CHAPTER 19

The First Law of Thermodynamics

PROBLEMS AND SOLUTIONS

19–1. Suppose that a 10-kg mass of iron at 20°C is dropped from a height of 100 meters. What is the kinetic energy of the mass just before it hits the ground? What is its speed? What would be the final temperature of the mass if all its kinetic energy at impact is transformed into internal energy? Take the molar heat capacity of iron to be $\overline{C}_P = 25.1\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ and the gravitational acceleration constant to be $9.80\ \mathrm{m\cdot s^{-2}}$.

Just before the mass hits the ground, all of the potential energy that the mass originally had will be converted into kinetic energy. So

$$\mathrm{PE} = mgh = (10\ \mathrm{kg})(9.80\ \mathrm{m\cdot s^{-2}})(100\ \mathrm{m}) = 9.8\ \mathrm{kJ} = \mathrm{KE}$$

Since kinetic energy can be expressed as $mv^2/2$, the speed of the mass just before hitting the ground is

$$v_f = \left(\frac{2\mathrm{KE}}{m}\right)^{1/2} = \left[\frac{2(9.8\ \mathrm{kJ})}{10\ \mathrm{kg}}\right]^{1/2} = 44\ \mathrm{m\cdot s^{-1}}$$

For a solid, the difference between $\overline{C}_V$ and $\overline{C}_P$ is small, so we can write $\Delta U = n\overline{C}_P\Delta T$ (Equation 19.39). Then

$$\Delta T = \frac{9.8\ \mathrm{kJ}}{\left(\dfrac{1\times 10^4\ \mathrm{g}}{55.85\ \mathrm{g\cdot mol^{-1}}}\right)(25.1\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}})} = 2.2\ \mathrm{K}$$

The final temperature of the iron mass is then 22.2°C.

19–2. Consider an ideal gas that occupies $2.50\ \mathrm{dm^3}$ at a pressure of 3.00 bar. If the gas is compressed isothermally at a constant external pressure, P_{ext}, so that the final volume is $0.500\ \mathrm{dm^3}$, calculate the smallest value P_{ext} can have. Calculate the work involved using this value of P_{ext}.

Since the gas is ideal, we can write

$$P_2 = \frac{P_1V_1}{V_2} = \frac{(3.00\ \mathrm{bar})(2.50\ \mathrm{dm^3})}{0.500\ \mathrm{dm^3}} = 15.0\ \mathrm{bar}$$

The smallest possible value of P_{ext} is P_2. The work done in this case is (Equation 19.1)

$$w = -P_{\mathrm{ext}}\Delta V = (-15.0\ \mathrm{bar})(-2.0\ \mathrm{dm^3})\left(\frac{8.3145\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}}{0.083145\ \mathrm{bar\cdot dm^3\cdot mol^{-1}\cdot K^{-1}}}\right) = 3000\ \mathrm{J}$$

19–3. A one-mole sample of $CO_2(g)$ occupies $2.00\ \text{dm}^3$ at a temperature of 300 K. If the gas is compressed isothermally at a constant external pressure, P_{ext}, so that the final volume is $0.750\ \text{dm}^3$, calculate the smallest value P_{ext} can have, assuming that $CO_2(g)$ satisfies the van der Waals equation of state under these conditions. Calculate the work involved using this value of P_{ext}.

The smallest value P_{ext} can have is P_2, where P_2 is the final pressure of the gas. We can use the van der Waals equation (Equation 16.5) and the constants given in Table 16.3 to find P_2:

$$\begin{aligned} P_2 &= \frac{RT_2}{\overline{V}_2 - b} - \frac{a}{\overline{V}_2^2} \\ &= \frac{(0.083145\ \text{dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300\ \text{K})}{0.750\ \text{dm}^3\cdot\text{mol}^{-1} - 0.042816\ \text{dm}^3\cdot\text{mol}^{-1}} - \frac{3.6551\ \text{dm}^6\cdot\text{bar}\cdot\text{mol}^{-2}}{(0.750\ \text{dm}^3\cdot\text{mol}^{-1})^2} \\ &= 28.8\ \text{bar} \end{aligned}$$

The work involved is (Equation 19.1)

$$w = -P\Delta V = -(28.8 \times 10^5\ \text{Pa})(-1.25 \times 10^{-3}\ \text{m}^3) = 3.60\ \text{kJ}$$

19–4. Calculate the work involved when one mole of an ideal gas is compressed reversibly from 1.00 bar to 5.00 bar at a constant temperature of 300 K.

Using the ideal gas equation, we find that

$$V_1 = \frac{nRT}{P_1} \quad \text{and} \quad V_2 = \frac{nRT}{P_2}$$

We can therefore write $V_2/V_1 = P_1/P_2$. Now we substitute into Equation 19.2 to find

$$\begin{aligned} w &= -\int P_{\text{ext}}dV = -\int \frac{nRT}{V}dV \\ &= -nRT \ln\left(\frac{V_2}{V_1}\right) = -nRT \ln\left(\frac{P_1}{P_2}\right) \\ &= (-1\ \text{mol})(8.315\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300\ \text{K}) \ln 0.2 = 4.01\ \text{kJ} \end{aligned}$$

19–5. Calculate the work involved when one mole of an ideal gas is expanded reversibly from $20.0\ \text{dm}^3$ to $40.0\ \text{dm}^3$ at a constant temperature of 300 K.

We can integrate Equation 19.2 to find the work involved:

$$\begin{aligned} w &= -nRT \ln\left(\frac{V_2}{V_1}\right) \\ &= (-1\ \text{mol})(8.315\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300\ \text{K}) \ln 2 = -1.73\ \text{kJ} \end{aligned}$$

19–6. Calculate the minimum amount of work required to compress 5.00 moles of an ideal gas isothermally at 300 K from a volume of $100\ \text{dm}^3$ to $40.0\ \text{dm}^3$.

We note that the minimum amount of work required is the amount of work needed to reversibly compress the gas, so we can write Equation 19.2 as

$$\begin{aligned} w_{\text{min}} = w_{\text{rev}} &= -nRT \ln\left(\frac{V_2}{V_1}\right) \\ &= (-5.00\ \text{mol})(8.315\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(300\ \text{K}) \ln 0.400 = 11.4\ \text{kJ} \end{aligned}$$

19–7. Consider an ideal gas that occupies 2.25 L at 1.33 bar. Calculate the work required to compress the gas isothermally to a volume of 1.50 L at a constant pressure of 2.00 bar followed by another isothermal compression to 0.800 L at a constant pressure of 3.75 bar (Figure 19.4). Compare the result with the work of compressing the gas isothermally and reversibly from 2.25 L to 0.800 L.

We can use Equation 19.2 to describe the work involved with the compressions under different circumstances.

a. Two-step process, each step at constant external pressure

  i. From (2.25 L, 1.33 bar) to (1.50 L, 2.00 bar),

$$w = -\int P_{\text{ext}}dV = (-2.00\ \text{bar})(1.50\ \text{L} - 2.25\ \text{L})(100\ \text{J}\cdot\text{bar}^{-1}\cdot\text{dm}^{-3}) = 150\ \text{J}$$

  ii. From (1.50 L, 2.00 bar) to (0.800 L, 2.50 bar),

$$w = -\int P_{\text{ext}}dV = (-3.75\ \text{bar})(0.800\ \text{L} - 1.50\ \text{L})(100\ \text{J}\cdot\text{bar}^{-1}\cdot\text{dm}^{-3}) = 263\ \text{J}$$

The total work involved in the two-step process is +413 J.

b. Reversible process

Because the gas is ideal, $PV = nRT$. We can then write

$$PV = (2.25\ \text{L})(1.33\ \text{bar})(100\ \text{J}\cdot\text{bar}^{-1}\cdot\text{dm}^{-3}) = 299.25\ \text{J} = nRT$$

and use Equation 19.2 to find w:

$$w = -\int PdV = -nRT \ln\left(\frac{V_2}{V_1}\right) = -(299.25\ \text{J}) \ln\left(\frac{0.800}{2.25}\right) = 309\ \text{J}$$

The total work involved in the reversible process is +309 J. Note that the work involved in the reversible process is less than the work involved at constant external pressure, as is expected.

19–8. Show that for an isothermal reversible expansion from a molar volume $\overline{V}_1$ to a final molar volume $\overline{V}_2$, the work is given by

$$w = -RT \ln\left(\frac{\overline{V}_2 - B}{\overline{V}_1 - B}\right) - \frac{A}{BT^{1/2}} \ln\left[\frac{(\overline{V}_2 + B)\overline{V}_1}{(\overline{V}_1 + B)\overline{V}_2}\right]$$

for the Redlich-Kwong equation.

For the Redlich-Kwong equation,

$$P = \frac{RT}{\overline{V} - B} - \frac{A}{T^{1/2}\overline{V}(\overline{V} + B)} \tag{16.7}$$

We can then use Equation 19.2 to find w.

$$
\begin{aligned}
w &= \int_{\overline{V}_1}^{\overline{V}_2} \left[-\frac{RT}{\overline{V}-B} + \frac{A}{T^{1/2}\overline{V}(\overline{V}+B)} \right] d\overline{V} \\
&= -RT \ln\left(\frac{\overline{V}_2 - B}{\overline{V}_1 - B}\right) - \frac{A}{T^{1/2}B}\left[\ln\left(\frac{\overline{V}_1}{\overline{V}_1+B}\right) - \ln\left(\frac{\overline{V}_2}{\overline{V}_2+B}\right)\right] \\
&= -RT \ln\left(\frac{\overline{V}_2 - B}{\overline{V}_1 - B}\right) - \frac{A}{BT^{1/2}} \ln\left[\frac{(\overline{V}_2+B)\overline{V}_1}{(\overline{V}_1+B)\overline{V}_2}\right]
\end{aligned}
$$

19–9. Use the result of Problem 19–8 to calculate the work involved in the isothermal reversible expansion of one mole of $CH_4(g)$ from a volume of 1.00 $dm^3 \cdot mol^{-1}$ to 5.00 $dm^3 \cdot mol^{-1}$ at 300 K. (See Table 16.4 for the values of A and B.)

