Chemistry 431
Problem Set 3
Fall 2023
Solutions

1. One mole of an ideal monatomic gas at 25.°C and 20. bar pressure is expanded adiabatically against a constant external pressure of 1.0 bar until equilibrium is reached. Calculate $q, w, \Delta U$ and ΔH for the process.
   Answer:
$$\frac{3}{2}nR(T_f - 298\text{ K}) = -1.0\text{ bar}\left(\frac{nRT_f}{P_f} - \frac{nRT_i}{P_i}\right)$$
$$\frac{3}{2}(T_f - 298\text{ K}) = -\left(T_f - \frac{298\text{ K}}{20}\right)$$
$$T_f = 185\text{ K}$$
$$q = 0$$
$$w = \Delta U = C_V\Delta T = \frac{3}{2}(1\text{ mol})(8.3144\text{ J mol}^{-1}\text{K}^{-1})(185\text{ K} - 298\text{ K}) = -1409\text{ J}$$
$$\Delta H = C_p\Delta T = \frac{5}{3}\Delta U = -2349\text{ J}$$

2. Three moles of an ideal monatomic gas at an initial pressure of 10.0 bar and an initial temperature of 100.°C are expanded adiabatically against a constant external pressure of 2.0 bar until equilibrium is reached. Calculate the final temperature of the gas.
   Answer:
$$w = -P_{ext}(V_f - V_i) = \Delta U = C_V(T_f - T_i)$$
$$-(2.0\text{ bar})\left(\frac{nRT_f}{2.0\text{ bar}} - \frac{nR(373\text{ K})}{10.0\text{ bar}}\right) = \frac{3}{2}nR(T_f - 373\text{ K})$$
$$-(T_f - 74.6\text{ K}) = \frac{3}{2}T_f - 559.5\text{ K}$$
$$\frac{5}{2}T_f = 634.1\text{ K}$$
$$T_f = 253.6\text{ K}$$

3. Calculate $q, w, \Delta U$ and ΔH for the adiabatic reversible compression of 3.0 moles of an ideal diatomic gas from 5.0 liters at 35.°C to 1.0 liter.
Answer:

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$\gamma = \frac{7}{5}$$

$$308 \text{ K}(5)^{2/5} = T(1)^{2/5}$$

$$T = 586 \text{ K}$$

$$q = 0$$

$$w = \Delta U = C_V \Delta T = \frac{5}{2}(3 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(586 \text{ K} - 308 \text{ K}) = 17335 \text{ J}$$

$$\Delta H = C_p \Delta T = \frac{7}{5}\Delta U = 24270 \text{ J}$$

4. A cylinder fitted with a frictionless piston contains 2.00 moles of an ideal monatomic gas at an initial pressure of 5.00 bar and an initial temperature of 298 K. The gas is first expanded adiabatically against a constant external pressure of 1.00 bar until equilibrium is reached, followed by an adiabatic, reversible compression until the final gas pressure equals the initial gas pressure of 5.00 bar. Calculate $q, w, \Delta U$ and ΔH for the overall, two-step process.
Answer:

$$q = 0$$

Step 1

$$w_1 = \Delta U_1 = -P_{ext}\Delta V = C_V \Delta T$$

$$-1.00 \text{ bar}\left(\frac{nRT_f}{1.00 \text{ bar}} - \frac{nR(298 \text{ K})}{5.00 \text{ bar}}\right) = \frac{3}{2}nR(T_f - 298 \text{ K}) \qquad T_f = 203 \text{ K}$$

$$V_f = \frac{nRT_f}{P_f} = \frac{(2.00 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(203 \text{ K})}{1.00 \text{ bar}} = 33.7 \text{ L}$$

Step 2

$$P_i = 1.00 \text{ bar} \qquad V_i = 33.7 \text{ L}$$

$$P_i V_i^{\gamma} = P_f V_f^{\gamma} \quad \text{with} \quad \gamma = \frac{C_P}{C_V} = \frac{5/2\ nR}{3/2\ nR} = \frac{5}{3}$$

$$(1.00 \text{ bar})(33.7 \text{ L})^{5/3} = (5.00 \text{ bar})V_f^{5/3}$$

$$V_f = 12.8 \text{ L} \qquad T_f = \frac{P_f V_f}{nR} = \frac{(5.00 \text{ bar})(12.8 \text{ L})}{(2.00 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})} = 386.\text{ K}$$

Overall

$$q = 0$$

$$\Delta U = w = C_V \Delta T = \frac{3}{2}(2.00 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(386 \text{ K} - 298 \text{ K}) = 2195 \text{ J}$$

$$\Delta H = C_P \Delta T = \frac{5}{3}\Delta U = 3658 \text{ J}$$

5. One mole of an ideal monatomic gas at 1.0 bar pressure and a temperature of 25.°C is taken through the following series of steps:

   (a) A heating at constant volume to 100.°C;

   (b) An adiabatic compression against a constant external pressure of 25. bar until the volume is halved;

   (c) A cooling at constant pressure until the final temperature is 35.°C.

