Segment $3 \rightarrow 1$

For this segment, $\Delta U_{3 \rightarrow 1} = 0$ and $\Delta H_{3 \rightarrow 1} = 0$ as noted earlier and $w_{3 \rightarrow 1} = -q_{3 \rightarrow 1}$. Because this is a reversible isothermal compression,

$$w_{3 \rightarrow 1} = -nRT \ln \frac{V_1}{V_3} = -2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 79.9 \text{ K}$$

$$\times \ln \frac{1.00 \times 10^{-3}\text{m}^3}{25.0 \times 10^{-3}\text{m}^3}$$

$$= 5.35 \text{ kJ}$$

The results for the individual segments and for the cycle in the indicated direction are given in the following table. If the cycle is traversed in the reverse fashion, the magnitudes of all quantities in the table remain the same, but all signs change.

Path	q (kJ)	w (kJ)	ΔU (kJ)	ΔH (kJ)
$1 \rightarrow 2$	139.4	−39.8	99.6	139.4
$2 \rightarrow 3$	−99.6	0	−99.6	−139.4
$3 \rightarrow 1$	−5.35	5.35	0	0
Cycle	34.5	−34.5	0	0

EXAMPLE PROBLEM 2.6

In this example, 2.50 mol of an ideal gas with $C_{V,m} = 12.47$ J mol^{-1} K^{-1} is expanded adiabatically against a constant external pressure of 1.00 bar. The initial temperature and pressure of the gas are 325 K and 2.50 bar, respectively. The final pressure is 1.25 bar. Calculate the final temperature, q, w, ΔU, and ΔH.

Solution

Because the process is adiabatic, $q = 0$, and $\Delta U = w$. Therefore,

$$\Delta U = nC_{v,m}(T_f - T_i) = -P_{external}(V_f - V_i)$$

Using the ideal gas law,

$$nC_{v,m}(T_f - T_i) = -nRP_{external}\left(\frac{T_f}{P_f} - \frac{T_i}{P_i}\right)$$

$$T_f\left(nC_{v,m} + \frac{nRP_{external}}{P_f}\right) = T_i\left(nC_{v,m} + \frac{nRP_{external}}{P_i}\right)$$

$$T_f = T_i \left(\frac{C_{v,m} + \dfrac{RP_{external}}{P_i}}{C_{v,m} + \dfrac{RP_{external}}{P_f}} \right)$$

$$= 325 \text{ K} \times \left(\frac{12.47 \text{ J mol}^{-1}\text{K}^{-1} + \dfrac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 1.00 \text{ bar}}{2.50 \text{ bar}}}{12.47 \text{ J mol}^{-1}\text{K}^{-1} + \dfrac{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 1.00 \text{ bar}}{1.25 \text{ bar}}} \right) = 268 \text{ K}$$

We calculate $\Delta U = w$ from

$$\Delta U = nC_{V,m}(T_f - T_i) = 2.5 \text{ mol} \times 12.47 \text{ J mol}^{-1}\text{K}^{-1} \times (268 \text{ K} - 325 \text{ K})$$

$$= -1.78 \text{ kJ}$$

Because the temperature falls in the expansion, the internal energy decreases:

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + nR(T_2 - T_1)$$

$$= -1.78 \times 10^3 \text{J} + 2.5 \text{ mol} \times 8.314 \text{ J mol}^{-1}\text{K}^{-1}$$

$$\times (268 \text{ K} - 325 \text{ K}) = -2.96 \text{ kJ}$$

2.10 THE REVERSIBLE ADIABATIC EXPANSION AND COMPRESSION OF AN IDEAL GAS

The adiabatic expansion and compression of gases is an important meteorological process. For example, the cooling of a cloud as it moves upward in the atmosphere can be modeled as an adiabatic process because the heat transfer between the cloud and the rest of the atmosphere is slow on the timescale of its upward motion.

