / \partial P)_v \rightarrow 0$ as $T \rightarrow 0$. From the fourth of the Maxwell's relations,

$$(\partial v / \partial T)_P = -(\partial s / \partial P)_T, \text{ so that } (\partial v / \partial T)_P \rightarrow 0.$$

Similarly, using the third Maxwell's relation and the cyclic relations it may be shown that $(\partial P / \partial T)_v = -((\partial v / \partial T) / (\partial v / \partial P)) = (\partial s / \partial v)_T \rightarrow 0$ as $T \rightarrow 0$. Since $\partial v / \partial T \rightarrow 0$, it is apparent that $\partial v / \partial P \rightarrow 0$ as $T \rightarrow 0$.

Remark

The experimentally measured values of β_P and β_T both tend to 0 as $T \rightarrow 0$. Using the Maxwell's relations the reverse can be shown, i.e., $(\partial s/\partial T)_v \rightarrow 0$ and $(\partial s/\partial P)_v \rightarrow 0$.

Example 4

When a refrigerant is throttled from the saturated liquid phase using a short orifice, a two-phase mixture of quality x is formed. We are asked to determine the choking flow conditions for the two-phase mixture, which occurs when the mixture reaches the sound speed ($c^2 = -v^2 (\partial P/\partial v)_s$). We must also derive an expression for the speed of sound in a two-phase mixture. Assume ideal gas behavior for the vapor phase and that the liquid phase is incompressible.

Solution

During the elemental expansion of a two phase mixture of a specified quality x from P to $P + dP$, and v to $v + dv$,

$$dh = Tds + v dP, \text{ and} \quad (\text{A})$$

$$du = Tds - Pd v. \quad (\text{B})$$

Since,

$$dh_f = d(u_f + Pv_f)$$

For incompressible liquids,

$$dh_f = du_f + v_f dP.$$

For a two phase mixture of vapor and liquid,

$$dh = x dh_g + (1 - x) dh_f = x dh_g + (1 - x)(du_f + v_f dP).$$

Assuming ideal gas behavior for the vapor phase, and if $du_f = cdT$, then

$$dh = x c_{p,o} dT + (1 - x)(cdT + v_f dP). \quad (\text{C})$$

Similarly,

$$du = x c_{v,o} dT + (1 - x) cdT. \quad (\text{D})$$

Considering constant entropy in Eqs. (A) and (B), using Eqs. (C) and (D), dividing by dT , we obtain the relation

$$(dP/dT)_s = (x c_{p,o} + (1 - x) c)/(v - (1 - x)v_f), \text{ i.e.,} \quad (\text{E})$$

$$(dv/dT)_s = -(x c_{v,o} + (1 - x)c)/P. \quad (\text{F})$$

Dividing Eq. (E) by Eq. (F), we obtain the relation

$$-(dP/dv)_s = (x c_{p,o} + (1 - x)c)(P/(v - (1 - x)v_f))/(x c_{v,o} + (1 - x)c). \quad (\text{G})$$

Using the definition of the sound speed,

$$c'^2 = -v^2(dP/dv)_s,$$

where

$$v = xv_g + (1 - x)v_f, \quad (\text{H})$$

Eq. (G) can be written as

$$c'^2 = v^2(xc_{p,o} + (1 - x)c) P/((v - (1 - x)v_f)(xc_{v,o} + (1 - x)c). \quad (\text{I})$$

Since $v_g = RT/P$,

$$v = (xRT/P + (1 - x)v_f), \text{ and}$$

$$c'^2 = RT(x + (1 - x)(Pv_f/(RT)))^2 (xc_{p,o} + (1 - x)c)/(x(xc_{v,o} + (1 - x)c)). \quad (\text{J})$$

If $x=1$, then, as expected,

$$c^2 = c_{p,o} RT/c_{v,o} = \gamma RT. \quad (\text{K})$$

If $x \rightarrow 0$, then

$$c^2 = RT(Pv_f/RT)^2/x \rightarrow \infty.$$

Using tabulated values for R-134A,

$$c = 1.464 \text{ kJ kg}^{-1} \text{ K}^{-1}, \text{ and } c_{p,o} \text{ at } 298 \text{ K} = 0.851 \text{ kJ kg}^{-1} \text{ K}^{-1}.$$