From Table 16.4, $A = 32.205\ dm^6 \cdot bar \cdot mol^{-2} \cdot K^{1/2}$ and $B = 0.029850\ dm^3 \cdot mol^{-1}$. Then, using the equation for w from the previous problem,

$$
\begin{aligned}
w &= -RT \ln\left(\frac{\overline{V}_2 - B}{\overline{V}_1 - B}\right) - \frac{A}{BT^{1/2}} \ln\left[\frac{(\overline{V}_2+B)\overline{V}_1}{(\overline{V}_1+B)\overline{V}_2}\right] \\
&= -RT \ln 5.1231 - \frac{A}{BT^{1/2}} \ln 0.97681 \\
&= -(39.3\ dm^3 \cdot bar \cdot mol^{-1})(100\ J \cdot bar^{-1} \cdot dm^{-3}) = -3.93\ kJ \cdot mol^{-1}
\end{aligned}
$$

19–10. Repeat the calculation in Problem 19–9 for a van der Waals gas.

From Equation 16.5,

$$
P = \frac{RT}{\overline{V}-b} - \frac{a}{\overline{V}^2}
$$

Then (Equation 19.2)

$$
\begin{aligned}
w &= \int -P d\overline{V} = \int_{\overline{V}_1}^{\overline{V}_2} \left(-\frac{RT}{\overline{V} - b} + \frac{a}{\overline{V}^2} \right) d\overline{V} \\
&= -RT \ln \frac{\overline{V}_2 - b}{\overline{V}_1 - b} + \frac{a(\overline{V}_2 - \overline{V}_1)}{\overline{V}_2 \overline{V}_1}
\end{aligned}
$$

From Table 16.3, for methane $a = 2.3026\ dm^6 \cdot bar \cdot mol^{-2}$ and $b = 0.043067\ dm^3 \cdot mol^{-1}$. Then

$$
w = -39.18\ dm^3 \cdot bar \cdot mol^{-1} = -3.92\ kJ \cdot mol^{-1}
$$

19–11. Derive an expression for the reversible isothermal work of an expansion of a gas that obeys the Peng-Robinson equation of state.

The Peng-Robinson equation of state is

$$
P = \frac{RT}{\overline{V}-\beta} - \frac{\alpha}{\overline{V}(\overline{V}+\beta) + \beta(\overline{V}-\beta)} \tag{16.7}
$$

Substituting into Equation 19.2 gives

$$
\begin{aligned}
w_{rev} &= -\int_1^2 d\overline{V} \left[\frac{RT}{\overline{V}-\beta} - \frac{\alpha}{\overline{V}(\overline{V}+\beta) + \beta(\overline{V}-\beta)} \right] \\
&= -RT \ln\left(\frac{\overline{V}_2 - \beta}{\overline{V}_1 - \beta}\right) - \alpha \int_1^2 d\overline{V} \frac{1}{\overline{V}^2 + 2\overline{V}\beta - \beta^2} \\
&= -RT \ln\left(\frac{\overline{V}_2 - \beta}{\overline{V}_1 - \beta}\right) - \frac{\alpha}{(8\beta^2)^{1/2}} \ln \left. \frac{2\overline{V} + 2\beta - (8\beta^2)^{1/2}}{2\overline{V} + 2\beta + (8\beta^2)^{1/2}} \right|_{\overline{V}_1}^{\overline{V}_2} \\
&= -RT \ln\left(\frac{\overline{V}_2 - \beta}{\overline{V}_1 - \beta}\right) - \frac{\alpha}{(8\beta^2)^{1/2}} \ln \frac{(\overline{V}_2 - 0.4142\beta)(\overline{V}_1 + 2.414\beta)}{(\overline{V}_2 + 2.414\beta)(\overline{V}_1 - 0.4142\beta)}
\end{aligned}
$$

19–12. One mole of a monatomic ideal gas initially at a pressure of 2.00 bar and a temperature of 273 K is taken to a final pressure of 4.00 bar by the reversible path defined by $P/V =$ constant. Calculate the values of ΔU, ΔH, q, and w for this process. Take $\overline{C}_V$ to be equal to 12.5 $J \cdot mol^{-1} \cdot K^{-1}$.

Let $P/\overline{V} = C$. Then, since the gas is ideal, we can write

$$
\begin{aligned}
T_1 &= \frac{P_1 V_1}{R} = \frac{P_1^2}{CR} \\
C &= \frac{4.00\ bar^2}{(273\ K)R}
\end{aligned}
$$

Since $P/\overline{V}$ is constant throughout the process, we can also write

$$
T_2 = \frac{P_2 V_2}{R} = \frac{P_2^2}{CR} = \frac{16\ bar^2}{CR} = \frac{(16.0\ bar^2)(273\ K)R}{(4.00\ bar^2)R} = 1092\ K
$$

Because the $\overline{C}_V$ we are given is temperature-independent, we can write (by the definition of molar heat capacity)

$$
\begin{aligned}
\Delta U &= n \int_{T_1}^{T_2} \overline{C}_V dT \\
&= (1\ mol)(12.5\ J \cdot mol^{-1} \cdot K^{-1})(1092\ K - 273\ K) = 10.2\ kJ
\end{aligned}
$$

Now we can use Equation 19.2 to calculate w, using the equality $P/\overline{V} = C$. Note that $\overline{V} = V$, since we are taking one mole of the gas.

$$
\begin{aligned}
w &= -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} CV dV = -\frac{C}{2}(V_2^2 - V_1^2) \\
&= -\frac{C}{2}\left(\frac{P_2^2}{C^2} - \frac{P_1^2}{C^2}\right) = -\frac{16.0\ bar^2 - 4.00\ bar^2}{2C} \\
&= -\frac{(12.0\ bar^2)(1\ mol)(273\ K)(0.083145\ bar \cdot dm^3 \cdot mol^{-1} \cdot K^{-1})}{2(4.00\ bar^2)} \\
&= -3.40\ kJ
\end{aligned}
$$

Finally, we can find q from Equation 19.10 and ΔH from Equation 19.35, letting $PV = nRT$.

$$
\begin{aligned}
q &= \Delta U - w = 13.6\ \text{kJ} \\
\Delta H &= \Delta U + nR\Delta T = 10.2\ \text{kJ} + (1\ \text{mol})(8.3145\ \text{J}\cdot\text{mol}^{-1}\text{K}^{-1})(819\ \text{K}) \\
&= 17.0\ \text{kJ}
\end{aligned}
$$

19–13. The isothermal compressibility of a substance is given by

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{1}$$

For an ideal gas, $\beta = 1/P$, but for a liquid, β is fairly constant over a moderate pressure range. If β is constant, show that

$$\frac{V}{V_0} = e^{-\beta(P-P_0)} \tag{2}$$

where V_0 is the volume at a pressure P_0. Use this result to show that the reversible isothermal work of compressing a liquid from a volume V_0 (at a pressure P_0) to a volume V (at a pressure P) is given by

$$
\begin{aligned}
w &= -P_0(V - V_0) + \beta^{-1}V_0\left(\frac{V}{V_0}\ln\frac{V}{V_0} - \frac{V}{V_0} + 1\right) \\
&= -P_0V_0[e^{-\beta(P-P_0)} - 1] + \beta^{-1}V_0\{1 - [1 + \beta(P - P_0)]e^{-\beta(P-P_0)}\}
\end{aligned}
\tag{3}
$$

(You need to use the fact that $\int \ln x dx = x \ln x - x$.) The fact that liquids are incompressible is reflected by β being small, so that $\beta(P - P_0) \ll 1$ for moderate pressures. Show that

$$
\begin{aligned}
w &= \beta P_0V_0(P - P_0) + \frac{\beta V_0(P - P_0)^2}{2} + O(\beta^2) \\
&= \frac{\beta V_0}{2}(P^2 - P_0^2) + O(\beta^2)
\end{aligned}
\tag{4}
$$

Calculate the work required to compress one mole of toluene reversibly and isothermally from 10 bar to 100 bar at 20°C. Take the value of β to be $8.95 \times 10^{-5}\ \text{bar}^{-1}$ and the molar volume to be $0.106\ \text{L}\cdot\text{mol}^{-1}$ at 20°C.

We begin with Equation 1 and integrate both sides, letting β be constant with respect to pressure.

$$
\begin{aligned}
\int -\beta dP &= \int V^{-1}dV \\
-\beta(P - P_0) &= \ln\left(\frac{V}{V_0}\right) \\
\frac{V}{V_0} &= e^{-\beta(P-P_0)} \\
P &= -\beta^{-1}\ln\left(\frac{V}{V_0}\right) + P_0
\end{aligned}
$$

Now we wish to find the reversible isothermal work of compressing a liquid from (P_0, V_0) to (P, V). We know that $\delta w = -PdV$ (Equation 19.2), so we use the expression we found above for P to write

$$
\begin{aligned}
\delta w &= -\left[-\beta^{-1}\ln\left(\frac{V}{V_0}\right) + P_0\right]dV \\
&= -P_0dV + \beta^{-1}\ln\left(\frac{V}{V_0}\right)dV
\end{aligned}
$$

Integrating both sides of this equation gives

$$
\begin{aligned}
w &= -P_0(V - V_0) + \beta^{-1}\int \ln V dV - \beta^{-1}\int \ln V_0 dV \\
&= -P_0(V - V_0) + \beta^{-1}\left[V\ln V - V - (V_0\ln V_0 - V_0)\right] - \beta^{-1}(V - V_0)\ln V_0 \\
&= -P_0(V - V_0) + \beta^{-1}\left(V\ln V - V - V_0\ln V_0 + V_0 - V\ln V_0 + V_0\ln V_0\right) \\
&= -P_0(V - V_0) + \beta^{-1}V_0\left(\frac{V}{V_0}\ln\frac{V}{V_0} - \frac{V}{V_0} + 1\right)
\end{aligned}
$$

Substitution for V then yields the result

$$w = -P_0V_0\left[e^{-\beta(P-P_0)} - 1\right] + \beta^{-1}V_0\left\{1 - \left[1 + \beta(P - P_0)\right]e^{-\beta(P-P_0)}\right\}$$

which is Equation 3 in the text of the problem. Now let $x = -\beta(P - P_0)$. Because $-\beta(P - P_0) \ll 1$, $x \ll 1$. We can now write Equation 3 as

$$
\begin{aligned}
w &= -P_0V_0(e^x - 1) + \beta^{-1}V_0\left\{1 - \left[1 + \beta(P - P_0)\right]e^x\right\} \\
&= -P_0V_0(e^x - 1) + \beta^{-1}V_0 - \beta^{-1}V_0e^x - V_0(P - P_0)e^x
\end{aligned}
$$

Now, recall from MathChapter I that if x is small, we can write e^x as $1 + x + x^2/2 + O(x^3)$ (Equation I.2). Notice that to find w to $O(\beta^2)$, we must expand e^x to $O(x^3)$, since one of the above terms multiplies e^x by β^{-1}. Expanding the above equation gives

$$
\begin{aligned}
w &= -P_0V_0\left[x + O(x^2)\right] + \beta^{-1}V_0 - \beta^{-1}V_0\left[1 + x + \frac{x^2}{2} + O(x^3)\right] - V_0(P - P_0)\left[1 + x + O(x^2)\right] \\
&= \beta P_0V_0(P_0 - P_0) + V_0(P - P_0) - \frac{\beta V_0(P - P_0)^2}{2} - V_0(P - P_0) + \beta V_0(P - P_0)^2 + O(\beta^2) \\
&= \beta P_0V_0(P - P_0) + \frac{\beta V_0(P - P_0)^2}{2} + O(\beta^2) \\
&= \frac{\beta V_0}{2}(P^2 - P_0^2) + O(\beta^2)
\end{aligned}
$$

Now, for one mole of toluene [to $O(\beta^2)$], we use the parameters given in the problem to find

$$w = \frac{(8.95 \times 10^{-5}\ \text{bar}^{-1})(0.106\ \text{mol}\cdot\text{L}^{-1})^{-1}}{2}\left[(100\ \text{bar})^2 - (10\ \text{bar})^2\right] = 418\ \text{J}$$

19–14. In the previous problem, you derived an expression for the reversible, isothermal work done when a liquid is compressed. Given that β is typically $O(10^{-4})\ \text{bar}^{-1}$, show that $V/V_0 \approx 1$ for pressures up to about 100 bar. This result, of course, reflects the fact that liquids are not very compressible. We can exploit this result by substituting $dV = -\beta VdP$ from the defining equation of β into $w = -\int PdV$ and then treating V as a constant. Show that this approximation gives Equation 4 of Problem 19–13.