   Calculate $q, w, \Delta U$ and ΔH for the overall process "a" + "b" + "c." [Hint: Think about state functions before solving this problem. Do not "brute force" the solution.]
   Answer:

$$\Delta U = C_V \Delta T = \frac{3}{2}(1 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(10 \text{ K}) = 125 \text{ J}$$

$$\Delta H = C_p \Delta T = \frac{5}{3}\Delta U = 208 \text{ J}$$

$$V_i = \frac{nRT_i}{P_i} = \frac{(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(298 \text{ K})}{1 \text{ bar}} = 24.78 \text{ L}$$

$$q_a = C_V \Delta T = \frac{3}{2}(1 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(75 \text{ K}) = 935 \text{ J}$$

$$q_b = 0$$

$$P_i = (1 \text{ bar})\frac{373}{298} = 1.25 \text{ bar}$$

$$V_i = \frac{nRT}{P} = \frac{(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(373 \text{ K})}{1.25 \text{ bar}} = 24.81 \text{ L}$$

$$V_f = 0.5V_i = 12.39 \text{ L}$$

$$-25 \text{ bar}(12.39 \text{ L} - 24.81 \text{ L}) = \frac{3}{2}(1 \text{ mol})(0.08314 \text{ L bar mol}^{-1}\text{K}^{-1})(T - 373 \text{ K})$$

$$T = 2863 \text{ K}$$

$$q_c = C_p \Delta T = \frac{5}{2}(1 \text{ mol})(8.3144 \text{ J mol}^{-1}\text{K}^{-1})(308 \text{ K} - 2863 \text{ K}) = -53108 \text{ J}$$

$$q = q_a + q_b + q_c = -52173 \text{ J}$$

$$w = \Delta U - q = (125 \text{ J} + 52173 \text{ J}) = 52298 \text{ J}$$

6. 2.00 moles of an ideal diatomic gas at a temperature of 298.K and a pressure of 5.00 bar are expanded adiabatically against a constant external pressure of 2.00 bar until equilibrium is reached. The gas is then compressed adiabatically and reversibly until the change in the enthalpy ΔH for the two step process (first expansion, then compression) is 0. Calculate the final volume after the completion of the two-step process.
Answer: Step 1

$$\Delta U = C_V(T_f - T_i) = w = -P_{ext}\left(\frac{nRT_f}{P_{ext}} - \frac{nRT_i}{P_i}\right)$$

$$\frac{5}{2}nR(T_f - 298.\text{ K}) = nR\left(-T_f + T_i\frac{P_{ext}}{P_i}\right)$$

$$\frac{5}{2}T_f - 745.\text{ K} = -T_f + 119.2\text{ K} \qquad T_f = 247.\text{ K}$$

$$\text{After Step 1} \quad V = \frac{nRT}{P} = \frac{(2.00\text{ mol})(0.08314\text{ L bar mol}^{-1}\text{K}^{-1})(247.\text{ K})}{2.00\text{ bar}} = 20.5\text{ L}$$

Overall Process, final temperature:

$$\Delta H = 0 \qquad \text{for the overall process, so that} \qquad T_f = 298.\text{ K}$$

Reversible, adiabatic step

$$T_iV_i^{\gamma-1} = T_fV_f^{\gamma-1}$$

$$T_i = 247.\text{ K}, T_f = 298.\text{ K}, V_i = 20.5\text{ L}, \gamma - 1 = \frac{7}{5} - 1 = \frac{2}{5}$$

$$247.(20.5\text{ L})^{2/5} = 298.V_f^{2/5} \qquad V_f = 12.8\text{ L}$$

7. Two containers are joined together as in the Joule experiment. One contains 1.0 moles of He at 75.°C, and the other contains 2.0 moles of N_2 at 25.°C. The gases are allowed to diffuse into each other adiabatically. Assuming the gases to be ideal, what is the final temperature of the system?
Answer:

$$\Delta U = 0 = C_{V,He}\Delta T_{He} + C_{V,N_2}\Delta T_{N_2}$$

$$\frac{3}{2}(1\text{ mol})R(T_f - 348\text{ K}) + \frac{5}{2}(2\text{ mol})R(T_f - 298\text{ K}) = 0$$

$$T_f = 310\text{ K}$$