

Chemistry 2720 Fall 2001 Assignment 2

Solutions

1. Temperature is a property of objects which correlates with our intuitive sense of hotness. Heat is an interaction between systems which changes their states but is not work. Heat flows spontaneously from hotter to colder bodies.
2. (a) Because the external pressure is constant during the expansion, we just have to calculate $w = -P_{\text{ext}}\Delta V$, i.e. we need the change in volume. The first three bits of data tell us the initial volume:

$$\begin{aligned}P &= (1.08 \text{ atm})(101\,325 \text{ Pa/atm}) = 109\,431 \text{ Pa} \\T &= 20 + 273.15 \text{ K} = 293 \text{ K} \\ \therefore V_i &= \frac{nRT}{P} \\ &= \frac{(18 \text{ mol})(8.314510 \text{ JK}^{-1}\text{mol}^{-1})(293 \text{ K})}{109\,431 \text{ Pa}} \\ &= 0.40 \text{ m}^3\end{aligned}$$

The final volume is calculated analogously:

$$\begin{aligned}P &= (0.35 \text{ atm})(101\,325 \text{ Pa/atm}) = 35\,464 \text{ Pa} \\ \therefore V_f &= \frac{nRT}{P} \\ &= \frac{(18 \text{ mol})(8.314510 \text{ JK}^{-1}\text{mol}^{-1})(293 \text{ K})}{35\,464 \text{ Pa}} \\ &= 1.23 \text{ m}^3\end{aligned}$$

The work is then

$$\begin{aligned}w &= -P_{\text{ext}}\Delta V = -P_{\text{ext}}(V_f - V_i) \\ &= -(35\,464 \text{ Pa})(1.23 - 0.40 \text{ m}^3) \\ &= -29 \text{ kJ}\end{aligned}$$

The negative sign tells us that work is done *by* the system, i.e. that the system expends energy in the form of work. This makes sense since the volume increases. The system pushes out against its surroundings to expand, and this requires work.

- (b) If the system (the nitrogen gas) performs work, then in principle this work can be used to raise a mass. Thus, the mass is raised by

$$h = \frac{w}{mg} = \frac{29 \times 10^3 \text{ J}}{(2.3 \text{ kg})(9.80665 \text{ m/s}^2)} = 1.3 \text{ km.}$$

3. The molar work is

$$\bar{w} = - \int_{\bar{V}_i}^{\bar{V}_f} P d\bar{V}.$$

We can easily substitute the equation for P into this equation and it's reasonably easy also to do the integral. However, we also need \bar{V}_i and \bar{V}_f . These are obtained from the equation of state itself:

$$\begin{aligned} P &= \frac{1}{\kappa_T} \ln \left(\frac{\bar{V}^\circ}{\bar{V}} \right) + P^\circ \\ \therefore \kappa_T(P - P^\circ) &= \ln \left(\frac{\bar{V}^\circ}{\bar{V}} \right) \\ \therefore \frac{\bar{V}^\circ}{\bar{V}} &= e^{\kappa_T(P - P^\circ)} \\ \therefore \bar{V} &= \bar{V}^\circ e^{-\kappa_T(P - P^\circ)} \end{aligned}$$

The initial pressure is 1 atm (101 325 Pa), so the initial molar volume is

$$\bar{V}_i = (7.093 \times 10^{-6} \text{ m}^3/\text{mol})e^0 = 7.093 \times 10^{-6} \text{ m}^3/\text{mol}.$$

The final pressure is 1000 atm (1.013×10^8 atm), so the final molar volume is

$$\begin{aligned} \bar{V}_f &= (7.093 \times 10^{-6} \text{ m}^3/\text{mol})e^{-(7.25 \times 10^{-12} \text{ Pa}^{-1})(1.013 \times 10^8 - 101325 \text{ Pa})} \\ &= 7.088 \times 10^{-6} \text{ m}^3/\text{mol}. \end{aligned}$$

The work is then

$$\begin{aligned} \bar{w} &= - \int_{\bar{V}_i}^{\bar{V}_f} P d\bar{V} \\ &= - \int_{\bar{V}_i}^{\bar{V}_f} \left[\frac{1}{\kappa_T} \ln \left(\frac{\bar{V}^\circ}{\bar{V}} \right) + P^\circ \right] d\bar{V} \\ &= - \left[\frac{1}{\kappa_T} \left(\bar{V} \ln \left(\frac{\bar{V}^\circ}{\bar{V}} \right) + \bar{V} \right) + P^\circ \bar{V} \right]_{\bar{V}_i}^{\bar{V}_f} \\ &= -(9.783453 \times 10^5 - 9.783455 \times 10^5 \text{ J}) \\ &= 0.2 \text{ J.} \end{aligned}$$

The work is tiny, especially when we consider the enormous change in pressure. Ignoring pressure-volume terms for solids should therefore be safe.