

Solution to problem 2.2

For the given equation of state, $P\left(\frac{V}{n} - b\right) = RT$, and by using the Maxwell relations, we find:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{\frac{V}{n} - b} = \frac{P}{T}.$$

For an isothermal change, we find:

$$\Delta S = \int \left(\frac{\partial S}{\partial V}\right)_T dV = \int \frac{P}{T} dV = \int \frac{R}{\frac{V}{n} - b} dV = nR \ln \left(\frac{V_{\text{final}} - nb}{V_{\text{initial}} - nb} \right) = nR \ln \left(\frac{P_{\text{initial}}}{P_{\text{final}}} \right)$$

$$\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P = - \frac{nR}{P}.$$

This gives the same expression for ΔS as above.

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P = 0.$$

Consequently,

$$\Delta U = 0.$$

For the following derivative, we use the definition of the enthalpy H : $U = H - PV$:

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T - \left(\frac{\partial(PV)}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T - V = -T \frac{nR}{P} - P \frac{\partial}{\partial P} \left[n \left(\frac{RT}{P} + b \right) \right]_T = 0.$$

Again we find that $\Delta U = 0$.

$$\left(\frac{\partial H}{\partial P}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_P = V - T \frac{nR}{P} = nb.$$

For an isothermal change, we find:

$$\Delta H = \int \left(\frac{\partial H}{\partial P}\right)_T dP = \int nb dP = nb \Delta P.$$

The changes in Gibbs energy (G) and Helmholtz energy (A) are found from the definitions of G and A and the results above:

$$\begin{aligned} \Delta G &= \Delta H - T \Delta S = nb \Delta P - nRT \ln \left(\frac{P_{\text{initial}}}{P_{\text{final}}} \right) \\ \Delta A &= \Delta U - T \Delta S = -nRT \ln \left(\frac{P_{\text{initial}}}{P_{\text{final}}} \right) \end{aligned}$$

Solution to problem 2.5

Since the entropy is constant, we may express the entropy as function of volume and temperature, differentiate, use some of the Maxwell relations, and require that the differential is equal to zero:

$$\begin{aligned}
S &= S(V, T) \\
dS &= \left(\frac{\partial S}{\partial V} \right)_T dV + \left(\frac{\partial S}{\partial T} \right)_V dT = \left(\frac{\partial P}{\partial T} \right)_V dV + \frac{C_V}{T} dT = 0
\end{aligned}$$

The exhaust temperature cannot depend on the amount of substance flowing through the turbine, and for convenience we choose one mole gas as basis in this calculation. With the Van der Waals equation, we find for one mole gas:

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

This gives the following differential equation between v and T at constant S :

$$\frac{dv}{v-b} = -\frac{c_V}{R} \frac{dT}{T}$$

This is the adiabatic equation of state for a Van der Waals gas. Integration gives:

$$\ln \left(\frac{v_{\text{final}} - b}{v_{\text{initial}} - b} \right) = -\frac{c_V}{R} \ln \left(\frac{T_{\text{final}}}{T_{\text{initial}}} \right)$$

where T_{final} and v_{final} are unknown. It is given that the final pressure is atmospheric, and by using the equation of state, we could express v_{final} by P_{final} . This is, however, a little cumbersome, but since the exhaust pressure is low, we try first by assuming that the exhaust gas is an ideal gas. This gives:

$$\begin{aligned}
\ln \left(\frac{T_{\text{final}}}{T_{\text{initial}}} \right) &= -\frac{R}{c_V} \ln \left(\frac{v_{\text{final}}^{\text{ideal gas}} - b}{v_{\text{initial}} - b} \right) \approx -\frac{R}{c_V} \ln \left(\frac{RT_{\text{final}}}{P_{\text{final}}(v_{\text{initial}} - b)} \right) \\
&= -\frac{R}{c_V} \ln T_{\text{final}} - \frac{R}{c_V} \ln \left(\frac{R}{P_{\text{final}}(v_{\text{initial}} - b)} \right)
\end{aligned}$$

where we have approximated $v_{\text{final}}^{\text{ideal gas}} - b \approx v_{\text{final}}^{\text{ideal gas}}$. Rearrangement gives

$$\begin{aligned}
\ln T_{\text{final}} + \frac{R}{c_V} \ln T_{\text{final}} &= \ln T_{\text{initial}} - \frac{R}{c_V} \ln \left(\frac{R}{P_{\text{final}}(v_{\text{initial}} - b)} \right) \\
\left(1 + \frac{R}{c_V} \right) \ln T_{\text{final}} &= \left(1 + \frac{R}{c_V} \right) \ln T_{\text{initial}} - \frac{R}{c_V} \ln \left(\frac{RT_{\text{initial}}}{P_{\text{final}}(v_{\text{initial}} - b)} \right) \\
\ln \left(\frac{T_{\text{final}}}{T_{\text{initial}}} \right) &= -\frac{R}{c_P} \ln \left(\frac{RT_{\text{initial}}}{P_{\text{final}}(v_{\text{initial}} - b)} \right)
\end{aligned}$$