Using the values for $P = 690 \text{ kPa}$, $R = 0.08149 \text{ kJ kg}^{-1} \text{ K}^{-1}$, $c_{v,o} = 0.7697 \text{ kJ kg}^{-1} \text{ K}^{-1}$, $v_f = 0.000835 \text{ m}^3 \text{ kg}^{-1}$, and $\gamma = 1.1$. For the conditions $x = 1$, $T = 298 \text{ K}$,

$$c^2 = 163.4 \text{ m s}^{-1}.$$

a. *Example 5*

Derive an expression for the sound speed ($c^2 = -v^2(\partial P/\partial v)_s = v/\beta_s$) in terms of the measurable properties of a simple compressible substance.
 Show that $c_p/c_v = k = \beta_T/\beta_s$.
 Determine a relation for the sound speed for an ideal gas.
 Determine a relation for the sound speed for a VW gas.

Solution

Recall that speed of sound is derived as

$$c^2 = -v^2(\partial P/\partial v)_s = v/\beta_s$$

$$ds = 0 = c_v dT/T + (\partial P/\partial T)_v dv, \text{ and} \quad (\text{A})$$

$$ds = 0 = c_p dT/T - (\partial v/\partial T)_p dP. \quad (\text{B})$$

We multiply Eq. (A) by (T/c_v) and Eq. (B) by (T/c_p) and then subtract one of the resulting relations from the other to obtain

$$(\partial P/\partial T)_v (T/c_v) dv_s + (\partial v/\partial T)_p (T/c_p) dP_s = 0, \text{ or} \quad (\text{C})$$

$$(\partial P/\partial v)_s = -k (\partial P/\partial T)_v / (\partial v/\partial T)_p, \text{ where} \quad (\text{D})$$

$$k(T,v) = c_p(T,v)/c_v(T,v). \quad (\text{E})$$

Applying the expression for the speed of sound $c^2 = -v^2(\partial P/\partial v)_s = v/\beta_s$ in Eq. (D),

$$c^2 = v^2 k(T,v) (\partial P/\partial T)_v / (\partial v/\partial T)_p. \quad (\text{F})$$

Using the cyclical rule

$$(\partial P/\partial v)_T (\partial v/\partial T)_p (\partial T/\partial P)_v = -1 \quad (\text{G})$$

we obtain

$$(\partial v/\partial T) = - (\partial P/\partial T) / (\partial P/\partial v) \quad (\text{H})$$

Substituting from Eq. (H) in Eq. (F),

$$c^2 = -k(T,v) v^2 (\partial P/\partial v)_T = k(T,v) v/\beta_T \quad (\text{I})$$

Letting $c^2 = v/\beta_s$, in Eq. (I)

$$v/\beta_s = k(T,v) v/\beta_T, \text{ or } k(T,v) = \beta_T/\beta_s.$$

In the case of ideal gases,

$$k = - (c^2/v^2) / (-RT/v^2) = c^2/RT \text{ or } c^2 = kRT. \quad (\text{J})$$

Typically we denote c as c_0 for ideal gases.

For a VW gas,

$$\partial P/\partial v = -RT/(v-b)^2 + 2a/v^3 \quad (\text{K})$$

Thereafter, combining Eqs. (1) and (K)

$$c^2 = k(T, v) v^2 \{RT/(v - b)^2 + a/v^3\} \quad (L)$$

Remarks

If, in the VW state relation, $a = b = 0$, the expression reduces to the sound speed for an ideal gas. In that case, $k = k(T)$.

High pressures often develop within the clearance space in turbine seals, and gas leaks are governed by the resulting choked flow conditions. The value of the sound speed through a real gas is required in order to evaluate this condition.

In the case of liquids and solids, a very large pressure is required to cause a small change in the volume so that $(\partial P/\partial v)_T \rightarrow \infty$ and, consequently, $c \rightarrow \infty$. Therefore, sound travels at faster speeds in liquids and solids.