We are given that $\beta \sim O(10^{-4}\ \text{bar}^{-1})$, and the largest pressure differential that can occur under the given conditions is on the order of $O(10^2\ \text{bar})$. Then, using Equation 2 of Problem 19.13, we find

$$\frac{V}{V_0} = e^{-\beta(P-P_0)} = e^{-O(10^{-2})} \approx 0.990$$

Therefore, $V/V_0 \approx 1$ for pressures ranging from 1 to 100 bar. Now $dV = -\beta V dP$, so

$$w = -\int P dV = \beta V_0 \int P dP = \frac{\beta V_0}{2}(P^2 - P_0^2)$$

as in Equation 4 of Problem 19.13.

19–15. Show that

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/\overline{C}_V}$$

for a reversible adiabatic expansion of an ideal gas.

For an adiabatic expansion $\delta q = 0$, so $dU = \delta w$. By definition, $dU = n\overline{C}_V dT$, and for an ideal gas (Equation 19.2)

$$\delta w = -PdV = -nRTV^{-1}dV$$

We can then write

$$\begin{aligned} n\overline{C}_V dT &= -nRTV^{-1}dV \\ \int \frac{\overline{C}_V}{T} dT &= \int -\frac{R}{V} dV \\ \overline{C}_V \ln\left(\frac{T_2}{T_1}\right) &= -R\ln\left(\frac{V_2}{V_1}\right) \\ \ln\left(\frac{T_2}{T_1}\right)^{\overline{C}_V} &= \ln\left(\frac{V_2}{V_1}\right)^{-R} \end{aligned}$$

Finally, exponentiating both sides gives

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_1}\right)^{-R/\overline{C}_V} = \left(\frac{V_1}{V_2}\right)^{R/\overline{C}_V}$$

19–16. Show that

$$\left(\frac{T_2}{T_1}\right)^{3/2} = \frac{\overline{V}_1 - b}{\overline{V}_2 - b}$$

for a reversible, adiabatic expansion of a monatomic gas that obeys the equation of state $P(\overline{V} - b) = RT$. Extend this result to the case of a diatomic gas.

For an adiabatic expansion $\delta q = 0$, so $dU = \delta w$. By definition, $dU = n\overline{C}_V dT$, and for this gas Equation 19.2 becomes

$$\delta w = -PdV = -n\frac{RT}{\overline{V} - b}d\overline{V}$$

Setting dU and δw equal to one another gives

$$\begin{aligned} n\overline{C}_V dT &= -\frac{nRT}{\overline{V} - b} d\overline{V} \\ \int \frac{\overline{C}_V}{T} dT &= \int -\frac{R}{\overline{V} - b} d\overline{V} \\ \overline{C}_V \ln\left(\frac{T_2}{T_1}\right) &= -R\ln\left(\frac{\overline{V}_2 - b}{\overline{V}_1 - b}\right) \\ \left(\frac{T_2}{T_1}\right)^{\overline{C}_V/R} &= \frac{\overline{V}_1 - b}{\overline{V}_2 - b} \end{aligned}$$

For a monatomic gas, $\overline{C}_V = 3R/2$, and for a diatomic gas, $\overline{C}_V = 5R/2$. Thus

$$\left(\frac{T_2}{T_1}\right)^{3/2} = \frac{\overline{V}_1 - b}{\overline{V}_2 - b}$$

for a monatomic gas, and

$$\left(\frac{T_2}{T_1}\right)^{5/2} = \frac{\overline{V}_1 - b}{\overline{V}_2 - b}$$

for a diatomic gas.

19–17. Show that

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P}$$

for a reversible adiabatic expansion of an ideal gas.

For an ideal gas, $\overline{C}_V + R = \overline{C}_P$ and

$$\frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2}$$

From Problem 19–15, we can write

$$\begin{aligned} \left(\frac{T_2}{T_1}\right)^{\overline{C}_V/R} &= \left(\frac{V_1}{V_2}\right) \\ \frac{P_1}{P_2}\left(\frac{T_2}{T_1}\right)^{\overline{C}_V/R} &= \frac{P_1 V_1}{P_2 V_2} = \frac{T_1}{T_2} \end{aligned}$$

Then

$$\begin{aligned} \frac{P_1}{P_2} &= \left(\frac{T_1}{T_2}\right)^{(\overline{C}_V + R)/R} = \left(\frac{T_1}{T_2}\right)^{\overline{C}_P/R} \\ \left(\frac{P_1}{P_2}\right)^{R/\overline{C}_P} &= \frac{T_1}{T_2} \end{aligned}$$

and, finally,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P}$$

19–18. Show that

$$P_1 V_1^{(\overline{C}_V+R)/\overline{C}_V} = P_2 V_2^{(\overline{C}_V+R)/\overline{C}_V}$$

for an adiabatic expansion of an ideal gas. Show that this formula reduces to Equation 19.23 for a monatomic gas.

For an ideal gas,

$$\frac{P_1V_1}{P_2V_2} = \frac{T_1}{T_2}$$

We can substitute this expression into the equation from Problem 19–15 to write

$$\frac{P_1V_1}{P_2V_2} = \left(\frac{V_1}{V_2}\right)^{R/\overline{C}_V}$$

Taking the reciprocal gives

$$\frac{P_1V_1}{P_2V_2} = \left(\frac{V_2}{V_1}\right)^{R/\overline{C}_V}$$

and rearranging yields

$$P_1 V_1^{\left(1+R/\overline{C}_V\right)} = P_2 V_2^{\left(1+R\overline{C}_V\right)}$$

For a monatomic ideal gas, $\overline{C}_V = \frac{3}{2}R$, so

$$P_1 V_1^{5/3} = P_2 V_2^{5/3} \tag{19.23}$$

19–19. Calculate the work involved when one mole of a monatomic ideal gas at 298 K expands reversibly and adiabatically from a pressure of 10.00 bar to a pressure of 5.00 bar.

Because this process is adiabatic, $\delta q = 0$. This means that

$$\delta w = dU = n\overline{C}_V dT$$

where $\overline{C}_V$ is temperature-independent (since the gas is ideal). We can use the equation from Problem 19–17 to write

$$T_2 = T_1\left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P}$$

For an ideal gas, $\overline{C}_P = 5R/2$, so

$$T_2 = (298\text{ K})\left(\frac{5.00\text{ bar}}{10.00\text{ bar}}\right)^{2/5} = 226\text{ K}$$

Substituting into the expression for δw ($\overline{C}_V = 3R/2$) gives

$$w = n\overline{C}_V\int_{T_1}^{T_2} dT = \frac{3}{2}(8.314\text{ J}\cdot\text{K}^{-1})(226\text{ K} - 298\text{ K}) = -900\text{ J}$$

19–20. A quantity of $N_2(g)$ at 298 K is compressed reversibly and adiabatically from a volume of 20.0 dm^3 to 5.00 dm^3. Assuming ideal behavior, calculate the final temperature of the $N_2(g)$. Take $\overline{C}_V = 5R/2$.

Using $\overline{C}_V$ given in the problem, we find that (by definition)

$$dU = n\overline{C}_V dT = \frac{5}{2}nR\,dT$$

and Equation 19.2 gives δw as

$$\delta w = -P\,dV = -\frac{nRT}{V}dV$$

For a reversible adiabatic compression, $\delta q = 0$, and so $dU = dw$. Then

$$\begin{aligned}
\frac{5}{2}nR\,dT &= -\frac{nRT}{V}dV \\
\frac{5}{2}\frac{dT}{T} &= -\frac{dV}{V} \\
\frac{5}{2}\ln\frac{T_2}{T_1} &= -\ln\frac{V_2}{V_1} \\
\ln\frac{T_2}{T_1} &= -\frac{2}{5}\ln\frac{5.00\text{ dm}^3}{20.0\text{ dm}^3} \\
T_2 &= 519\text{ K}
\end{aligned}$$

19–21. A quantity of $CH_4(g)$ at 298 K is compressed reversibly and adiabatically from 50.0 bar to 200 bar. Assuming ideal behavior, calculate the final temperature of the $CH_4(g)$. Take $\overline{C}_V = 3R$.

From Problem 19–17, we have

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P}$$

Assuming ideal behavior, $\overline{C}_P = R + \overline{C}_V = 4R$. Then

$$T_2 = \left(\frac{200\text{ bar}}{50.0\text{ bar}}\right)^{1/4}(298\text{ K}) = 421\text{ K}$$

19–22. One mole of ethane at 25°C and one atm is heated to 1200°C at constant pressure. Assuming ideal behavior, calculate the values of w, q, ΔU, and ΔH given that the molar heat capacity of ethane is given by

$$\begin{aligned}
\overline{C}_P/R = {} & 0.06436 + (2.137\times10^{-2}\text{ K}^{-1})T \\
& - (8.263\times10^{-6}\text{ K}^{-2})T^2 + (1.024\times10^{-9}\text{ K}^{-3})T^3
\end{aligned}$$

over the above temperature range. Repeat the calculation for a constant-volume process.

