ChemE 2200 - Physical Chemistry II for Engineers – Spring 2025

Solution to Homework Assignment 5

1. (A) For expansion against a constant external pressure, $w = -P_{\text{ext}}\Delta V$. We need to determine the final volume, when P = 1 atm. Because the gas is ideal and the temperature is constant,

$$V = \frac{nRT}{P} = \frac{(2.0\text{ g})(1\text{ mol/16 g})(0.0821\text{ L}\cdot\text{atm}/(\text{K}\cdot\text{mol}))(298\text{ K})}{1\text{ atm}} = 3.06\text{ L}$$

$$w = -P_{\text{ext}}\Delta V = -(1\text{ atm})(3.06\text{ L} - 1.17\text{ L}) = -1.89\text{ L}\cdot\text{atm}\frac{101\text{ J}}{1\text{ L}\cdot\text{atm}} = -191\text{ J}$$

(B) For the isothermal reversible expansion of an ideal gas,

$$w = -nRT\ln\frac{V_{\text{final}}}{V_{\text{inital}}} = -(2.0\text{ g})(1\text{ mol/16 g})(8.314\text{ J}/(\text{K}\cdot\text{mol}))(298\text{ K})\ln\frac{3.06\text{ L}}{1.17\text{ L}} = -298\text{ J}$$

Exercise adapted from P. Atkins, *Physical Chemistry*, 6th edition, 1997.

2. For an ideal gas U depends on temperature only, so $\Delta U = 0$ for an isothermal process. Thus $q = -w = 1.0$ kJ. The work done by an ideal gas in a reversible isothermal expansion is

$$w = -nRT\ln\frac{V_{\text{final}}}{V_{\text{inital}}}$$

Solve for T and substitute the specifics.

$$T = \frac{-w}{nR\ln(V_{\text{final}}/V_{\text{initial}})} = -\frac{1000.\text{ J}}{(1\text{ mol})(8.314\text{ J}/(\text{K}\cdot\text{mol}))\ln(2V_{\text{initial}}/V_{\text{initial}})} = 174\text{ K}$$

Exercise adapted from K. J. Laidler and J. H. Meiser, *Physical Chemistry*, 3rd edition, 1999.

3. (A) The work done on the gas in cylinder section B during the isothermal compression is

$$w_{\text{B}} = -nRT\ln\frac{V_1}{V_2} = -(2.0\text{ mol})(8.314\text{ J}/(\text{K}\cdot\text{mol}))(300\text{ K})\ln\frac{1.0\text{ L}}{2.0\text{ L}} = 3.5\times10^3\text{ J}$$

(B) Because the temperature in cylinder section B is constant and because the gas is ideal, $\Delta U_{\text{B}} = 0$.

(C) Begin with the expression for ΔU and solve for q_{B}.

$$\Delta U_{\text{B}} = q_{\text{B}} + w_{\text{B}}$$

$$q_{\text{B}} = \Delta U_{\text{B}} - w_{\text{B}} = 0 - 3.5\times10^3\text{ J} = -3.5\times10^3\text{ J}$$

(D) Because the piston moves reversibly, $w_{\text{B}} = -w_{\text{A}}$. Thus $w_{\text{A}} = -3.5\times10^3$ J.

(E) To calculate ΔU for the gas in cylinder section A we need only calculate the change in temperature because the internal energy for an ideal gas depends only on the temperature. We know the final volume of cylinder section A (3.0 L), so we only need to find the pressure in cylinder section A to calculate the temperature. The volume of cylinder section B decreases by a factor of 2 at constant temperature (300 K). Therefore the pressure in cylinder section B doubles; $P_{\text{B, final}} = 2P_{\text{B, initial}}$. Because the piston moves freely the pressure in each section must be equal; $P_{\text{B, initial}} = P_{\text{A, initial}}$ and $P_{\text{B, final}} = P_{\text{A, final}}$, so $P_{\text{A, final}} = 2P_{\text{A, initial}}$. Use the ideal gas law to obtain a ratio of the state of gas A initially to the state of gas A finally.

$$PV = nRT$$

$$\frac{P_{\text{A,initial}}V_{\text{A,initial}}}{P_{\text{A,final}}V_{\text{A,final}}} = \frac{T_{\text{A,initial}}}{T_{\text{A,final}}}$$

$$T_{\text{A,final}} = T_{\text{A,initial}}\frac{P_{\text{A,final}}V_{\text{A,final}}}{P_{\text{A,initial}}V_{\text{A,initial}}} = (300\text{ K})\frac{2P_{\text{A,initial}}(3.0\text{ L})}{P_{\text{A,initial}}(2.0\text{ L})} = 900\text{ K}$$

$$\Delta U_{\text{A}} = n\int_{T_{\text{initial}}}^{T_{\text{final}}}\overline{C}_{\text{V}}\,dT_{\text{A}} = n\overline{C}_{\text{V}}(T_{\text{final}} - T_{\text{initial}}) = (2.0\text{ mol})(20\text{ J}/(\text{K}\cdot\text{mol}))(900\text{ K} - 300\text{ K}) = 2.4\times10^{4}\text{ J}$$