Applying Eq. (L) to the case of an ideal gas, $c_o^2 = k(T) RT$, and dividing Eq.(I) by c_o^2 ,
 $(c^2/c_o^2) = - (k(T_R, v_R)/(k_o(T_R) T_R)) v_R^2 (\partial P_R/\partial v_R)_{TR}$.

b. Example 6

The state of a copper bar is initially at a pressure of 1 bar and temperature of 250 K. It is compressed so that the exerted pressure is 1000 bar. Assume that the compression is adiabatic and reversible (i.e., the material reverts to its original state once the load is removed) with, and that $\beta_P = 48 \times 10^{-6} \text{ K}^{-1}$, $\beta_T = 7.62 \times 10^{-7} \text{ bar}^{-1}$, $v = 1.11 \times 10^{-4} \text{ m}^3 \text{ kg}^{-1}$, $c_p = 0.372 \text{ kJ kg}^{-1} \text{ K}^{-1}$, and $c_v = 0.364 \text{ kJ kg}^{-1} \text{ K}^{-1}$. Determine the change in the internal energy and the intermolecular potential energy of the solid.

Solution

$$v_2 - v_1 \approx -\beta_T v_1 (P_2 - P_1) \quad (A)$$

With $\beta_T = -\frac{1}{v} \left(\frac{\partial v}{\partial P} \right)_T$, and integrating $\ln \left(\frac{v_2}{v_1} \right) = -\beta_T (P_2 - P_1)$ solving for v_2

$$v_2 = 1.1109 \times 10^{-4} \text{ m}^3 \text{ g}^{-1}.$$

From Eq. (37) and integrating $\ln \frac{T_2}{T_1} = -\frac{\beta_P}{\beta_T C_v} (V_2 - V_1)$ or $(T_2 - T_1) \approx -\frac{\beta_P}{\beta_T} \frac{T_1}{C_v} (V_2 - V_1)$

Using results from (A)

$$T_2 \approx T_1 \frac{\beta_P}{C_v} (P_2 - P_1) = 0.375 \text{ K} \quad (B)$$

c.) For an adiabatic reversible process, the first law yields,

$$\begin{aligned} \Delta u &= - \int P dv = - \int P (\partial v/\partial P) dP = \int \beta_T P v dP = \left(P_2^2 - P_1^2 \right) \frac{\beta_T v}{2} \\ &= ((1000 \times 100)^2/2 - 100^2/2) \times 1.11 \times 10^{-4} \times 7.62 \times 10^{-9} \\ &= 0.00423 \text{ kJ kg}^{-1} \text{ or } 4.23 \text{ J kg}^{-1}. \end{aligned}$$

d.) Note that one may use following equation also, which is similar to the result in Example 7.

$$du = c_v dT + (T \beta_P/\beta_T - P) dv.$$

Now, thermal part of change in “u” is given as,

$$c_v dT = 0.364 \times 0.38 = 0.138 \text{ kJ kg}^{-1}, \quad (D)$$

The intermolecular potential energy of the solid

$$\Delta(\text{ipe}) = (T \beta_P/\beta_T - P) dv$$

where second term is same as the answer in part (c)

$$= (250 \text{ K} \times 48 \times 10^{-6} \text{ K}^{-1} \div 7.62 \times 10^{-7} \text{ bar}^{-1}) * 8.8 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1} * 100 \text{ kPa bar}^{-1} - 0.00423$$

$$\Delta (\text{ipe}) = 0.1398 - 0.00423 = -0.13 \text{ kJ kg}^{-1} \quad (\text{E})$$

Therefore, the net change in the internal energy of the solid is

$$du = 0.138 - 0.1356 = 0.00239 \text{ kJ kg}^{-1},$$

At the minimum intermolecular potential energy, compression should cause the "ipe" to increase. Since the ipe decreases with compression, this indicates that the solid is not at that minimum value. In this example, the temperature increases by 0.38 K, increasing the thermal portion of the internal energy by 0.138 kJ, but the IPE decreases by 0.13 kJ.

$$v_2 - v_1 \approx -\beta_T v_1 (P_2 - P_1)$$

Recall that

$$(\partial T / \partial v)_s = -T \beta_p / (\beta_T c_v) \text{ so that } dv_s = -dT_s \beta_T c_v / (T \beta_p).$$

Likewise, since $(\partial T / \partial P)_s = T v \beta_p / c_p$, $dT_s = dP_s (T v \beta_p / c_p)$.