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a. For a constant-pressure process, $q_P = \Delta H$ and $d\overline{H} = \overline{C}_P dT$. Then

$$\begin{aligned}\Delta\overline{H} &= \int \overline{C}_P dT \\ &= R\left[0.06436T + \frac{1}{2}(2.137\times10^{-2})T^2 - \frac{1}{3}(8.263\times10^{-6})T^3 + \frac{1}{4}(1.024\times10^{-9})T^4\right]\Bigg|_{298\text{ K}}^{1473\text{ K}} \\ \Delta\overline{H} &= 122.9\text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

We now use Equation 19.36, remembering that the gas is behaving ideally:

$$\begin{aligned}\Delta\overline{H} &= \Delta\overline{U} + P\Delta\overline{V} = \Delta\overline{U} + R\Delta T \\ \Delta\overline{U} &= 122.9\text{ kJ}\cdot\text{mol}^{-1} - (8.3145\times10^{-3}\text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(1473\text{ K} - 298\text{ K}) \\ &= 113.1\text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Finally, we use the expression $\Delta U = q + w$ to write

$$w = \Delta\overline{U} - q = 113.1\text{ kJ}\cdot\text{mol}^{-1} - 122.9\text{ kJ}\cdot\text{mol}^{-1} = -9.8\text{ kJ}\cdot\text{mol}^{-1}$$

b. For a constant-volume process, $w = 0$, and so $\Delta\overline{U} = q$. $\Delta\overline{H}$ is the same as in the previous situation, so $\Delta\overline{H} = 122.9\text{ kJ}\cdot\text{mol}^{-1}$. We can use Equation 19.36, remembering that the gas behaves ideally, to write

$$\begin{aligned}\Delta\overline{H} &= \Delta\overline{U} + \overline{V}\Delta P = \Delta\overline{U} + R\Delta T \\ \Delta U &= 122.9\text{ kJ}\cdot\text{mol}^{-1} - (8.3145\times10^{-3}\text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(1473\text{ K} - 298\text{ K}) \\ &= 113.1\text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Note that the value of $\Delta\overline{U}$ is the same as in part a, because U depends only on temperature for an ideal gas.

19–23. The value of $\Delta_r H^\circ$ at 25°C and one bar is +290.8 kJ for the reaction

$$2\,\text{ZnO(s)} + 2\,\text{S(s)} \longrightarrow 2\,\text{ZnS(s)} + \text{O}_2\text{(g)}$$

Assuming ideal behavior, calculate the value of $\Delta_r U^\circ$ for this reaction.

Because both reactants are solid, $V_1 \approx 0$. The final volume will depend only on the amount of oxygen present; assuming it behaves ideally, we write

$$V_2 \approx \frac{nRT}{P} = \frac{(1\text{ mol})(0.08314\text{ dm}^3\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(298\text{ K})}{1\text{ bar}} = 24.78\text{ dm}^3$$

Then $\Delta V \approx 24.78\text{ dm}^3$ for the reaction. Using Equation 19.36, we write

$$\begin{aligned}\Delta_r U^\circ &= \Delta_r H^\circ - P\Delta V \\ &= 290.8\text{ kJ} - (1\text{ bar})(24.776\text{ dm}^3)\left(\frac{1\text{ kJ}}{10\text{ dm}^3\cdot\text{bar}}\right) \\ &= 288.3\text{ kJ}\end{aligned}$$

19–24. Liquid sodium is being considered as an engine coolant. How many grams of sodium are needed to absorb 1.0 MJ of heat if the temperature of the sodium is not to increase by more than 10°C. Take $\overline{C}_P = 30.8\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for Na(l) and $75.2\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for H_2O(l).

We must have a coolant which can absorb 1.0×10^6 J without changing its temperature by more than 10 K. The smallest amount of sodium required will allow the temperature to change by exactly 10 K. We can consider this a constant-pressure process, because liquids are relatively incompressible. Then, substituting $\Delta T = 10$ K into Equation 19.40, we find

$$\Delta\overline{H} = \overline{C}_P\Delta T = 308\text{ J}\cdot\text{mol}^{-1}$$

We require one mole of sodium to absorb 308 J of heat. Therefore, to absorb 1.0 MJ of heat, we require

$$(1.0\times10^6\text{ J})\left(\frac{1\text{ mol}}{308\text{ J}}\right)\left(\frac{22.99\text{ g}}{1\text{ mol}}\right) = 74.6\text{ kg}$$

74.6 kg of liquid sodium is needed.

19–25. A 25.0-g sample of copper at 363 K is placed in 100.0 g of water at 293 K. The copper and water quickly come to the same temperature by the process of heat transfer from copper to water. Calculate the final temperature of the water. The molar heat capacity of copper is $24.5\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and that of water is $75.2\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

The heat lost by the copper is gained by the water. Since $\Delta H = n\overline{C}_P\Delta T$ (Equation 19.40), we can let x be the final temperature of the system and write the heat lost by the copper as

$$\left(\frac{25.0\text{ g}}{63.546\text{ g}\cdot\text{mol}^{-1}}\right)(24.5\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(363\text{ K} - x)$$

and the heat gained by the water as

$$\left(\frac{100.0\text{ g}}{18.0152\text{ g}\cdot\text{mol}^{-1}}\right)(75.3\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(x - 293\text{ K})$$

Equating these two expressions gives

$$\begin{aligned}3495\text{ J} - (9.628\text{ J}\cdot\text{K}^{-1})x &= (418.0\text{ J}\cdot\text{K}^{-1})x - 1.224\times10^5\text{ J} \\ 1.259\times10^5\text{ K} &= 427.6x \\ 295\text{ K} &= x\end{aligned}$$

The final temperature of the water is 295 K.

19–26. A 10.0-kg sample of liquid water is used to cool an engine. Calculate the heat removed (in joules) from the engine when the temperature of the water is raised from 293 K to 373 K. Take $\overline{C}_P = 75.2\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for H_2O(l).

We can use Equation 19.40, where $\Delta T = 373\text{ K} - 293\text{ K} = 80$ K. This gives

$$\Delta H = n\overline{C}_P\Delta T = \left(\frac{10.0\times10^3\text{ g}}{18.0152\text{ g}\cdot\text{mol}^{-1}}\right)(75.2\text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(80\text{ K}) = 3340\text{ kJ}$$

3340 kJ of heat is removed by the water.

19–27. In this problem, we will derive a general relation between C_P and C_V. Start with $U = U(P, T)$ and write

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT \qquad (1)$$

We could also consider V and T to be the independent variables of U and write

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \qquad (2)$$

Now take $V = V(P, T)$ and substitute its expression for dV into Equation 2 to obtain

$$dU = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP + \left[\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V\right] dT$$

Compare this result with Equation 1 to obtain

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T \qquad (3)$$

and

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \qquad (4)$$

Last, substitute $U = H - PV$ into the left side of Equation (4) and use the definitions of C_P and C_V to obtain

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P$$

Show that $C_P - C_V = nR$ if $(\partial U/\partial V)_T = 0$, as it is for an ideal gas.

We can write the total derivatives of $V(P, T)$ and $U(V, T)$ as (MathChapter H)

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT \qquad (a)$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \qquad (b)$$

Substituting dV from Equation a into Equation b gives

$$\begin{aligned} dU &= \left(\frac{\partial U}{\partial V}\right)_T \left[\left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT\right] + \left(\frac{\partial U}{\partial T}\right)_V dT \\ &= \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T dP + \left[\left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V\right] dT \end{aligned}$$

We can also express U as a function of P and T, in which case the total derivative dU is

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT$$

Because the coefficients of dP and dT in both expressions for dU are equal, we can write

$$\left(\frac{\partial U}{\partial P}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

and

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V \qquad (c)$$

Substituting $H - PV$ for U into the left side of Equation c gives

$$\left(\frac{\partial [H - PV]}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$$

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

Using the definitions of C_P and C_V (Equations 19.39 and 19.40), this expression becomes

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

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \left(\frac{\partial V}{\partial T}\right)_P \qquad (d)$$

If $(\partial U/\partial V) = 0$, then Equation d becomes

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P$$

Using the ideal gas equation to find $P(\partial V/\partial T)_P$, we find that

$$\begin{aligned} PV &= nRT \\ P\left(\frac{\partial V}{\partial T}\right)_P + V\left(\frac{\partial P}{\partial T}\right)_P &= nR\left(\frac{\partial T}{\partial T}\right)_P \\ P\left(\frac{\partial V}{\partial T}\right)_P &= nR \\ C_P - C_V &= nR \end{aligned}$$

19–28. Following Problem 19–27, show that

$$C_P - C_V = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right] \left(\frac{\partial P}{\partial T}\right)_V$$

We can write the total derivatives of $P(V, T)$ and $H(P, T)$ as (MathChapter H)

$$dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT \qquad (a)$$

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \qquad (b)$$

Substituting dP from Equation a into Equation b gives

$$\begin{aligned} dH &= \left(\frac{\partial H}{\partial P}\right)_T \left[\left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT\right] + \left(\frac{\partial H}{\partial T}\right)_P dT \\ &= \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T dV + \left[\left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P\right] dT \end{aligned}$$

We can also express H as a function of V and T, in which case the total derivative dH is

$$dH = \left(\frac{\partial H}{\partial V}\right)_T dV + \left(\frac{\partial H}{\partial T}\right)_V dT$$

Because the coefficients of dV and dT in both expressions for dH are equal, we can write

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

and

$$\left(\frac{\partial H}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P \qquad \text{(c)}$$

Substituting $U + PV$ for H into the left side of Equation c gives

$$\left(\frac{\partial [U + PV]}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P$$

$$\left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_V + V\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial H}{\partial T}\right)_P$$

Using the definitions of C_P and C_V (Equations 19.39 and 19.40), this expression becomes

$$C_V + V\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + C_P$$

$$C_P - C_V = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V$$

which is the desired result.

19–29. Starting with $H = U + PV$, show that

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

Interpret this result physically.

Take the partial derivative of both sides of this equation with respect to T, holding P constant, and substitute C_P for $(\partial H/\partial T)_P$.

$$H = U + PV$$

$$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

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

This expression tells us how the total energy of a constant-pressure system changes with respect to temperature. Recall that for a constant pressure process, $dH = \delta q$. Then $C_P = (\partial q/\partial T)$. Because $dU = \delta q + \delta w$, the work involved in the process must be $-P(\partial V/\partial T)_P$. The equation above is equivalent to the statement

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial [q + w]}{\partial T}\right)_P$$

19–30. Given that $(\partial U/\partial V)_T = 0$ for an ideal gas, prove that $(\partial H/\partial V)_T = 0$ for an ideal gas.

