1. Exercise E3.3 (p. 148). Also, as part (d), calculate $\Delta S$ for the process given in part (c).

**Answer**

(a) From the relationship given on p. 130, we write

$$C_{p,m} = C_{V,m} + T \left( \frac{\partial p}{\partial T} \right)_{V_m} \left( \frac{\partial V_m}{\partial T} \right)_{p}$$

$$= \frac{3}{2} R + T \left( \frac{\partial p}{\partial T} \right)_{V_m} \left( \frac{\partial V_m}{\partial T} \right)_{p}$$

From the given equation of state, $p = \left( RT - a \right)/V_m$ and, therefore,

$$\left( \frac{\partial p}{\partial T} \right)_{V_m} = \frac{R}{V_m}.$$  

Also from the equation of state, $V_m = \left( RT - a \right)/p$ and so

$$\left( \frac{\partial V_m}{\partial T} \right)_{V_m} = \frac{R}{p}.$$  

Substituting into Eq. (1) above, we get

$$C_{p,m} = \frac{3}{2} R + \frac{R^2 T}{p V_m}.$$  

Since the equation of state can be written as $p V_m + a = RT$, we obtain $p V_m = RT - a$. Therefore,

$$C_{p,m} = \frac{3}{2} R + \frac{R^2 T}{RT - a} = \frac{3}{2} R + \frac{R}{1 - a/(RT)}.$$  

(b) The thermodynamic equation of state for isothermal internal energy change is [Eq. (3.25)]:

$$\left( \frac{\partial U_m}{\partial V_m} \right)_T = T \left( \frac{\partial p}{\partial T} \right)_{V_m} - p.$$  

From the equation of state given,

$$\left( \frac{\partial U_m}{\partial V_m} \right)_T = \frac{RT}{V_m} - p = \frac{a}{V_m}.$$  

Therefore,

$$dU_m = \frac{a}{V_m} dV_m,$$

$$\Delta U_m = a \ln \left( \frac{V_m,2}{V_m,1} \right).$$  

(c) Let us first convert the parameter $a$ to more convenient units so that we can use $R = 0.083145$ L bar K$^{-1}$ mol$^{-1}$ (1 dm$^3$ = 1 L).

$$a = 0.304 \, \text{dm}^3 \, \text{MPa} \, \text{mol}^{-1} \times \left( \frac{1 \text{ bar}}{0.100 \, \text{MPa}} \right) = 3.04 \, \text{L bar} \, \text{mol}^{-1}.$$
From the equation of state, we calculate the molar volumes corresponding to the initial and final states:

\[
V_{m,1} = \frac{(RT - a)}{p_1} = \frac{(0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} - 3.04 \text{ L bar mol}^{-1})}{10.0 \text{ bar}} = 2.19 \text{ L mol}^{-1}
\]

and \( V_{m,2} = \frac{(RT - a)}{p_2} = 21.90 \text{ L mol}^{-1} \). Now,

\[
\begin{align*}
    w &= - \int_{V_{m,1}}^{V_{m,2}} p \, dV_m = -(RT - a) \int_{V_{m,1}}^{V_{m,2}} \frac{dV_m}{V_m} \\
    &= -(RT - a) \ln \left( \frac{V_{m,2}}{V_{m,1}} \right) \\
    &= -21.90 \text{ L bar mol}^{-1} \times \ln \left( \frac{21.90}{2.19} \right) \times \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}} \\
    &= -5042.7 \text{ J mol}^{-1}.
\end{align*}
\]

\[
\Delta U_m = 3.04 \text{ L bar mol}^{-1} \times \ln \left( \frac{21.90}{2.19} \right) \times \frac{8.3145 \text{ J K}^{-1} \text{ mol}^{-1}}{0.083145 \text{ L bar K}^{-1} \text{ mol}^{-1}} \\
= 699.98 \text{ J mol}^{-1}.
\]

The heat \( q \) is calculated using the first law:

\[
q = \Delta U_m - w = 5742.7 \text{ J mol}^{-1}.
\]

The enthalpy change is most conveniently calculated using the equation of state

\[
\left( \frac{\partial H_m}{\partial p} \right)_T = V_m - T \left( \frac{\partial V_m}{\partial T} \right)_p.
\]

From the equation of state, we get

\[
dH_m = \frac{RT - a}{p} \, dp - \frac{RT}{p} \, dp = -a \frac{dp}{p} \\
\Delta H_m = -a \ln \left( \frac{p_2}{p_1} \right) = 699.98 \text{ J mol}^{-1}.
\]

