

CHEM 3410: Physical Chemistry I — Fall 2009

**Homework 2 — Model Solutions**

1. (a) The process is performed at a constant pressure (P), so the work can be calculated as follows:

$$w = - \int P dV = -P \int V = -P\Delta V = (5 \text{ atm})(1 \text{ L} - 4 \text{ L}) = 20 \text{ L} \cdot \text{atm}$$

We would like to get our work in the same units as the give heat flow (in Joules). Remembering the gas constant,  $R$ , in both units allows us to convert:

$$20 \text{ L} \cdot \text{atm} \times \frac{8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}}}{0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}} = 2025 \text{ J}$$

$$\boxed{w = 2025 \text{ J}}$$

From the first law, we know that  $\Delta U = q + w$ , so:

$$\Delta U = -5000 \text{ J} + 2025 \text{ J}$$

$$\boxed{\Delta U = -2975 \text{ J}}$$

- (b) The initial and final temperature are the only two parameters we do now know. Using the ideal gas law, we can find them both. For example, the initial temperature is:

$$T_i = \frac{PV}{nR} = \frac{(5 \text{ atm})(5 \text{ L})}{(1 \text{ mole})(0.0821 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}})} = 305 \text{ K}$$

Similarly, the final temperature is 61 K.

$$\boxed{T_i = 305 \text{ K and } T_f = 61 \text{ K}}$$

- (c) i. For the roundabout process, the starting and ending states is the same as the direct process in part (a). Since internal energy is a state function, the change is the same for both processes.

$$\boxed{\Delta U = -2975 \text{ J}}$$

- ii. It is easiest to find the total work done in roundabout process since we know that for steps 1 and 3,  $dV = 0$  and therefore  $w_1 = w_3 = 0$ . For the second step, the work can be calculated in the same way as part (a), but using a different constant pressure, namely 1 atm.

$$w = - \int P dV = -P \int V = -P\Delta V = (1 \text{ atm})(1 \text{ L} - 4 \text{ L}) = 4 \text{ L} \cdot \text{atm}$$

Converting to Joules we get:

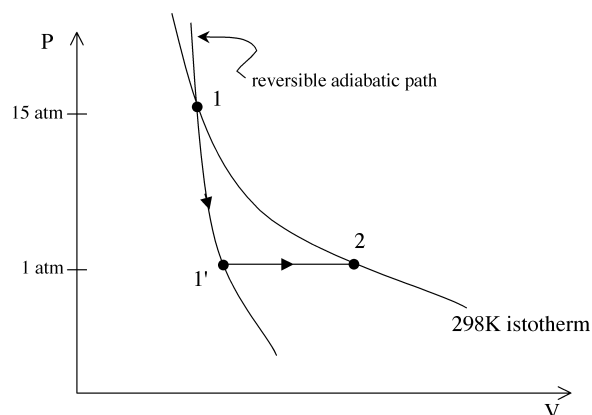
$$\boxed{w_{total} = w_3 = 405 \text{ J}}$$

It is now fairly straightforward to find  $q$  for the roundabout process since we know both  $\Delta U$  and  $w$ :

$$q = \Delta U - w = -2975 \text{ J} - 405 \text{ J} = -3380 \text{ J}$$

$$\boxed{q = -3380 \text{ J}}$$

This result shows that even though internal energy is a state function, the values for the work done and the heat flow are both path dependent.



2. For this problem we are dealing with an diatomic ideal gas, so  $C_p = \frac{7}{2}R$  and  $C_v = \frac{5}{2}R$ . The process would look something like the figure above when the pressure is plotted versus the volume.

We can consider each step in the process separately.

1 to 1' A good place to start would be to determine the number of moles of gas we are working with. We have T, P, and V of the initial state, so using the ideal gas law we can determine the number of moles of gas in our sample. Remember, we have to use  $R$  in the correct units. Since we are given the volume in cubic meters, it will be helpful to use Pa for pressure (1 atm = 101,325 Pa):

$$n = \frac{PV}{RT} = \frac{(15 * 101325 \text{ Pa})(1 \text{ m}^3)}{(8.314 \text{ J/molK})(298)} = 615 \text{ moles}$$

Now we can find  $P$ ,  $V$ , and  $T$  for the final state (1') using the information about the initial state. For an adiabatic expansion (thermally insulated) the relationship between the initial and final states is given by Equation 2.44:

$$P_i V_i^\gamma = P_f V_f^\gamma$$

where  $\gamma = \frac{C_p}{C_v} = \frac{7}{5}$ . Using the heat capacities for a diatomic ideal gas we get the final volume to be:

$$V_f^\gamma = \frac{P_i V_i^\gamma}{P_f} = \frac{(15 * 101325 \text{ Pa})(1 \text{ m}^3)^{\frac{7}{5}}}{101325 \text{ Pa}}$$

$$V_f = 6.92 \text{ m}^3$$

With ideal gas law, we can find the final temperature, giving us the following values for P, V, and T:

Table 1: default

	1	1'
P (Pa)	$1.52 \times 10^6$	$1.01 \times 10^5$
V ( $\text{m}^3$ )	1	6.919
T (K)	298	137

We can now find the work done in going from state 1 to 1' in one of two ways. It is important to remember that the work is **not** a state function, so its value is path dependent.

Method 1: Use the definition of PV work. This involves a bit of integration, but isn't too scary. We can write  $P$  as a function of  $V$  using Equation 2.44 as above:

$$PV^\gamma = P_1 V_1^\gamma$$

$$P = P(V) = \frac{P_1 V_1^\gamma}{V^\gamma}$$

Simple expansion expression work is given by:

$$w = \int_1^{1'} -PdV = \int_1^{1'} -\frac{P_1V_1^\gamma}{V^\gamma}dV = -P_1V_1^\gamma \int_1^{1'} \frac{dV}{V^\gamma}$$

Performing the integration:

$$w = \left[ \frac{P_1V_1^\gamma}{\gamma-1} \left( \frac{1}{V^{\gamma-1}} \right) \right]_1^{1'} = \frac{P_1V_1^\gamma}{\gamma-1} \left( \frac{1}{V_1'^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right)$$

Inserting values from the table above, we get:

$$w = -2.03 \text{ MJ}$$

Method 2: It is an adiabatic expansion of an ideal gas, so  $q = 0$ . Therefore:

$$\Delta U = q + w = w$$

But for an ideal gas, the internal energy is only a function of temperature:

$$\Delta U = w = \int nC_v dT$$

Assuming  $C_v$  is constant over our temperature range, this reduces to:

$$w = nC_v\Delta T = nC_v(T_{1'} - T_1)$$

Inserting out values from the table above, we get:

$$w = -2.03 \text{ MJ}$$

Thankfully, the answers are identical. Both approaches are valid. The first is more general and would work in most cases. The second is a special case since we are dealing with an ideal gas.

1' to 2 This step is done at constant pressure, so it is a bit more straight forward than above:

$$w = \int_{1'}^2 -PdV = -P \int_{1'}^2 dV = -P(V_2 - V_{1'})$$

To find  $V_2$  we can use the ideal gas law again:

$$V = \frac{nRT}{P} = 15 \text{ m}^3$$

So,

$$w = -1.01 \times 10^5 (15 \text{ m}^3 - 6.919 \text{ m}^3)$$

$$w = -819 \text{ kJ}$$

The total work done in both processes is then:

$$-2030 \text{ kJ} + -819 \text{ kJ} = -2849 \text{ kJ}$$

The sign of the work done in each step and the over all process should make sense. The gas is expanding, therefore it is doing work on the surroundings and work is “flowing” out of the system, hence the negative sign.