Begin with Equation 19.35 and use the ideal gas law to write

$$H = U + PV = U + nRT$$

Now take the partial derivative of both sides with respect to volume (note that for an ideal gas, U is dependent only upon temperature) to find

$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + nR\left(\frac{\partial T}{\partial V}\right)_T = 0$$

19–31. Given that $(\partial U/\partial V)_T = 0$ for an ideal gas, prove that $(\partial C_V/\partial V)_T = 0$ for an ideal gas.

We define C_V as $(\partial U/\partial V)_T$ (Equation 19.39). Therefore,

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial^2 U}{\partial V \partial T} = \frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T$$

Since $(\partial U/\partial V)_T = 0$ for an ideal gas, $(\partial C_V/\partial V)_T = 0$.

19–32. Show that $C_P - C_V = nR$ if $(\partial H/\partial P)_T = 0$, as is true for an ideal gas.

From Problem 19.28,

$$C_P - C_V = \left[V - \left(\frac{\partial H}{\partial P}\right)_T\right]\left(\frac{\partial P}{\partial T}\right)_V = V\left(\frac{\partial P}{\partial T}\right)_V$$

where, as stated in the problem, $(\partial H/\partial P)_T = 0$. Substituting $P = nRTV^{-1}$ into the above expression gives

$$C_P - C_V = V\left(\frac{\partial [nRTV^{-1}]}{\partial T}\right)_V = nR$$

19–33. Differentiate $H = U + PV$ with respect to V at constant temperature to show that $(\partial H/\partial V)_T = 0$ for an ideal gas.

(Notice that this problem has you prove the same thing as Problem 19.30 without assuming that $(\partial U/\partial V)_T = 0$ for an ideal gas.) We can use the ideal gas equation to write Equation 19.35 as

$$H = U + PV = U + nRT$$

For an ideal gas, U is dependent only on temperature, and the product nRT is also dependent only on temperature. Therefore, H is a function only of temperature, and differentiating H at constant temperature will yield the result

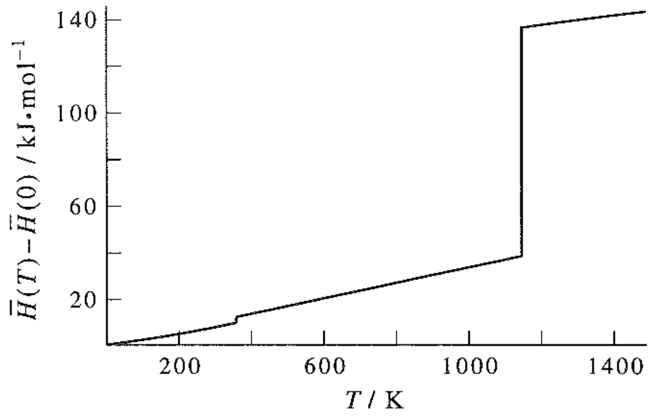
$$\left(\frac{\partial H}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + nR\left(\frac{\partial T}{\partial V}\right)_T = 0$$

19–34. Given the following data for sodium, plot $\overline{H}(T)-\overline{H}(0)$ against T for sodium: melting point, 361 K; boiling point, 1156 K; $\Delta_{\text{fus}}H^\circ = 2.60\ \text{kJ·mol}^{-1}$; $\Delta_{\text{vap}}H^\circ = 97.4\ \text{kJ·mol}^{-1}$; $\overline{C}_P(\text{s}) = 28.2\ \text{J·mol}^{-1}\text{·K}^{-1}$; $\overline{C}_P(\text{l}) = 32.7\ \text{J·mol}^{-1}\text{·K}^{-1}$; $\overline{C}_P(\text{g}) = 20.8\ \text{J·mol}^{-1}\text{·K}^{-1}$.

We can use an extended form of Equation 19.46:

$$\overline{H}(T)-\overline{H}(0) = \int_0^{T_{\text{fus}}} \overline{C}_P(\text{s})dT + \Delta_{\text{fus}}\overline{H} + \int_{T_{\text{fus}}}^{T_{\text{vap}}} \overline{C}_P(\text{l})dT + \Delta_{\text{vap}}\overline{H} + \int_{T_{\text{vap}}}^{T} \overline{C}_P(\text{g})dT$$

Notice the very large jump between the liquid and gaseous phases.



19–35. The Δ_rH° values for the following equations are

$$2\,\text{Fe(s)} + \tfrac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} \qquad \Delta_rH^\circ = -206\ \text{kJ·mol}^{-1}$$

$$3\,\text{Fe(s)} + 2\,\text{O}_2\text{(g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)} \qquad \Delta_rH^\circ = -136\ \text{kJ·mol}^{-1}$$

Use these data to calculate the value of Δ_rH for the reaction described by

$$4\,\text{Fe}_2\text{O}_3\text{(s)} + \text{Fe(s)} \longrightarrow 3\,\text{Fe}_3\text{O}_4\text{(s)}$$

Set up the problem so that the summation of two reactions will give the desired reaction:

$$\begin{array}{ll} 4[\text{Fe}_2\text{O}_3\text{(s)} \rightarrow 2\,\text{Fe(s)} + \tfrac{3}{2}\text{O}_2\text{(g)}] & \Delta_rH = 4(206)\ \text{kJ} \\ +\,3[3\,\text{Fe(s)} + 2\,\text{O}_2\text{(g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)}] & \Delta_rH = 3(-136)\ \text{kJ} \\ \hline 4\,\text{Fe}_2\text{O}_3\text{(s)} + \text{Fe(s)} \longrightarrow 3\,\text{Fe}_3\text{O}_4\text{(s)} & \Delta_rH = 416\ \text{kJ} \end{array}$$

19–36. Given the following data,

$$\tfrac{1}{2}\text{H}_2\text{(g)} + \tfrac{1}{2}\text{F}_2\text{(g)} \rightarrow \text{HF(g)} \qquad \Delta_rH^\circ = -273.3\ \text{kJ·mol}^{-1}$$

$$\text{H}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{H}_2\text{O(l)} \qquad \Delta_rH^\circ = -285.8\ \text{kJ·mol}^{-1}$$

calculate the value of Δ_rH for the reaction described by

$$2\,\text{F}_2\text{(g)} + 2\,\text{H}_2\text{O(l)} \longrightarrow 4\,\text{HF(g)} + \text{O}_2\text{(g)}$$

Set up the problem so that the summation of two reactions will give the desired reaction:

$$\begin{array}{lll} & 4[\tfrac{1}{2}\text{H}_2\text{(g)} + \tfrac{1}{2}\text{F}_2\text{(g)} \rightarrow \text{HF(g)}] & \Delta_rH = 4(-273.3)\ \text{kJ} \\ + & 2[\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{(g)} + \tfrac{1}{2}\text{O}_2\text{(g)}] & \Delta_rH = 2(285.8)\ \text{kJ} \\ \hline & 2\,\text{F}_2\text{(g)} + 2\,\text{H}_2\text{O(l)} \longrightarrow 4\,\text{HF(g)} + \text{O}_2\text{(g)} & \Delta_rH = -521.6\ \text{kJ} \end{array}$$

19–37. The standard molar heats of combustion of the isomers m-xylene and p-xylene are $-4553.9\ \text{kJ·mol}^{-1}$ and $-4556.8\ \text{kJ·mol}^{-1}$, respectively. Use these data, together with Hess's Law, to calculate the value of Δ_rH° for the reaction described by

$$m\text{-xylene} \longrightarrow p\text{-xylene}$$

Because m-xylene and p-xylene are isomers, their combustion equations are stoichiometrically equivalent. We can therefore write

$$\begin{array}{ll} m\text{-xylene} \rightarrow \text{combustion products} & \Delta_rH = -4553.9\ \text{kJ} \\ +\,\text{combustion products} \rightarrow p\text{-xylene} & \Delta_rH = +4556.8\ \text{kJ} \\ \hline m\text{-xylene} \longrightarrow p\text{-xylene} & \Delta_rH = +2.9\ \text{kJ} \end{array}$$

19–38. Given that $\Delta_rH^\circ = -2826.7$ kJ for the combustion of 1.00 mol of fructose at 298.15 K,

$$\text{C}_6\text{H}_{12}\text{O}_6\text{(s)} + 6\,\text{O}_2\text{(g)} \longrightarrow 6\,\text{CO}_2\text{(g)} + 6\,\text{H}_2\text{O(l)}$$

and the Δ_fH° data in Table 19.2, calculate the value of Δ_fH° for fructose at 298.15 K.

We are given Δ_rH° for the combustion of fructose in the statement of the problem. We use the values given in Table 19.2 for CO_2(g), H_2O(l), and O_2(g):

$$\Delta_fH^\circ[\text{CO}_2\text{(g)}] = -393.509\ \text{kJ·mol}^{-1} \qquad \Delta_fH^\circ[\text{H}_2\text{O(l)}] = -285.83\ \text{kJ·mol}^{-1}$$
$$\Delta_fH^\circ[\text{O}_2\text{(g)}] = 0$$

Now, by Hess's law, we write

$$\Delta_rH^\circ = \sum \Delta_fH^\circ[\text{products}] - \sum \Delta_fH^\circ[\text{reactants}]$$
$$-2826.7\ \text{kJ·mol}^{-1} = 6(-393.509\ \text{kJ·mol}^{-1}) + 6(-285.83\ \text{kJ·mol}^{-1}) - \Delta_fH^\circ[\text{fructose}]$$
$$\Delta_fH^\circ[\text{fructose}] = 1249.3\ \text{kJ·mol}^{-1}$$

19–39. Use the Δ_fH° data in Table 19.2 to calculate the value of Δ_cH° for the combustion reactions described by the equations:

a. $\text{CH}_3\text{OH(l)} + \tfrac{3}{2}\text{O}_2\text{(g)} \longrightarrow \text{CO}_2\text{(g)} + 2\,\text{H}_2\text{O(l)}$

b. $\text{N}_2\text{H}_4\text{(l)} + \text{O}_2\text{(g)} \longrightarrow \text{N}_2\text{(g)} + 2\,\text{H}_2\text{O(l)}$

Compare the heat of combustion per gram of the fuels $\text{CH}_3\text{OH(l)}$ and $\text{N}_2\text{H}_4\text{(l)}$.