where we have used this relation between c_P and c_V : $c_P = c_V + R$. With the given numbers, we find

$$\begin{aligned}
\ln \left(\frac{T_{\text{final}}}{(350 + 273) \text{ K}} \right) &= -\frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{33.5 \text{ J K}^{-1} \text{ mol}^{-1}} \ln \left(\frac{82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1} (350+273) \text{ K}}{1 \text{ atm} (600-45) \text{ cm}^3 \text{ mol}^{-1}} \right) = -1.123 \\
\underline{\underline{T_{\text{final}}}} &= 623 \text{ K exp}(-1.123) = \underline{\underline{203 \text{ K}}}
\end{aligned}$$

Checking the ideal-gas assumption:

$$\begin{aligned}
V_{\text{final}}^{\text{ideal gas}} &= \frac{RT_{\text{final}}}{P_{\text{final}}} = \frac{82.06 \text{ cm}^3 \text{ atm mol}^{-1} \text{ K}^{-1} 203 \text{ K}}{1 \text{ atm}} = 16700 \text{ cm}^3 \text{ mol}^{-1} \\
V_{\text{final}}^{\text{VdW}} &= 16400 \text{ cm}^3 \text{ mol}^{-1}
\end{aligned}$$

(The Van der Waals result was found by an iterative solution of the cubic equation in V at 203 K and 1 atm.)

If we want to improve the ideal-gas assumption, we may insert $V_{\text{final}}^{\text{VdW}} = 16400 \text{ cm}^3 \text{ mol}^{-1}$ into the equation above:

$$\ln\left(\frac{T_{\text{final}}}{T_{\text{initial}}}\right) = -\frac{R}{c_V} \ln\left(\frac{v_{\text{final}}^{\text{VdW}} - b}{v_{\text{initial}} - b}\right) = -\frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{25.2 \text{ J K}^{-1} \text{ mol}^{-1}} \ln\left(\frac{(16400 - 45) \text{ cm}^3 \text{ mol}^{-1}}{(600-45) \text{ cm}^3 \text{ mol}^{-1}}\right) = -1.117$$

$$\underline{\underline{T_{\text{final}}}} = 623 \text{ K} \exp(-1.117) = \underline{\underline{204 \text{ K}}}$$

Solution to problem 2.6

The virial expansion of the compression factor is

$$z = \frac{Pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v^2} + \dots$$

The compression factor for the Van der Waals gas is

$$z^{\text{VdW}} = \frac{v}{RT} \left(\frac{RT}{v-b} - \frac{a}{v^2} \right) = \frac{1}{1 - \frac{b}{v}} - \frac{a}{RT} \frac{1}{v}$$

We recognize the first term on the right-hand side as the sum of a geometric series:

$$\frac{1}{1 - \frac{b}{v}} = 1 + \frac{b}{v} + \left(\frac{b}{v}\right)^2 + \dots$$

Ordering the Van der Waals compression factor in increasing powers of $\frac{1}{v}$ gives

$$z^{\text{VdW}} = 1 + \left(b - \frac{a}{RT}\right) \frac{1}{v} + \left(\frac{b}{v}\right)^2 + \dots$$

and we conclude that

$$B = b - \frac{a}{RT}.$$

Solution to problem 2.7

We start by recovering one result from Problem 2.2:

$$\left(\frac{\partial U}{\partial P}\right)_T = -T \left(\frac{\partial V}{\partial T}\right)_P - P \left(\frac{\partial V}{\partial P}\right)_T.$$

From the given equation of state, the volume is

$$z = \frac{Pv}{RT} = 1 + \frac{BP}{RT} \therefore v = \frac{RT}{P} \left(1 + \frac{BP}{RT}\right) = \frac{RT}{P} + a - \frac{b}{T^2}$$

From this we find:

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_P &= \frac{R}{P} + \frac{2b}{T^3} \\ \left(\frac{\partial V}{\partial P}\right)_T &= -\frac{RT}{P^2} \\ \left(\frac{\partial U}{\partial P}\right)_T &= -T \left(\frac{R}{P} + \frac{2b}{T^3}\right) - P \left(-\frac{RT}{P^2}\right) = -\frac{2b}{T^2} \end{aligned}$$

Integration at the constant temperature τ then gives:

$$\underline{\underline{\Delta U(\tau)}} = \int_0^\pi \left(\frac{\partial U}{\partial P} \right)_{T=\tau} d\underline{\underline{P}} = -\underline{\underline{\frac{2b}{\tau^2} \pi}}$$