(d) Since the temperature is constant during the process, the entropy change can be calculated directly from the \( q \) calculated above, as

\[
\Delta S = \frac{q}{T} = \frac{5742.7 \text{ J mol}^{-1}}{300 \text{ K}} = 19.14 \text{ J K}^{-1} \text{ mol}^{-1}.
\]

2. Exercise E3.7 (p. 149).

**Answer**

We make use of the fundamental equation in calorimetry: heat lost (by the copper block) = –heat gained (by the water). We denote the masses of the copper block and water as \( m_{Cu} \) and \( m_w \), the respective
specific heats as $s_{Cu}$ and $s_w$, the initial and final temperatures of the copper block as $T_{iCu}$ and $T_{fCu}$, and that of water as $T_{iw}$ and $T_{fw}$. Then, we can write

$$m_{Cu}s_{Cu}(T_{fCu} - T_{iCu}) = -m_{w}s_{w}(T_{fw} - T_{iw}).$$

The only unknown is the final temperature of the water. Therefore, we solve for it:

\[50 \text{ g} \times 0.389 \text{ J K}^{-1} \text{ g}^{-1} \times (323 - 373) \text{ K} = -100 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times (T_{fw} - 298) \text{ K}.
\]

\[T_{fw} - 298 = 2.32 \text{ K} \quad T_{fw} = 300.32 \text{ K}.
\]

Now, the entropy changes for each component is calculated as

$$dS = \frac{dq_{rev}}{T} = msdT/T.$$

Therefore, for copper, we get

$$\Delta S_{Cu} = 50 \text{ g} \times 0.389 \text{ J K}^{-1} \text{ g}^{-1} \times \ln \left(\frac{323}{373}\right) = -2.80 \text{ J K}^{-1}.$$

$$\Delta S_{w} = 100 \text{ g} \times 4.18 \text{ J K}^{-1} \text{ g}^{-1} \times \ln \left(\frac{300.32}{298}\right) = 3.24 \text{ J K}^{-1}.$$

The net entropy change in the isolated system is, therefore, $\Delta S_{Cu} + \Delta S_{w} = 0.44 \text{ J K}^{-1}$. Since no heat transfer occurs between the system (isolated!) and the surroundings, this is also equal to $\Delta S_{univ}$, which confirms that the transfer of heat from a hot body to a cooler body is a spontaneous process.

3. A reversible Joule cycle consists of the following four steps: (i) isobaric expansion, (ii) adiabatic expansion, (iii) isobaric compression, (iv) adiabatic compression. Helium gas with the equation of state $pV_m = RT + Bp$ (where $B > 0$) is carried through a Joule cycle.

(a) Sketch the paths taken by the system in the following sets of coordinates: (i) $(p, V)$, (ii) $(U, V)$, and (iii) $(T, S)$. [For the sketches, only the general shapes and slopes of the lines are important, not the actual values of the variables at the end of each step.]

(b) If $B = 0.015$ L mol$^{-1}$, $T_h = 500$ K, and $T_c = 298$ K, calculate $w$, $q$, $\Delta U$, $\Delta H$, and $\Delta S$ for each step and for the total cycle.

(c) What is the efficiency of this engine? Can it be expressed as a function of the two temperatures only?

**Answer**

(a) See the last page for the sketches.

(b) The question does not provide the initial and final pressures (or volumes) and, therefore, numerical results cannot be obtained. However, let us derive the expressions required. The Joule cycle involves (i) an isobaric expansion (by constant pressure heating) from $(p_h, V_h, T_h)$ to $(p_h, V_1, T_1)$, (ii) adiabatic expansion to $(p_c, V_c, T_c)$, (iii) isobaric compression (by constant pressure cooling) to $(p_c, V_2, T_2)$, and finally (iv) adiabatic compression back to $(p_h, V_h, T_h)$. The following expressions are useful for our analysis:

For an isobaric process:

$$dq = dH = C_p dT.$$

$$dS = \frac{C_p}{T} dT.$$
\[ dU = C_V dT = dw + dq \]
\[ dw = -pdV = -p \left( \frac{R}{p} \right) dT = -RdT \]
\[ dq - dU = -dw = (C_p - C_v) dT \]

Therefore, \( C_p - C_v = R \).

Thus, assuming \( C_V,m = (3/2)R \), we can evaluate \( w, q, \Delta U, \Delta H, \) and \( \Delta S \) for the isobaric expansion and compression processes, provided the temperatures \( T_1 \) and \( T_2 \) are known.