We will need the following values from Table 19.2:

$$\Delta_f H^\circ[CO_2(g)] = -393.509\ \text{kJ}\cdot\text{mol}^{-1} \qquad \Delta_f H^\circ[H_2O(l)] = -285.83\ \text{kJ}\cdot\text{mol}^{-1}$$
$$\Delta_f H^\circ[N_2H_4(l)] = +50.6\ \text{kJ}\cdot\text{mol}^{-1} \qquad \Delta_f H^\circ[CH_3OH(l)] = -239.1\ \text{kJ}\cdot\text{mol}^{-1}$$
$$\Delta_f H^\circ[N_2(g)] = 0$$

a. Using Hess's law,

$$\begin{aligned}\Delta_r H^\circ &= \sum \Delta_f H^\circ[\text{products}] - \sum \Delta_f H^\circ[\text{reactants}]\\ &= 2(-285.83\ \text{kJ}) + (-393.5\ \text{kJ}) - (-239.1\ \text{kJ})\\ &= \left(\frac{-726.1\ \text{kJ}}{\text{mol methanol}}\right)\left(\frac{1\ \text{mol}}{32.042\ \text{g}}\right) = -22.7\ \text{kJ}\cdot\text{g}^{-1}\end{aligned}$$

b. Again, by Hess's law,

$$\begin{aligned}\Delta_r H^\circ &= \sum \Delta_f H^\circ[\text{products}] - \sum \Delta_f H^\circ[\text{reactants}]\\ &= 2(-285.83\ \text{kJ}) - (+50.6\ \text{kJ})\\ &= \left(\frac{-622.3\ \text{kJ}}{\text{mol}\ N_2H_4}\right)\left(\frac{1\ \text{mol}}{32.046\ \text{g}}\right) = -19.4\ \text{kJ}\cdot\text{g}^{-1}\end{aligned}$$

More energy per gram is produced by combusting methanol.

19–40. Using Table 19.2, calculate the heat required to vaporize 1.00 mol of $CCl_4(l)$ at 298 K.

$$CCl_4(l) \longrightarrow CCl_4(g)$$

We can subtract $\Delta_f H^\circ[CCl_4(l)]$ from $\Delta_f H^\circ[CCl_4(g)]$ to find the heat required to vaporize CCl_4:

$$\Delta_{vap} H^\circ = -102.9\ \text{kJ} + 135.44\ \text{kJ} = 32.5\ \text{kJ}$$

19–41. Using the $\Delta_f H^\circ$ data in Table 19.2, calculate the values of $\Delta_r H^\circ$ for the following:

a. $C_2H_4(g) + H_2O(l) \longrightarrow C_2H_5OH(l)$

b. $CH_4(g) + 4\,Cl_2(g) \longrightarrow CCl_4(l) + 4\,HCl(g)$

In each case, state whether the reaction is endothermic or exothermic.

a. Using Hess's law,

$$\Delta_r H^\circ = -277.69\ \text{kJ} - (-285.83\ \text{kJ} + 52.28\ \text{kJ}) = -44.14\ \text{kJ}$$

This reaction is exothermic.

b. Again, by Hess's law,

$$\Delta_r H^\circ = 4(-92.31\ \text{kJ}) - 135.44\ \text{kJ} - (-74.81\ \text{kJ}) = -429.87\ \text{kJ}$$

This reaction is also exothermic.

19–42. Use the following data to calculate the value of $\Delta_{vap} H^\circ$ of water at 298 K and compare your answer to the one you obtain from Table 19.2: $\Delta_{vap} H^\circ$ at 373 K $= 40.7\ \text{kJ}\cdot\text{mol}^{-1}$; $\overline{C}_P(l) = 75.2\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; $\overline{C}_P(g) = 33.6\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

We can create a figure similar to Figure 19.10 to illustrate this reaction:

$$\begin{tikzcd} H_2O(l) \arrow[r, "\Delta_{vap}H^\circ{,}373\ \text{K}"] & H_2O(g) \arrow[d, "\Delta H_3"] \\ H_2O(l) \arrow[u, "\Delta H_2"] \arrow[r, "\Delta_{vap}H^\circ{,}298\ \text{K}"] & H_2O(g) \end{tikzcd}$$

Now we use Hess's Law to determine the enthalpy of vaporization.

$$\begin{aligned}\Delta_{vap} H^\circ_{298\ \text{K}} &= \Delta H_2 + \Delta H_3 + \Delta_{vap} H^\circ_{373\ \text{K}}\\ &= (75\ \text{K})(75.2\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) + (-75\ \text{K})(33.6\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) + 40.7\ \text{kJ}\cdot\text{mol}^{-1}\\ &= 43.8\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

Using Table 19.2, we find

$$\begin{aligned}\Delta_{vap} H^\circ &= \Delta_f H^\circ[H_2O(g)] - \Delta_f H^\circ[H_2O(l)]\\ &= -241.8\ \text{kJ}\cdot\text{mol}^{-1} + 285.83\ \text{kJ}\cdot\text{mol}^{-1} = 44.0\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

These values are fairly close. (Using values of $\overline{C}_P$ which include temperature-dependent terms may further improve the agreement.)

19–43. Use the following data and the data in Table 19.2 to calculate the standard reaction enthalpy of the water-gas reaction at 1273 K. Assume that the gases behave ideally under these conditions.

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g)$$

$$C^\circ_P[CO(g)]/R = 3.231 + (8.379 \times 10^{-4}\ \text{K}^{-1})T - (9.86 \times 10^{-8}\ \text{K}^{-2})T^2$$

$$C^\circ_P[H_2(g)]/R = 3.496 + (1.006 \times 10^{-4}\ \text{K}^{-1})T + (2.42 \times 10^{-7}\ \text{K}^{-2})T^2$$

$$C^\circ_P[H_2O(g)]/R = 3.652 + (1.156 \times 10^{-3}\ \text{K}^{-1})T + (1.42 \times 10^{-7}\ \text{K}^{-2})T^2$$

$$\begin{aligned}C^\circ_P[C(s)]/R = -0.6366 &+ (7.049 \times 10^{-3}\ \text{K}^{-1})T - (5.20 \times 10^{-6}\ \text{K}^{-2})T^2\\ &+ (1.38 \times 10^{-9}\ \text{K}^{-3})T^3\end{aligned}$$

We can create a figure similar to Figure 19.10 to illustrate this reaction.

$$\begin{tikzcd} C(s) + H_2O(g) \arrow[r, "\Delta_r H^\circ{,}1273\ \text{K}"] \arrow[d, "\Delta H_1"] & CO(g) + H_2(g) \\ C(s) + H_2O(g) \arrow[r, "\Delta_r H^\circ{,}298\ \text{K}"] & CO(g) + H_2(g) \arrow[u, "\Delta H_2"] \end{tikzcd}$$

Now use Hess's Law to calculate the standard reaction enthalpy at 1273 K. To do the integrals, it is helpful to use a program like *Excel* or *Mathematica* (I used *Mathematica*), so that the tedium of adding and multiplying can be avoided.

$$\begin{aligned}\Delta_r H^\circ_{1273} &= \Delta_r H^\circ_{298} + \Delta H_1 + \Delta H_2\\ &= (-110.5\ \text{kJ}\cdot\text{mol}^{-1} + 241.8\ \text{kJ}\cdot\text{mol}^{-1})\\ &\qquad + R\int_{298}^{1273} \{\overline{C}_P[CO(g)] + \overline{C}_P[H_2(g)] - \overline{C}_P[H_2O(g)] - \overline{C}_P[C(s)]\}\, dT\\ &= 131.3\ \text{kJ}\cdot\text{mol}^{-1} + R\,[3725.01\ \text{K} + 3649.92\ \text{K} - 4542.43\ \text{K} - 2151.29\ \text{K}]\\ &= 131.3\ \text{kJ}\cdot\text{mol}^{-1} + 5.664\ \text{kJ}\cdot\text{mol}^{-1} = 136.964\ \text{kJ}\cdot\text{mol}^{-1}\end{aligned}$$

19–44. The standard molar enthalpy of formation of $CO_2(g)$ at 298 K is $-393.509\ \mathrm{kJ\cdot mol^{-1}}$. Use the following data to calculate the value of $\Delta_f H^\circ$ at 1000 K. Assume the gases behave ideally under these conditions.

$$\begin{aligned} C_P^\circ[\mathrm{CO_2(g)}]/R &= 2.593 + (7.661\times10^{-3}\ \mathrm{K^{-1}})T - (4.78\times10^{-6}\ \mathrm{K^{-2}})T^2 \\ &\quad + (1.16\times10^{-9}\ \mathrm{K^{-3}})T^3 \end{aligned}$$

$$C_P^\circ[\mathrm{O_2(g)}]/R = 3.094 + (1.561\times10^{-3}\ \mathrm{K^{-1}})T - (4.65\times10^{-7}\ \mathrm{K^{-2}})T^2$$

$$\begin{aligned} C_P^\circ[\mathrm{C(s)}]/R &= -0.6366 + (7.049\times10^{-3}\ \mathrm{K^{-1}})T - (5.20\times10^{-6}\ \mathrm{K^{-2}})T^2 \\ &\quad + (1.38\times10^{-9}\ \mathrm{K^{-3}})T^3 \end{aligned}$$

We can create a figure similar to Figure 19.10 to illustrate this reaction.

$$\begin{tikzcd} \mathrm{C(s)} + \mathrm{O_2(g)} \arrow[r, "\Delta_r H^\circ\text{,1000 K}"] \arrow[d, "\Delta H_1"'] & \mathrm{CO_2(g)} \\ \mathrm{C(s)} + \mathrm{O_2(g)} \arrow[r, "\Delta_r H^\circ\text{,298 K}"] & \mathrm{CO_2(g)} \arrow[u, "\Delta H_2"'] \end{tikzcd}$$

Now use Hess's Law to calculate the standard reaction enthalpy at 1000 K:

$$\begin{aligned} \Delta_r H^\circ_{1000} &= \Delta_r H^\circ_{298} + \Delta H_1 + \Delta H_2 \\ &= -393.509\ \mathrm{kJ\cdot mol^{-1}} + R\int_{298}^{1000}\{\overline{C}_P[\mathrm{CO_2(g)}] - \overline{C}_P[\mathrm{O_2(g)}] - \overline{C}_P[\mathrm{C(s)}]\}\,dT \\ &= -393.509\ \mathrm{kJ\cdot mol^{-1}} + R\,[4047.167\ \mathrm{K} - 2732.278\ \mathrm{K} - 1419.433\ \mathrm{K}] \\ &= -393.509\ \mathrm{kJ\cdot mol^{-1}} - 0.869\ \mathrm{kJ\cdot mol^{-1}} = -394.378\ \mathrm{kJ\cdot mol^{-1}} \end{aligned}$$

