1. Problem 19–7 in McQuarrie & Simon:

   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.

2. Problem 19–13 in McQuarrie & Simon:

   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, $\beta$ is fairly constant over a moderate pressure range. If $\beta$ 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

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

   (You need to use the fact that $\int \ln x\,dx = x\ln x - x$.)

   The fact that liquids are incompressible is reflected by $\beta$ being small, so that $\beta(P-P_0) \ll 1$ for moderate pressures. Show that

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

   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 $\beta$ to be $8.95\times10^{-5}\ \mathrm{bar}^{-1}$ and the molar volume to be $0.106\ \mathrm{mol\,L^{-1}}$ at 20 °C.

3. Problem 19–22 in McQuarrie & Simon:

   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 $w$, $q$, $\Delta U$, and $\Delta H$ given that the molar heat capacity of ethane is given by

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

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

4. Problem 19–27 in McQuarrie & Simon:

   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.

5. Problem 19–50 in McQuarrie & Simon:

   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.

6. Extra credit: Problem 19–55 in McQuarrie & Simon:

   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.

Expression from Problem 19–43:

$$C_P^\circ[\mathrm{CO(g)}]/R = 3.231 + \left(8.379\times10^{-4}\,\mathrm{K}^{-1}\right)T - \left(9.86\times10^{-8}\,\mathrm{K}^{-2}\right)T^2$$

Table 18.2: Molecular constants for several diatomic molecules. These parameters were obtained from a variety of sources and do not represent the most accurate values because they were obtained under the rigid rotator-harmonic oscillator approximation

| Molecule | Electronic state | $\Theta_{vib}/\mathrm{K}$ | $\Theta_{rot}/\mathrm{K}$ | $D_0/\mathrm{kJ\,mol^{-1}}$ | $D_e/\mathrm{kJ\,mol^{-1}}$ |
|---|---|---|---|---|---|
| $H_2$ | $^1\Sigma_g^+$ | 6215 | 85.3 | 432.1 | 457.6 |
| $D_2$ | $^1\Sigma_g^+$ | 4394 | 42.7 | 435.6 | 453.9 |
| $Cl_2$ | $^1\Sigma_g^+$ | 805 | 0.351 | 239.2 | 242.3 |
| $Br_2$ | $^1\Sigma_g^+$ | 463 | 0.116 | 190.1 | 191.9 |
| $I_2$ | $^1\Sigma_g^+$ | 308 | 0.0537 | 148.8 | 150.3 |
| $O_2$ | $^3\Sigma_g^-$ | 2256 | 2.07 | 493.6 | 503.0 |
| $N_2$ | $^1\Sigma_g^+$ | 3374 | 2.88 | 941.6 | 953.0 |
| CO | $^1\Sigma^+$ | 3103 | 2.77 | 1070 | 1085 |
| NO | $^2\Pi_{1/2}$ | 2719 | 2.39 | 626.8 | 638.1 |
| HCl | $^1\Sigma^+$ | 4227 | 15.02 | 427.8 | 445.2 |
| HBr | $^1\Sigma^+$ | 3787 | 12.02 | 362.6 | 377.7 |
| HI | $^1\Sigma^+$ | 3226 | 9.25 | 294.7 | 308.6 |
| $Na_2$ | $^1\Sigma_g^+$ | 229 | 0.221 | 71.1 | 72.1 |
| $K_2$ | $^1\Sigma_g^+$ | 133 | 0.081 | 53.5 | 54.1 |