For an adiabatic process:
\[ dq = 0 \]
\[ dS = 0. \]
\[ dU = C_V dT \]
\[ dH = C_p dT \]
\[ dw = dU \]

Once again, we can evaluate \( w, q, \Delta U, \Delta H, \) and \( \Delta S \) for the adiabatic expansion and compression processes, provided the temperatures \( T_1 \) and \( T_2 \) are known.

(c) The efficiency of a heat engine is defined as the ratio of the net work to the amount of heat absorbed in the expansion process:
\[
\epsilon = \frac{w_1 + w_2 + w_3 + w_4}{q_1 + q_2 - R(T_h - T_1) - C_V(T_c - T_1) - R(T_2 - T_c) - C_V(T_h - T_2)} - R(T_2 - T_c) - C_V(T_h - T_2) + 0.
\]

Without adequate information about the temperatures \( T_1 \) and \( T_2 \), it is not possible to verify if the efficiency can be expressed as a function of two temperatures only.

4. The model \( C_{p,m} = \alpha + \beta T + \gamma T^2 \) is applied to the data given in P4.3 (p. 199) in the range \( 14.98 \leq T \leq 50.20 \) K. The following parameters are found to be satisfactory for the range \( 14.98 \leq T \leq 50.20 \) K: \( \alpha = -18.6002, \beta = 1.95645, \) and \( \gamma = -0.0155003, \) in appropriate units.

(a) Find the parameter \( \alpha \) and the characteristic temperature \( T^* \) that will ensure the smooth continuation of this curve to absolute zero with the Debye equation, according to which \( C_{p,m} = aT^3 \). Plot the graph of \( aT^3 \) in the range \( 0 - T^* \) and \( \alpha + \beta T + \gamma T^2 \) from 14.98-50.20 K to verify that the function is smooth and continuous.

(b) Calculate \( H_{50.20 \, K} - H_{0 \, K} \) by integrating the Debye equation up to \( T^* \) and the expression given above for higher temperatures.

(c) Also, using the same assumption, calculate \( S_{50.20 \, K} - S_{0 \, K} \).

**Answer**

(a) In order to smoothly continue the \( C_{p,m} \) curve to 0 K, we impose conditions of continuity in the function as well as its derivative across the temperature \( T^* \) at which the match is made.
\[
aT^3 = \alpha + \beta T + \gamma T^2 \tag{2}
\]
\[
3aT^2 = \beta + 2\gamma T \tag{3}
\]

Dividing Eq. (2) by Eq. (3), we get
\[
\frac{T}{3} = \frac{\alpha + \beta T + \gamma T^2}{\beta + 2\gamma T}
\]
which rearranges to

$$\frac{1}{3} \gamma T^2 + \frac{2}{3} \beta T + \alpha = 0.$$  

Substituting the constants given, the roots are 15.1726 K and 237.268 K. Since the second root lies outside the domain of the data, the temperature $T^*$ is 15.1726 K. Substituting for $T^*$ in Eq. (3), we get $a = 0.0021518 \text{ J mol}^{-1} \text{ K}^{-4}$. The plot is given below.

(b) The enthalpy change $H_{50.20 \text{ K}} - H_{0 \text{ K}}$ is calculated as the integral of $C_{p,m}dT$ over the temperature range. We write

$$H_{50.20 \text{ K}} - H_{0 \text{ K}} = \int_0^{T^*} aT^3dT + \int_{T^*}^{50.20 \text{ K}} (\alpha + \beta T + \gamma T^2)dT$$

$$= \frac{a}{4}(15.17)^4 + \alpha (50.20 - 15.17) + \frac{\beta}{2}(50.20^2 - 15.17^2) + \frac{\gamma}{3}(50.20^3 - 15.17^3)$$

$$= 981.38 \text{ J mol}^{-1}$$  

(c) The absolute entropy at 50.20 K is evaluated as the integral of $(C_{p,m}/T)dT$ over the temperature range.

$$S_{50.20 \text{ K}} - S_{0 \text{ K}} = \int_0^{T^*} aT^2dT + \int_{T^*}^{50.20 \text{ K}} \left(\frac{\alpha}{T} + \beta + \gamma T\right)dT$$

$$= \frac{a}{3}(15.17)^3 + \alpha \ln\left(\frac{50.20}{15.17}\right) + \beta (50.20 - 15.17) + \frac{\gamma}{2}(50.20^2 - 15.17^2)$$

$$= 31.0325 \text{ J K}^{-1} \text{ mol}^{-1}$$

5