19–45. The value of the standard molar reaction enthalpy for

$$\mathrm{CH_4(g)} + 2\,\mathrm{O_2(g)} \longrightarrow \mathrm{CO_2(g)} + 2\,\mathrm{H_2O(g)}$$

is -802.2 kJ at 298 K. Using the heat-capacity data in Problems 19–43 and 19–44 in addition to

$$\begin{aligned} C_P^\circ[\mathrm{CH_4(g)}]/R &= 2.099 + (7.272\times10^{-3}\ \mathrm{K^{-1}})T + (1.34\times10^{-7}\ \mathrm{K^{-2}})T^2 \\ &\quad - (8.66\times10^{-10}\ \mathrm{K^{-3}})T^3 \end{aligned}$$

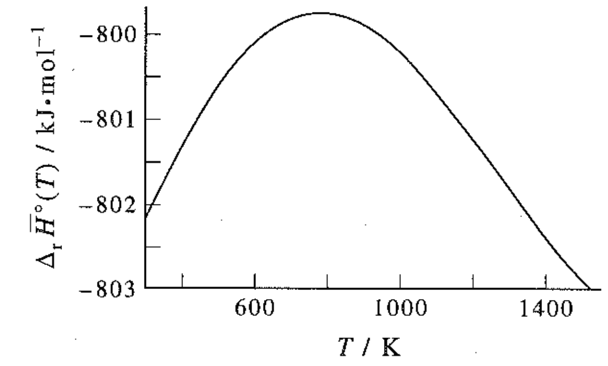
to derive a general equation for the value of $\Delta_r H^\circ$ at any temperature between 300 K and 1500 K. Plot $\Delta_r H^\circ$ versus T. Assume that the gases behave ideally under these conditions.

We can create a figure similar to Figure 19.10 to illustrate this reaction.

$$\begin{tikzcd} \mathrm{CH_4(s)} + 2\mathrm{O_2(g)} \arrow[r, "\Delta_r H^\circ"] \arrow[d, "\Delta H_1"'] & \mathrm{CO_2(g)} + 2\mathrm{H_2O(g)} \\ \mathrm{CH_4(s)} + 2\mathrm{O_2(g)} \arrow[r, "\Delta_r H^\circ\text{,298 K}"] & \mathrm{CO_2(g)} + 2\mathrm{H_2O(g)} \arrow[u, "\Delta H_2"'] \end{tikzcd}$$

Now use Hess's Law:

$$\begin{aligned} \Delta_r H^\circ &= \Delta_r H^\circ_{298} + \Delta H_1 + \Delta H_2 \\ &= -802.2\ \mathrm{kJ\cdot mol^{-1}} \\ &\qquad + R\int_{298}^{T}\{\overline{C}_P[\mathrm{CO_2(g)}] + 2\overline{C}_P[\mathrm{H_2O(g)}] - \overline{C}_P[\mathrm{CH_4(s)}] - 2\overline{C}_P[\mathrm{O_2(g)}]\}\ dT \\ &= -802.2\ \mathrm{kJ\cdot mol^{-1}} + R\int_{298}^{T}\left[1.610 - (4.21\times10^{-4}\ \mathrm{K^{-1}})T\right]dT \\ &\qquad + R\int_{298}^{T}\left[-(3.70\times10^{-6}\ \mathrm{K^{-2}})T^2 + (2.03\times10^{-9}\ \mathrm{K^{-3}})T^3\right]dT \\ &= -805.8\ \mathrm{kJ\cdot mol^{-1}} + (1.339\times10^{-2}\ \mathrm{kJ\cdot mol^{-1}\cdot K^{-1}})T \\ &\qquad -(1.750\times10^{-6}\ \mathrm{kJ\cdot mol^{-1}\cdot K^{-2}})T^2 - (1.025\times10^{-8}\ \mathrm{kJ\cdot mol^{-1}\cdot K^{-3}})T^3 \\ &\qquad +(4.211\times10^{-12}\ \mathrm{kJ\cdot mol^{-1}\cdot K^{-4}})T^4 \end{aligned}$$



19–46. In all the calculations thus far, we have assumed the reaction takes place at constant temperature, so that any energy evolved as heat is absorbed by the surroundings. Suppose, however, that the reaction takes place under adiabatic conditions, so that all the energy released as heat stays within the system. In this case, the temperature of the system will increase, and the final temperature is called the *adiabatic flame temperature*. One relatively simple way to estimate this temperature is to suppose the reaction occurs at the initial temperature of the reactants and then determine to what temperature the products can be raised by the quantity $\Delta_r H^\circ$. Calculate the adiabatic flame temperature if one mole of $CH_4(g)$ is burned in two moles of $O_2(g)$ at an initial temperature of 298 K. Use the results of the previous problem.

We know from Problem 19–45 that $802.2\ \mathrm{kJ\cdot mol^{-1}}$ of energy is produced when one mole of methane is burned in two moles of oxygen at 298 K. Now we determine how much the temperature of the products, one mole of CO_2 and two moles of H_2O, can be raised by this energy:

$$\begin{aligned} \Delta H(\text{products}) &= R\int_{298}^{T}\{\overline{C}_P[\mathrm{CO_2(g)}] + 2\overline{C}_P[\mathrm{H_2O(g)}]\}\,dT \\ 802.2\ \mathrm{kJ\cdot mol^{-1}} &= R\int_{298}^{T}\{\overline{C}_P[\mathrm{CO_2(g)}] + 2\overline{C}_P[\mathrm{H_2O(g)}]\}\,dT \\ &= R\int_{298}^{T}\left[9.897 + (9.97\times10^{-3}\ \mathrm{K^{-1}})T - (4.496\times10^{-6}\ \mathrm{K^{-2}})T^2 \right. \\ &\qquad \left. +(1.160\times10^{-9}\ \mathrm{K^{-3}})T^3\right]dT \\ &= -27.89\ \mathrm{kJ\cdot mol^{-1}} + (8.23\times10^{-2}\ \mathrm{kJ\cdot mol^{-1}\cdot K^{-1}})T + (4.15\times10^{-5}\ \mathrm{kJ\cdot mol^{-1}\cdot K^{-2}})T^2 \\ &\qquad -(1.25\times10^{-8}\ \mathrm{kJ\cdot mol^{-1}\cdot K^{-3}})T^3 + (2.41\times10^{-12}\ \mathrm{kJ\cdot mol^{-1}\cdot K^{-4}})T^4 \end{aligned}$$

We can solve this polynomial using Simpson's rule or a numerical software package. Working in *Mathematica*, we find that the final temperature will be 4040 K.

19–47. Explain why the adiabatic flame temperature defined in the previous problem is also called the maximum flame temperature.

The adiabatic flame temperature is the temperature of the system if all the energy released as heat stays within the system. Since we are considering an isolated system, the adiabatic flame temperature is also the maximum temperature which the system can achieve.

19–48. How much energy as heat is required to raise the temperature of 2.00 moles of $O_2(g)$ from 298 K to 1273 K at 1.00 bar? Take

$$\overline{C}_P[O_2(g)]/R = 3.094 + (1.561 \times 10^{-3}\ \mathrm{K}^{-1})T - (4.65 \times 10^{-7}\ \mathrm{K}^{-2})T^2$$

We can use Equation 19.44:

$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} n\overline{C}_P dT \\ &= (2.00\ \mathrm{mol})R \int_{298}^{1273} \left[3.094 + (1.561 \times 10^{-3}\ \mathrm{K}^{-1})T - (4.65 \times 10^{-7}\ \mathrm{K}^{-2})T^2\right] dT \\ &= 64.795\ \mathrm{kJ\cdot mol^{-1}}\end{aligned}$$

19–49. When one mole of an ideal gas is compressed adiabatically to one-half of its original volume, the temperature of the gas increases from 273 K to 433 K. Assuming that $\overline{C}_V$ is independent of temperature, calculate the value of $\overline{C}_V$ for this gas.

Equation 19.20 gives an expression for the reversible adiabatic expansion of an ideal gas:

$$\overline{C}_V dT = -\frac{RT}{V} dV$$

Integrating both sides and substituting the temperatures given, we find that

$$\begin{aligned}\int \frac{\overline{C}_V}{T} dT &= -\int \frac{R}{V} dV \\ \overline{C}_V \ln \frac{T_2}{T_1} &= -R \ln \frac{V_2}{V_1} \\ \overline{C}_V \ln \frac{433}{273} &= -R \ln 2 \\ \frac{\overline{C}_V}{R} &= 1.50\end{aligned}$$

19–50. Use the van der Waals equation to calculate the minimum work required to expand one mole of $CO_2(g)$ isothermally from a volume of 0.100 dm^3 to a volume of 100 dm^3 at 273 K. Compare your result with that which you calculate assuming ideal behavior.

In Problem 19–10, we found that the work done by a van der Waals gas was

$$w = -RT \ln \frac{\overline{V}_2 - b}{\overline{V}_1 - b} + \frac{a(\overline{V}_2 - \overline{V}_1)}{\overline{V}_2 \overline{V}_1}$$

Substituting $a = 3.6551\ \mathrm{dm^6\cdot bar\cdot mol^{-2}}$ and $b = 0.042816\ \mathrm{dm^3\cdot mol^{-1}}$ from Table 16.3 and using the parameters in the statement of the problem gives

$$\begin{aligned}w &= -(0.083145\ \mathrm{dm^3\cdot bar\cdot mol^{-1}\cdot K^{-1}})(273\ \mathrm{K}) \ln \frac{100\ \mathrm{dm^3\cdot mol^{-1}} - 0.042816\ \mathrm{dm^3\cdot mol^{-1}}}{0.100\ \mathrm{dm^3\cdot mol^{-1}} - 0.042816\ \mathrm{dm^3\cdot mol^{-1}}} \\ &\quad +3.6551\ \mathrm{dm^6\cdot bar\cdot mol^{-2}} \left[\frac{100\ \mathrm{dm^3\cdot mol^{-1}} - 0.100\ \mathrm{dm^3\cdot mol^{-1}}}{(100\ \mathrm{dm^3\cdot mol^{-1}})(0.100\ \mathrm{dm^3\cdot mol^{-1}})}\right] \\ &= (-169.5\ \mathrm{dm^3\cdot bar\cdot mol^{-1}} + 36.5\ \mathrm{dm^3\cdot bar\cdot mol^{-1}})(0.1\ \mathrm{kJ\cdot dm^{-3}\cdot bar^{-1}})(1\ \mathrm{mol}) \\ &= -13.3\ \mathrm{kJ}\end{aligned}$$

For an ideal gas,

$$\begin{aligned}w &= -\int P dV = -nRT \ln\left(\frac{V_2}{V_1}\right) \\ &= (-156.80\ \mathrm{dm^3\cdot bar})(0.1\ \mathrm{kJ\cdot bar^{-1}}) = -15.7\ \mathrm{kJ}\end{aligned}$$

The work needed to expand the van der Waals gas is greater than that needed for the ideal gas.