Hence, $\Delta T = 0.36 \text{ K}$. Consequently, the temperature following compression is 250.36 K.

The internal energy change

$$du_s = -(P dv_s) = (P \beta_T c_v / (T \beta_p)) dT_s.$$

An approximate solution for the internal energy change is as follows:

$$\begin{aligned} du_s &= -P dv_s = (P \beta_T c_v / (T \beta_p)) dT_s \\ &= 1000 \text{ bar} \times 7.62 \times 10^{-7} \text{ bar}^{-1} \times 0.364 \text{ kJ}^{-1} \text{ kg}^{-1} \text{ K}^{-1} \times 0.36 \text{ K} \div (250 \text{ K} \times 48 \times 10^{-6} \text{ K}^{-1}) \\ &= 0.00832 \text{ kJ kg}^{-1}. \end{aligned}$$

A more accurate evaluation is as follows

$$dv = -7.62 \times 10^{-7} \times 1000 \times 1.11 \times 10^{-4} = -8.46 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}.$$

Therefore,

$$\begin{aligned} \Delta u &= -\int P dv = -\int P (\partial v / \partial P) dP = \int \beta_T P v dP \\ &= ((1000 \times 100)^2 \div 2 - 100^2 \div 2) \times 1.11 \times 10^{-4} \times 7.62 \times 10^{-9} \\ &= 0.00423 \text{ kJ kg}^{-1} \text{ or } 4.23 \text{ J kg}^{-1}. \end{aligned}$$

Note that

$$du = c_v dT + (T \beta_p / \beta_T - P) dv.$$

Now,

$$c_v dT = 0.364 \times 0.36 = 0.131 \text{ kJ kg}^{-1}, \text{ and}$$

the intermolecular potential energy of the solid

$$\begin{aligned} \text{ipe} &= (T \beta_p / \beta_T - P) dv \\ &= (250 \text{ K} \times 48 \times 10^{-6} \text{ K}^{-1} \div 7.62 \times 10^{-7} \text{ bar}^{-1} - 1000 \text{ bar}) \\ &\quad \times 100 \text{ bar kPa}^{-1} \times (-8.46 \times 10^{-8} \text{ m}^3 \text{ kg}^{-1}). \\ &= -0.125 \text{ kJ kg}^{-1}. \end{aligned}$$

Therefore, the net change in the internal energy of the solid is

$$du = 0.131 - 0.125 = 0.006 \text{ kJ kg}^{-1},$$

At the minimum intermolecular potential energy, compression should cause the IPE to increase. Since the IPE decreases, this indicates that the solid is not at that minimum value. In this example, the temperature increases by 0.36 K, increasing the thermal portion of the internal energy by 0.131 kJ, but the IPE decreases by 0.125 kJ.

c. Example 7

Obtain an expression for dh and du for a liquid in terms of c_p , β_p , β_T , c_v , dT and dP . Simplify the relations for an incompressible liquid.

Solution

Rewriting Eq. (43),

$$dh = c_p dT + (v - T \beta_p v) dP, \quad (\text{A})$$

where $\beta_p = (\partial v / \partial T)_p$. Therefore,

$$du = dh - d(Pv) = c_p dT - Pd v - T \beta_p v dP$$

However, $v = v(T,P)$, so that

$$d v = (\partial v / \partial T)_P dT + (\partial v / \partial P)_T dP = v (\beta_p dT - \beta_T dP). \quad (B)$$