Consider the adiabatic expansion of an ideal gas. Because $q = 0$, the first law takes the form

$$\Delta U = w \quad \text{or} \quad C_V\, dT = -P_{external}\, dV \tag{2.39}$$

For a reversible adiabatic process, $P = P_{external}$, and

$$C_V\, dT = -nRT \frac{dV}{V} \quad \text{or, equivalently,} \quad C_V \frac{dT}{T} = -nR \frac{dV}{V} \tag{2.40}$$

Integrating both sides of this equation between the initial and final states,

$$\int_{T_i}^{T_f} C_V \frac{dT}{T} = -nR \int_{V_i}^{V_f} \frac{dV}{V} \tag{2.41}$$

If C_V is constant over the temperature interval $T_f - T_i$, then

$$C_V \ln \frac{T_f}{T_i} = -nR \ln \frac{V_f}{V_i} \tag{2.42}$$

Because $C_P - C_V = nR$ for an ideal gas, Equation (2.42) can be written in the form

$$\ln\left(\frac{T_f}{T_i}\right) = -(\gamma - 1)\ln\left(\frac{V_f}{V_i}\right) \quad \text{or, equivalently,} \quad \frac{T_f}{T_i} = \left(\frac{V_f}{V_i}\right)^{1-\gamma} \tag{2.43}$$

where $\gamma = C_{P,m}/C_{V,m}$. Substituting $T_f/T_i = P_f V_f / P_i V_i$ in the previous equation, we obtain

$$P_i V_i^{\gamma} = P_f V_f^{\gamma} \tag{2.44}$$

for the adiabatic reversible expansion or compression of an ideal gas. Note that our derivation is only applicable to a reversible process, because we have assumed that $P = P_{external}$.

Reversible adiabatic compression of a gas leads to heating, and reversible adiabatic expansion leads to cooling. Adiabatic and isothermal expansion and compression are compared in Figure 2.13 in which two systems containing 1 mol of an ideal gas have the same volume at $P = 1$ atm. One system undergoes adiabatic compression or expansion, and the other undergoes isothermal compression or expansion. Under isothermal conditions, heat flows out of the system as it is compressed to $P > 1$ atm, and heat flows into the system as it is expanded to $P < 1$ atm to keep T constant. Because no heat flows into or out of the system under adiabatic conditions, its temperature increases in compression and decreases in expansion. Because $T > T_{isothermal}$ for a compression starting at 1 atm, $P_{adiabatic} > P_{isothermal}$ for a given volume of the gas. Similarly, in a reversible adiabatic expansion originating at 1 atm, $P_{adiabatic} < P_{isothermal}$ for a given volume of the gas.

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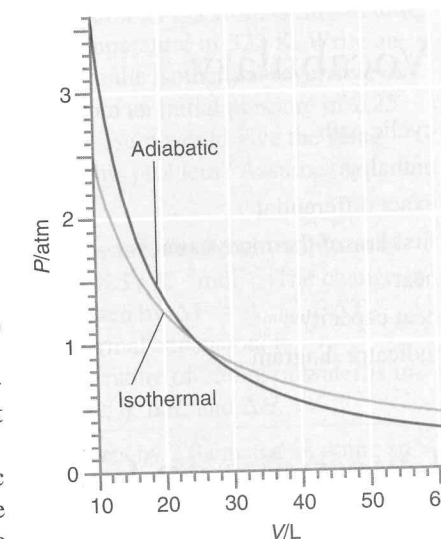**2.6** Reversible adiabatic heating and cooling

FIGURE 2.13

Two systems containing 1 mol of N_2 have the same P and V values at 1 atm. The red curve corresponds to reversible expansion and compression about $P = 1$ atm under adiabatic conditions. The yellow curve corresponds to reversible expansion and compression about $P = 1$ atm under isothermal conditions.

EXAMPLE PROBLEM 2.7

A cloud mass moving across the ocean at an altitude of 2000. m encounters a coastal mountain range. As it rises to a height of 3500. m to pass over the mountains, it undergoes an adiabatic expansion. The pressure at 2000. and 3500. m is 0.802 and 0.602 atm, respectively. If the initial temperature of the cloud mass is 288 K, what is the cloud temperature as it passes over the mountains? Assume that $C_{P,m}$ for air is 28.86 J K^{-1} mol^{-1} and that air obeys the ideal gas law. If you are on the mountain, should you expect rain or snow?