19–51. Show that the work involved in a reversible, adiabatic pressure change of one mole of an ideal gas is given by

$$w = \overline{C}_V T_1 \left[\left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P} - 1\right]$$

where T_1 is the initial temperature and P_1 and P_2 are the initial and final pressures, respectively.

For a reversible, adiabatic pressure change of an ideal gas, $\delta q = 0$, so $dU = dw$. Since $d\overline{U}$ is defined as $\overline{C}_V dT$,

$$dw = \overline{C}_V dT$$

for one mole of an ideal gas. Integrating, we find

$$w = \overline{C}_V T_2 - \overline{C}_V T_1 = \overline{C}_V (T_2 - T_1) = \overline{C}_V T_1 \left(\frac{T_2}{T_1} - 1\right)$$

From Problem 19.17, we know that

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P}$$

and so substituting gives

$$w = \overline{C}_V T_1 \left[\left(\frac{P_2}{P_1}\right)^{R/\overline{C}_P} - 1\right]$$

19–52. In this problem, we will discuss a famous experiment called the *Joule-Thomson experiment*. In the first half of the 19th century, Joule tried to measure the temperature change when a gas is expanded into a vacuum. The experimental setup was not sensitive enough, however, and he found that there was no temperature change, within the limits of his error. Soon afterward, Joule and Thomson devised a much more sensitive method for measuring the temperature change upon expansion. In their experiments (see Figure 19.11), a constant applied pressure P_1 causes a quantity of gas to flow slowly from one chamber to another through a porous plug of silk or cotton. If a volume, V_1, of gas is pushed through the porous plug, the work done on the gas is P_1V_1. The pressure on the other side of the plug is maintained at P_2, so if a volume V_2 enters the right-side chamber, then the net work is given by

$$w = P_1V_1 - P_2V_2$$

The apparatus is constructed so that the entire process is adiabatic, so $q = 0$. Use the First Law of Thermodynamics to show that

$$U_2 + P_2V_2 = U_1 + P_1V_1$$

or that $\Delta H = 0$ for a Joule-Thomson expansion. Starting with

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

show that

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

Interpret physically the derivative on the left side of this equation. This quantity is called the *Joule-Thomson coefficient* and is denoted by μ_{JT}. In Problem 19–54 you will show that it equals zero for an ideal gas. Nonzero values of $(\partial T/\partial P)_H$ directly reflect intermolecular interactions. Most gases cool upon expansion [a positive value of $(\partial T/\partial P)_H$] and a Joule-Thomson expansion is used to liquefy gases.

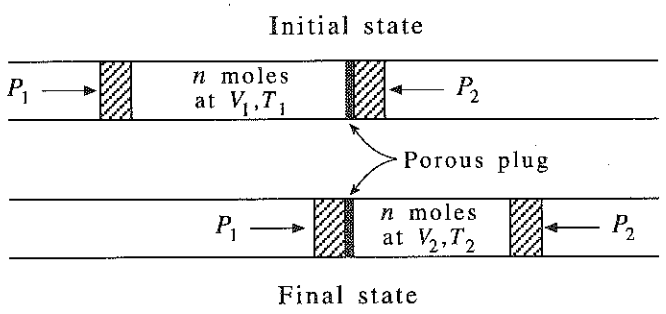


FIGURE 19.11
A schematic description of the Joule-Thomson experiment.

The net work is $w = P_1V_1 - P_2V_2$. Since $q = 0$, $U = w$, so

$$U_2 - U_1 = P_1V_1 - P_2V_2$$
$$U_2 + P_2V_2 = U_1 + P_1V_1$$

Since $\Delta H = U_1 + P_1V_1 - (U_2 + P_2V_2)$, $\Delta H = 0$. Now we write the total derivative of H as a function of P and T:

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT$$

Using the definition of C_P, we write this as

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + C_P dT$$
$$-C_P dT = \left(\frac{\partial H}{\partial P}\right)_T dP - dH$$
$$dT = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T dP + \frac{1}{C_P} dH$$

Keep H constant and divide through by dP to obtain

$$\left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T + 0$$

The Joule-Thomson coefficient is a measure of the change of temperature of a gas with respect to the change in pressure in a Joule-Thomson expansion (or compression).

19–53. The Joule-Thomson coefficient (Problem 19–52) depends upon the temperature and pressure, but assuming an average constant value of 0.15 K·bar^{-1} for $N_2(g)$, calculate the drop in temperature if $N_2(g)$ undergoes a drop in pressure of 200 bar.

$$(0.15\ \text{K}\cdot\text{bar}^{-1})(-200\ \text{bar}) = -30\ \text{K}$$

19–54. Show that the Joule-Thomson coefficient (Problem 19–52) can be written as

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

Show that $(\partial T/\partial P)_H = 0$ for an ideal gas.

From Problem 19–52,

$$\mu_{JT} = -\frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

Since $H = U + PV$,

$$\mu_{JT} = -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$
$$= -\frac{1}{C_P}\left[\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial (PV)}{\partial P}\right)_T\right]$$

For an ideal gas, U and PV depend only on temperature, so $\mu_{JT} = 0$.

19–55. Use the rigid rotator-harmonic oscillator model and the data in Table 18.2 to plot $\overline{C}_P(T)$ for CO(g) from 300 K to 1000 K. Compare your result with the expression given in Problem 19–43.

From Example 19–8, we know that for an ideal gas

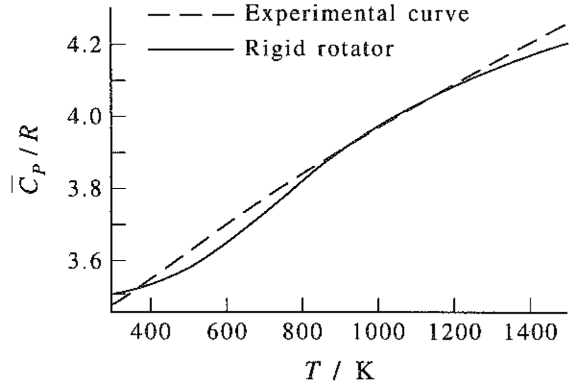
$$\overline{C}_P = \overline{C}_V + R \tag{19.43}$$

And from Chapter 18, we know that for a linear polyatomic ideal gas

$$\frac{\overline{C}_V}{R} = \frac{5}{2} + \left(\frac{\Theta_{\text{vib}}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib}}/T}}{(1-e^{\Theta_{\text{vib}}/T})^2} \tag{18.41}$$

Therefore, since $\Theta_{\text{vib}}(\text{CO}) = 3103$ K, we wish to graph

$$\frac{\overline{C}_P}{R} = \frac{7}{2} + \left(\frac{3103\text{ K}}{T}\right)^2 \frac{e^{-3103\text{ K}/T}}{(1-e^{-3103\text{ K}/T})^2}$$



19–56. Use the rigid rotator-harmonic oscillator model and the data in Table 18.4 to plot $\overline{C}_P(T)$ for CH_4(g) from 300 K to 1000 K. Compare your result with the expression given in Problem 19–45.

Again, for an ideal gas

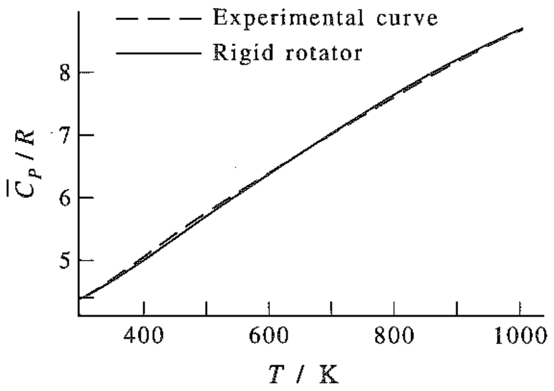
$$\overline{C}_P = \overline{C}_V + R \tag{19.43}$$

And from Chapter 18, we know that for a nonlinear polyatomic ideal gas

$$\frac{\overline{C}_V}{R} = \frac{3}{2} + \frac{3}{2} + \sum_{j=1}^{3n-6} \left(\frac{\Theta_{\text{vib},j}}{T}\right)^2 \frac{e^{-\Theta_{\text{vib},j}/T}}{(1-e^{-\Theta_{\text{vib},j}/T})^2} \tag{18.62}$$

Using the values given in the problem, we wish to graph

$$\frac{\overline{C}_P}{R} = 4 + \left(\frac{4170\text{ K}}{T}\right)^2 \frac{e^{-4170\text{ K}/T}}{(1-e^{-4170\text{ K}/T})^2} + 2\left(\frac{2180\text{ K}}{T}\right)^2 \frac{e^{-2180\text{ K}/T}}{(1-e^{-2180\text{ K}/T})^2}$$
$$+3\left(\frac{4320\text{ K}}{T}\right)^2 \frac{e^{-4320\text{ K}/T}}{(1-e^{-4320\text{ K}/T})^2} + 3\left(\frac{1870\text{ K}}{T}\right)^2 \frac{e^{-1870\text{ K}/T}}{(1-e^{-1870\text{ K}/T})^2}$$



19–57. Why do you think the equations for the dependence of temperature on volume for a reversible adiabatic process (see Equation 19.22 and Example 19.6) depend upon whether the gas is a monatomic gas or a polyatomic gas?

For an adiabatic process, no energy is transferred as heat, so the change in internal energy is equal to the change in work. The internal energy of a monatomic gas (in the electronic ground state) is entirely in the translational degrees of freedom, which is directly related to the temperature of the gas. If the volume of the system increases, work is done by the system, and so the internal energy of the system must decrease. The only way for it to do so is by decreasing the amount of energy in the translational degrees of freedom, which decreases the observed temperature of the gas. The internal energy of a polyatomic gas (in the electronic ground state) is in the rotational, vibrational, and translational degrees of freedom. These vibrational, rotational, and translational energy levels are not necessarily in equilibrium (see Problem 18–37). If the volume of a polyatomic gas is increased, work is done by the system, as before, and the internal energy of the gas must again decrease. However, the gas can lose energy in the rotational or vibrational levels, which will not decrease the observed temperature of the gas. It can also lose energy in the translational levels, which will decrease the observed temperature of the gas, but the other available methods of decreasing the energy of the system will change the dependence of temperature on volume for a polyatomic gas from that observed for a monatomic gas.