Hence,

$$du = (c_p - P v \beta_p) dT + v (P \beta_T - T \beta_p) dP \quad (C)$$

For incompressible liquids $\beta_p = \beta_T = 0$, and Eqs. (A) can be expressed in the form

$$dh = c_p dT + v dP., \text{ i.e., } h = h(T,P), \text{ and} \quad (D)$$

Further,

$$(dh/dT)_P = c_p. \quad (E)$$

For an incompressible fluid Eq. (C) assumes the form

$$du/dT = c_p, \text{ i.e., } u = u(T) \text{ alone.} \quad (F)$$

Upon comparing Eqs. (E) and (F),

$$(\partial h / \partial T)_P = du/dT = c_p. \quad (G)$$

Note that $du/dT = (\partial u / \partial T)_v$, since v is constant. Therefore,

$$(\partial h / \partial T)_P = du/dT = c_p = c_v = c \quad (H)$$

d. Example 8

Determine the entropy of H₂O assuming the relation $s = 0$ for the saturated liquid at the triple point, and $h_{fg} = 2503 \text{ kJ kg}^{-1}$. If the ideal gas specific heat of water is reproduced by the relation $\bar{c}_{p,o} (\text{kJ kmole}^{-1} \text{ K}^{-1}) = 28.85 + 0.01206 T + 100,600/T^2$, determine its entropy at a pressure of 250 bar and a temperature of 873 K.

Solution

Typically, properties are tabulated with respect to arbitrary reference conditions, e.g., T_{ref} and P_{ref} . For saturated liquid water, it is customary to set that reference condition at the triple point, i.e., $T_{ref} = T_{TP} = 273 \text{ K}$ and $P_{TP} = 0.00611 \text{ bar}$ at which the entropy is assumed to have a value of zero. Since

$$T ds + v dP = dh,$$

during vaporization at a specified pressure,

$$ds = dh/T, \text{ i.e., } s_g - s_f = (h_g - h_f)/T = h_{fg}/T.$$

Therefore,

$$s_g(T_{TP}, P_{TP}) - 0 = h_{fg}/T = 2503 \div 273 = 9.17 \text{ kJ kg}^{-1} \text{ K}^{-1}.$$

Applying the RK equation at this state,

$$0.00611 = 0.08314 \times 273 \div (\bar{v} - 0.0211) - 142.64 \div (273^2 \times \bar{v} (\bar{v} + 0.0211)), \text{ i.e.,}$$

$$\bar{v} = 3715 \text{ m}^3 \text{ kmole}^{-1}.$$

The compressibility factor based on this value of the specific volume

$$Z(T_{TP}, P_{TP}) = P \bar{v} / (\bar{R} T) = 0.00611 \times 3715 \div (0.08314 \times 273) = 1.$$

Furthermore, employing Eq. (53),

$$s(273, 3715) - s_o(273, 3715) \approx 0, \text{ and}$$

using Eq. (57)

$$s(273, 0.00611) - s_o(273, 0.00611) \approx 0.$$

This result is expected, since the pressure is low so that the vapor behavior is like that of an ideal gas. Hence,

$$s(273, 0.00611) = s_o(273, 0.006 \text{ bar}) = 9.17 \text{ kJ kg}^{-1}. \quad (A)$$

Since.

$$d\bar{s}_o = \bar{c}_{p,o} dT/T - \bar{R} dP/P,$$

integrating this expression between the states (873 K, 250 bar) and (273 K, 0.00611 bar), we obtain the relation

$$\bar{s}_o(873, 250 \text{ bar}) - \bar{s}_o(273, 0.006 \text{ bar}) = \left(\int_{273}^{873} \bar{c}_{p,o} dT/T \right) - \bar{R} \ln(250 \div 0.006) \quad (\text{B})$$

Using the given relation for $\bar{c}_{p,o}$,

$$\begin{aligned} \bar{s}_o(873, 250 \text{ bar}) - \bar{s}_o(273, 0.006 \text{ bar}) &= \\ &= (28.85 \times \ln(873 \div 273) + 0.01206 \times (873 - 273) - (100600 + 2)(873^{-2} - 273^{-2})) - \\ &= (8.314 \times \ln(250 \div 0.006)) \\ &= 41.38 - 88.30 = -46.92 \text{ kJ kmole}^{-1} \text{ K}^{-1}. \end{aligned}$$