(F) Begin with the expression for ΔU and solve for q_{A}.

$$\Delta U_{\text{A}} = q_{\text{A}} + w_{\text{A}}$$

$$q_{\text{A}} = \Delta U_{\text{A}} - w_{\text{A}} = 2.4\times10^{4}\text{ J} - (-3.5\times10^{3}\text{ J}) = +2.75\times10^{4}\text{ J}$$

As expected, q_{A} is positive because heat flowed into section A.

Exercise adapted from P. Atkins, *Physical Chemistry*, 6th edition, 1997.

4. Begin by calculating the temperatures for states 2 and 3. For 1 → 2 the volume of the gas doubles at constant pressure. Because this is one mole of an ideal gas, $PV = RT$. Thus $P_1V_1 = RT_1$ and $P_2V_2 = RT_2$. Divide these two equations to yield

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

$$T_2 = T_1\frac{P_2V_2}{P_1V_1} = (273\text{ K})\frac{(1.0\text{ atm})(44.8\text{ L})}{(1.0\text{ atm})(22.4\text{ L})} = 546\text{ K}$$

Because the path from 3 to 1 is isothermal, $T_3 = T_1 = 273$ K.

(A) **The path 1 → 2.** The gas expands against a constant external pressure of 1.0 atm. Use the equation for work.

$$w_{1\to2} = -P_{\text{ext}}\Delta V = -(1.0\text{ atm})(44.8\text{ L} - 22.4\text{ L}) = -22.4\text{ L}\cdot\text{atm}\frac{0.101\text{ kJ}}{1\text{ L}\cdot\text{atm}} = -2.26\text{ kJ}$$

Calculate ΔU. Because the gas is ideal, U depends only on temperature and because the gas is monatomic, $\overline{C}_{\text{V}} = (3/2)R$.

$$\Delta U_{1\to2} = n\int_{T_1}^{T_2}\overline{C}_{\text{V}}\,dT = n\frac{3}{2}R(T_2 - T_1) = (1.0\text{ mol})\frac{3}{2}(8.314\text{ J}/(\text{K}\cdot\text{mol}))(546\text{ K} - 273\text{ K}) = 3.40\text{ kJ}$$

We can now calculate q.

$$q_{1\to2} = \Delta U_{1\to2} - w_{1\to2} = 3.40\text{ kJ} - (-2.26\text{ kJ}) = 5.66\text{ kJ}$$

For a process at constant pressure, $\Delta H = q$.

$$\Delta H_{1\to2} = q_{1\to2} = 5.66\text{ kJ}$$

(B) **The path 2 → 3.** Because the volume does not change, $w_{2\to3} = 0$.

$$q_{2\to3} = \Delta U_{2\to3} = n\int_{T_2}^{T_3}C_{\text{V}}\,dT = n\frac{3}{2}R(T_3 - T_2)$$

$$= (1.0\text{ mol})\frac{3}{2}(8.314\text{ J}/(\text{K}\cdot\text{mol}))(273\text{ K} - 546\text{ K}) = -3.40\text{ kJ}$$

Use the definition of enthalpy to calculate $\Delta H_{2\to3}$.

$$\Delta H_{2\to3} = \Delta U_{2\to3} + \Delta(PV)_{2\to3} = \Delta U_{2\to3} + nR\Delta T_{2\to3}$$

$$= -3.40\ \text{kJ} + (1.0\ \text{mol})(8.314\ \text{J}/(\text{K}\cdot\text{mol}))(273\ \text{K} - 546\ \text{K}) = -5.66\ \text{kJ}$$

Alternatively, one could note that ΔU and ΔH must be zero for a complete cycle.

$$\Delta U_{\text{cycle}} = \Delta U_{1\to2} + \Delta U_{2\to3} + \Delta U_{3\to1} = 0$$

$$\Delta H_{\text{cycle}} = \Delta H_{1\to2} + \Delta H_{2\to3} + \Delta H_{3\to1} = 0$$

Because the path 3 → 1 is isothermal and the gas is ideal, $\Delta U_{3\to1} = \Delta H_{3\to1} = 0$. Thus

$$\Delta U_{2\to3} = -\Delta U_{1\to2} = -3.40\ \text{kJ}$$

$$\Delta H_{2\to3} = -\Delta H_{1\to2} = -5.66\ \text{kJ}$$

This agrees with our calculation above.