On a mass basis

$$\begin{aligned} s_o(873, 250 \text{ bar}) - s_o(273, 0.006 \text{ bar}) &= -46.92 \div 18.02 = -2.604 \text{ kJ kg}^{-1} \text{ K}^{-1}, \text{ and} \\ s_o(873 \text{ K}, 250 \text{ bar}) &= 9.17 - 2.604 = 6.566 \text{ kJ kg}^{-1} \text{ K}^{-1}. \end{aligned}$$

From the results of Example (16), at $P = 250$ bars, and $T = 873$ K,

$$\bar{v} = 0.245 \text{ m}^3 \text{ kmole}^{-1} \text{ and } Z = 0.844.$$

Thereafter, using Eq. (53)

$$\begin{aligned} \bar{s}(T, v) - \bar{s}_o(T, v) &= \bar{R} \ln(1 - (b/\bar{v})) - (1/2)(a/(bT^{3/2})) \ln(1 + (b/\bar{v})) \\ &= 8.314 \times \ln(1 - (0.0211 \div 0.245)) - \\ &= (0.5 \times 142.64 \times 100 \div (0.0211 \times 873^{1.5})) \ln(1 + (0.0211/0.245)) \\ &= -1.826 \text{ kJ kmole}^{-1} \text{ K}^{-1}. \end{aligned}$$

Then using Eq. (5),

$$\bar{s}(T, P) - \bar{s}_o(T, P) = s(T, v) - s_o(T, v) + \bar{R} \ln Z = -1.826 - 1.409 = -3.235 \text{ kJ kmole}^{-1} \text{ K}^{-1}.$$

or

$$\begin{aligned} s(T, P) - s_o(T, P) &= -0.180 \text{ kJ kg}^{-1} \text{ K}^{-1}, \text{ i.e.,} \\ s(T, P) &= 6.566 - 0.180 = 6.386 \text{ kJ kg}^{-1} \text{ K}^{-1}. \end{aligned}$$

Remarks

Using the RK equation, we determined the values of s at specified temperatures and pressures, and at specified temperatures and specific volumes. This enables the production of T - s diagrams along with superimposed isotherms, isobars, and isometric contours.

- Instead of the RK equation, we can use the entropy departure charts, at $P_R (= 250 \div 220.9) = 1.132$, and $T_R (= 873 \div 647) = 1.349$,

$$\{(s_o(T, P) - s(T, P))\} / R = 0.389. \quad (\text{C})$$

The value of $s(873 \text{ K}, 250 \text{ bar})$ can be calculated thereafter.

e. Example 9

Determine the relations for properties s , v , u , and h if $g(T, P)$ is known.

Solution

Using the relations $g = h - Ts$, and $dg = v dP - s dT$,

$$(\partial g / \partial T)_P = -s \text{ and } (\partial g / \partial P)_T = v \quad (\text{A})$$

Thereafter,

$$h = g + Ts \text{ and } u = h - Ts. \quad (\text{B})$$

Remarks

Manipulating the relations for $g (= h - Ts)$ and $dg (= -s dT + v dP)$, we obtain the expression

$$dg = v dP - (h - g) dT/T, \text{ i.e., } dg - g dT/T = v dP - h dT/T$$

Therefore,

$$T d(g/T) = v dP - h dT/T, \text{ or } d(g/RT) = v dP/RT - h dT/(RT^2), \text{ and} \\ (\partial(g/RT)/\partial T)_P = -h/RT^2. \quad (C)$$

Similarly,

$$(\partial(g_o/RT)/\partial T)_P = -h_o/RT^2 \text{ so that } (\partial(g_{C,R}/T_R)/\partial T_R)_{P_R} = -h_{C,R}/T_R^2, \text{ and} \\ (\partial g_{C,R}/\partial T_R)_{P_R} = -s_{C,R}, \text{ and } (\partial g_{C,R}/\partial P_R)_{T_R} = v_{C,R}. \quad (D,E)$$

a. Example 10

Determine the reversible work required for the steady reversible isothermal compression of methane at 230 K from $P_1 = 150$ bar to $P_2 = 250$ bar. You may use the Kesler charts.

Solution

We will use the conservation equation

$$\bar{q} - \bar{w}_s = \bar{h}_2 - \bar{h}_1 \text{ and } \delta \bar{q} = T d\bar{s}.$$

For an isothermal process,

$$\bar{q} = \int T d\bar{s} = T(\bar{s}_2 - \bar{s}_1).$$

Therefore,

$$-\bar{w}_s = (\bar{h}_2 - \bar{h}_1) - T(\bar{s}_2 - \bar{s}_1).$$

For methane, $T_c = 191$ K, and $P_c = 46.4$ bar. Hence,

$$T_{R,1} = T_{R,2} = 230 \div 191 = 1.2, P_{R,1} = 150 \div 46.4 = 3.2, P_{R,2} = 250 \div 46.4 = 5.4.$$

From the discussion in Chapter 2, using the enthalpy correction charts (Appendix Fig. B-3) or the Kesler tables (Table A-24A) at $T_{R,2} = 1.2$, $P_{R,2} = 5.4$, $Z_2 = 0.75$. Thus,

$$(\bar{h}_{o2} - \bar{h}_2)/\bar{R}T_c = 3.172$$

Similarly, at $T_{R,1} = 1.2$, $P_{R,1} = 3.2$, and

$$(\bar{h}_{o1} - \bar{h}_1)/\bar{R}T_c = 2.834.$$

Therefore,

$$\bar{h}_1 = \bar{h}_{o1} - 2.834 \times 8.314 \times 191 = (\bar{h}_{o1} - 4500) \text{ kJ kmole}^{-1},$$

$$(\bar{h}_2 = \bar{h}_{o2} - 3.172 \times 8.314 \times 191 = (\bar{h}_{o2} - 5037) \text{ kJ kmole}^{-1}, \text{ and}$$

$$\bar{h}_2 - \bar{h}_1 = (\bar{h}_{o2}(T_2) - \bar{h}_{o1}(T_1) - 537) \text{ kJ kmole}^{-1}.$$

Since $T_2 = T_1$, $\bar{h}_{o2}(T_2) = \bar{h}_{o1}(T_1)$, and

$$\bar{h}_2 - \bar{h}_1 = -537 \text{ kJ kmole}^{-1}.$$

For $T_{R,1} = 1.2$, $P_{R,1} = 3.2$, and $((\bar{s}_{o1} - \bar{s}_1)/\bar{R}) = 1.7379$ (Tables A-25A or Appendix Fig. B-4).

Therefore,

$$(\bar{s}_{o1} - \bar{s}_1) = 14.4 \text{ kJ kmole}^{-1} \text{ K}^{-1}.$$

For $T_{R,2} = 1.2$, $P_{R,2} = 5.4$, and $((\bar{s}_{o2} - \bar{s}_2)/\bar{R}) = 1.819$, and

$$(\bar{s}_{o2} - \bar{s}_2) = 15.1 \text{ kJ kmole}^{-1} \text{ K}^{-1}.$$

Consequently,

$$\bar{s}_2 - \bar{s}_1 = 4.95 \text{ kJ kmole}^{-1} \text{ K}^{-1}, \text{ and}$$

$$\bar{w}_s = -601 \text{ kJ kmole}^{-1}.$$

Remark

If the ideal gas state equation is used,

$$w_s = -\int \bar{v} dP = -\int (\bar{R}T/P) dP = -\bar{R}T \ln(P_2/P_1) = -8.314 \times 230 \ln(250 \div 150) \\ = -977 \text{ kJ kmole}^{-1}.$$

f. Example 11

Determine the fugacity of pure water for the following cases:

Saturated vapor at 100°C,

Saturated liquid at 100°C,

Compressed liquid at 100°C, and 200 bar.