(C) **The path 3 → 1.** As stated above, because the path is isothermal, $\Delta U_{3\to1} = \Delta H_{3\to1} = 0$.

$$q_{3\to1} = -w_{3\to1} = -nRT\ln\frac{V_1}{V_3} = -(1.0\ \text{mol})(8.314\ \text{J}/(\text{K}\cdot\text{mol}))(273\ \text{K})\ln\frac{1\ \text{L}}{0.5\ \text{L}} = -1.57\ \text{kJ}$$

$$w_{3\to1} = +1.57\ \text{kJ}$$

(D) **The cycle.** As stated above, $\Delta U_{\text{cycle}} = 0$ and $\Delta H_{\text{cycle}} = 0$ because internal energy and enthalpy are state functions. For heat and work, the net cycle is the sum of the paths.

$$q_{\text{cycle}} = q_{1\to2} + q_{2\to3} + q_{3\to1} = 5.67 - 3.40 - 1.57 = +0.70\ \text{kJ}$$

$$w_{\text{cycle}} = w_{1\to2} + w_{2\to3} + w_{3\to1} = -2.27 + 0 + 1.57 = -0.70\ \text{kJ}$$

This reversible cycle converts 0.70 kJ of heat into 0.70 kJ of work.

Exercise adapted from P. Atkins, *Physical Chemistry*, 6th edition, 1997.

5. We need to find the intersection of an isotherm that passes through the initial state and an adiabat that passes through the final state. The equation for the isotherm is

$$P = \frac{nRT}{V} = \frac{(1\ \text{mol})(0.0821\ \text{L}\cdot\text{atm}/(\text{K}\cdot\text{mol}))(298\ \text{K})}{V} = \frac{24.5\ \text{L}}{V}$$

The equation for a reversible adiabatic expansion of an ideal monatomic gas is

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

For an ideal monatomic gas,

$$\overline{C}_\text{V} = \frac{3}{2}R$$

$$1 + \frac{R}{\overline{C}_\text{V}} = 1 + \frac{2}{3} = \frac{5}{3}$$

Thus

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{5/3}$$

We need to determine the volume of the final state. Use the ideal gas law.

$$V = \frac{nRT}{P} = \frac{(1\ \text{mol})(0.0821\ \text{L}\cdot\text{atm}/(\text{K}\cdot\text{mol}))(253\ \text{K})}{2.0\ \text{atm}} = 10.39\ \text{L}$$

We can now derive the equation for the adiabat that passes through the final state (P = 2 atm, V = 10.39 L).

$$\frac{P}{2} = \left(\frac{10.39}{V}\right)^{5/3}$$

$$P = \frac{98.94}{V^{5/3}}$$

Find the intersection of the isotherm and the adiabat by setting the pressures equal.

$$\frac{24.5}{V} = \frac{98.94}{V^{5/3}}$$

$$V^{2/3} = 4.04$$

$$V = 4.04^{3/2} = 8.1\,\mathrm{L}$$

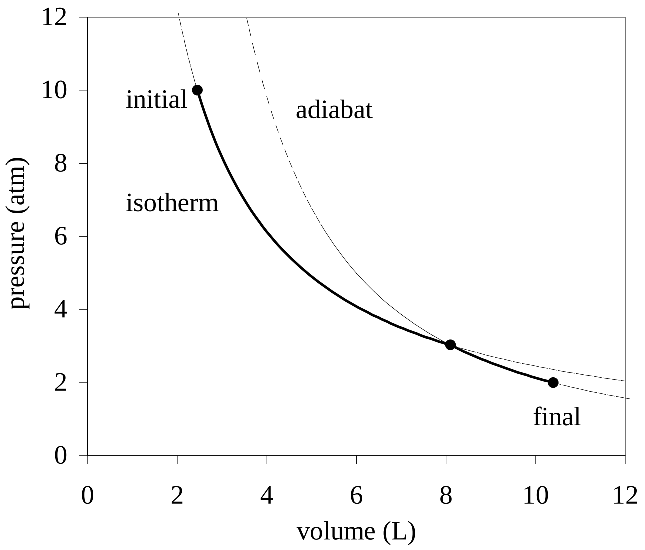
Find the pressure of the intermediate state by using the equation for the isotherm (or the equation for the adiabat).

$$P = \frac{24.5}{V} = \frac{24.5}{8.1\,\mathrm{L}} = 3.0\ \mathrm{atm}$$

Of course, the temperature of the intermediate state is 298 K. (The intermediate state is on the same isotherm as the initial state.)

Summary: the intermediate state on the reversible path is at 3 atm, 8.1 L and 298 K.

The isotherm and adiabat are shown in the graph below. The intermediate state is the intersection of the isotherm and the adiabat. The reversible paths are shown by the solid lines.



Exercise adapted from K. J. Laidler and J. H. Meiser, *Physical Chemistry*, 3rd edition, 1999.