Superheated vapor at 100°C, and 0.5 bar.
 Saturated vapor at 350°C.
 Super-cooled vapor at 90°C, 1 bar' assume ideal gas behavior

Solution

The saturation pressure at 100°C is $P^{\text{sat}} = 1$ bar. Since $P_c = 220.9$ bars, $P_R = P^{\text{sat}}/P_c \ll 1$, at this state water vapor $\text{H}_2\text{O}(\text{g})$ behaves as an ideal gas. Therefore,

$$f = P^{\text{sat}} = 100 \text{ kPa or } 1 \text{ bar.}$$

Since P and T are constant, f is unchanged during the phase change. Therefore, for the saturated liquid $\text{H}_2\text{O}(\text{l})$ $f = 100 \text{ kPa or } 1 \text{ bar.}$

At constant temperature,

$$d(\ln f) = v dP/(RT).$$

For liquids, $v \approx \text{constant}$. For this problem, $v = 0.001 \text{ m}^3 \text{ kg}^{-1}$. Integrating from the saturated liquid state at 100°C and 1 bar to the compressed liquid state at 100°C and 2 bar,

$$\ln (f(T,P)/f^{\text{sat}}(T)) = v(P - P^{\text{sat}})/(RT), \text{ i.e.,}$$

$$\ln (f(100^\circ\text{C}, 200 \text{ bar})/f^{\text{sat}}(100^\circ\text{C})) = ((0.001 \times (20,000 - 100))/(8.314 \times 373/18.02)) = 0.116.$$

Therefore,

$$(f(100^\circ\text{C}, 200 \text{ bar})/f^{\text{sat}}(100^\circ\text{C})) = \text{POY} = \exp(0.116) = 1.123, \text{ and}$$

$$f(100^\circ\text{C}, 200 \text{ bar}) \approx 1.123 \times f^{\text{sat}}(100^\circ\text{C}) = 1.123 \times 100 \text{ kPa} = 112.3 \text{ kPa} = 1.123 \text{ bar.}$$

Superheated vapor behaves as an ideal gas at low pressures. Therefore, the fugacity equals the pressure, i.e., $f = 0.5$ bar.

At 350°C, $P^{\text{sat}} = 165$ bar, $P_R = 165/220.9 = 0.75$, $T_R = 623/373 = 1.67$, and $Z \approx 0.3$. Therefore, under these conditions water vapor behaves as a real gas and $f \neq P$. Using the fugacity coefficient charts, $\phi = 0.74$, and $f = 0.74 \times 165 = 124 \text{ kPa} = 1.24 \text{ bar.}$

Since the behavior is ideal gas, $f = P^{\text{sat}}$ at 90°C = 0.7014 bars.

Remarks

The example illustrates that when the pressure is increased by a factor of 200, in the case of liquids f changes by only 12%. At a specified temperature the changes in the values of f with respect to pressure ($d \ln f = v_f dP$) are small, since the liquid specific volume v_f is small. However, for the gaseous state, v is much larger than v_f (oftentimes by three orders of magnitude) so that f changes significantly as the pressure is altered.

b. Example 12

Obtain a relation for h_{fg}/RT_c with respect to P_R for a substance using the RK state equation in terms of $v_{R,f}$, $v_{R,g}$, and T_R .

Solution

Consider the relation

$$h_{fg}/RT_c = (dP_{\text{ref}}^{\text{sat}}/dT_R) T_R (v_{R,g} - v_{R,f}). \tag{A}$$

During phase change $\int \{P(T,v)\} dv = P^{\text{sat}} (v_g - v_f)$, where $P(T,v)$ is given by any real gas state equation. Differentiating with temperature,

$$(dP^{\text{sat}}/dT) (v_g - v_f) - \int (\partial P/\partial T) dv = 0, \tag{B}$$

$$(dP_R^{\text{sat}}/dT_R) (v_{R,g} - v_{R,f}) - \int (\partial P_R/\partial T_R) dv_{R,f} = 0, \text{ and} \tag{C}$$

$$P_R = T_R/(v_{R,f} - 0.0864) - 0.4275/(T_R^2 v_{R,f} (v_{R,f} + 0.0864)). \tag{D}$$

Therefore, using Eq. (D) in Eq. (C) for $(\partial P_R/\partial T_R)$ and then applying Eq. (127) in reduced form

$$h_{fg}/(RT_c) = T_R \ln ((v_{R,f} - 0.0864)/(v_{R,f} - 0.0864)) + (2.4671/T_R^{3/2}) \ln ((v_{R,g} (v_{R,f} + 0.0864))/(v_{R,g} + 0.0864) v_{R,f}). \tag{E}$$

If v_g and v_f are known, h_{fg} can be determined.