

Problem Set 3A (due 9PM Tuesday, 1/17/12)

Q1) 1-mol sample of an ideal gas for which $C_{v,m} = \frac{3}{2}R$ undergoes the following two step process:

- a) From an initial state of the gas described by $T = 28^\circ\text{C}$ and $P = 2.0 \cdot 10^4 \text{ Pa}$, the gas undergoes an isothermal expansion against a constant external pressure of $1.0 \cdot 10^4 \text{ Pa}$ until the volume has doubled. Calculate q , w , and ΔU for this step of the process.

Begin with all the information up front: EoS, Laws 1A, 1B and definition of work.

$$PV = nRT \quad \Delta U = w + q \quad \Delta U = C_v \Delta T \quad w = -P_{ext} \Delta V$$

The process is one step, Iso-T, $P_{ext} = P_2$ from I.G. E.o.S.

$$\Delta U = 0 = w + q \Rightarrow q = -w = P_{ext} \Delta V = P_2 \Delta V$$

$$P_1 V_1 = P_2 V_2 = nRT = 8.3 \cdot 301 = 2.5 \text{ kJ}$$

$$P_2 \Delta V = P_2 V_2 - P_2 \frac{P_1}{P_2} V_1 = P_2 V_2 \left(1 - \frac{P_1}{P_2} \right) = \frac{1}{2} P_2 V_2$$

$$w = -\frac{1}{2} nRT = -1.25 \text{ kJ} \quad q = 1.25 \text{ kJ}$$

- b) Subsequently, the gas is cooled at constant volume (isochoric). The temperature falls to -40.5°C . Calculate q , w , and ΔU for this step of the overall process.

Use the same basic information as part a, system goes from state 2 to state 3.

Identify the process, Iso_V Beginning and End Temps are given so ΔU is knowable, and w can be easily determined because P is lowered to follow T , but $DV=0$ so the work is zero:

$$\Delta U = C_v \Delta T = w + q \quad \text{and} \quad w = -P_{ext} \Delta V = 0$$

$$V_3 = V_2 \quad \text{and} \quad T_2 P_3 = P_2 T_3$$

$$\Delta U = q = C_v \Delta T = -8.3 \cdot 68.5 = -0.57 \text{ kJ}$$

Heat is withdrawn from the system as internal system energy (the gas molecules slow down) and no work is done in the environment.

- c) Calculate q , w , and ΔU for the overall process.

We just add up the values of q , w , and ΔU from the two individual steps. For some suggestions on notation, we can use numbers to define the states and letter to label the transformation. So change A takes us from state 1 to state 2 and change B goes from state 2 to state 3.

$$\Delta U = \Delta U_A + \Delta U_B = -0.57 \text{ kJ}$$

$$w = w_A + w_B = -1.25 \text{ kJ}$$

$$q = q_A + q_B = +1.25 \text{ kJ} - 0.57 \text{ kJ} = +0.68 \text{ kJ}$$

Q2) Energy can be put into a gas by heating. The increase in temperature is related to the increase in internal energy according to the heat capacity.

- a) If one mole of an ideal monoatomic gas is raised from 25°C to 125°C how much does the internal energy of the gas increase?

$$C_{v,m} = \frac{3}{2}R \quad \Delta T = +100\text{K}$$

$$\Delta U = nC_{v,m} \cdot \Delta T = 1 \cdot \frac{3}{2} \cdot 8.3 \cdot 0.1\text{kJ} = 1.25\text{kJ}$$

- b) If the gas of part a is a diatomic molecule how much does the internal energy increase for the same temperature change.

For an ideal diatomic C_{vm} increases to $5/2R$

$$C_{v,m} = \frac{5}{2}R \quad \Delta T = +100\text{K}$$

$$\Delta U = nC_{v,m} \cdot \Delta T = 1 \cdot \frac{5}{2} \cdot 8.3 \cdot 0.1\text{kJ} = 2.08\text{kJ}$$

- c) Explain why the change is different for the two different types of gas.

The diatomic has more degrees of freedom (per molecule) being a more complicated molecule, and each of those DoFs can absorb the heat (transferred in) as internal energy when the temperature rises. Because heat is transferred in at constant volume there is no work so $\Delta U = q_v$.

- d) The heat capacity of a material is often somewhat temperature dependent. Use the temperature dependence of the heat capacity of chlorine gas (a diatomic molecule) to estimate the change in its internal energy when the temperature of one mole of chlorine gas is raised from 25°C to 125°C .

$$C = a + bT + cT^2$$

$$a = 25.635 \text{ J/mol-K}, \quad b = 10.144 \cdot 10^{-3} \text{ J/mol-K}^2, \quad c = -40.38 \cdot 10^{-7} \text{ J/mol-K}^3$$

Compare your result to part b. [Hint, again we use the principle $\Delta U = \int dU$]

$$C(T) = a + bT + cT^2$$

$$\Delta U = \int dU = \int_{T_1}^{T_2} C(T) dT = a\Delta T + b\frac{1}{2}(T_2^2 - T_1^2) + c\frac{1}{3}(T_2^3 - T_1^3)$$

$$\text{let } \bar{T} = \frac{1}{2}(T_1 + T_2)$$

$$\Delta U = a\Delta T + b\bar{T}\Delta T + c\frac{1}{3}(T_2^2 + T_1T_2 + T_1^2)\Delta T$$

$$\Delta U = \left\{ a + b\bar{T} + c\left(\bar{T}^2 + \frac{\Delta T^2}{12}\right) \right\} \Delta T = \left\{ C(\bar{T}) + c\left(\frac{\Delta T^2}{12}\right) \right\} \Delta T$$

Applying this “simplified” form to the example at hand, $C(\bar{T} = 348K) = 28.68 \text{ J/mole-K}$ and the “extra” term is $c\left(\frac{\Delta T^2}{12}\right) = -0.0034 \text{ J/mole-K}$. The extra term is inconsequential. The energy change in the chlorine is $\Delta U = 2.9 \text{ kJ}$, compared to the idea of 2.1 kJ in part B. Some of the additional modes of the gas are accessed.

Q3) Consider the gas in question 1, part a for which we found q , w , and ΔU . For the same gas, and a similar process compute the q , w , and ΔU . For (the same gas and same final and ending T and P as question 1a) one mole of a monoatomic gas that goes isothermally from an initial state described by $T = 28^\circ\text{C}$ and $P = 2.0 \cdot 10^4 \text{ Pa}$, to a state where the pressure of the gas is $1.0 \cdot 10^4 \text{ Pa}$. The process by which the change occurs is reversible: that is, the pressure is very slowly reduced so that the reversible path may be used.

- a) Compare the work done by the system for this process with the work done in question 1a. Which is “larger” and why?
b)

Solve for the work done by the gas as it expands two fold for isothermal reversible work:

$$PV = nRT \quad \Delta U = w + q \quad \Delta U = C_v \Delta T \quad w = -P_{ext} \Delta V$$

$$\Delta U = C_v \Delta T = 0 \Rightarrow q = -w$$

$$w = -\int P_{ext} dV = -\int P dV = -\int \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

$$w = -nRT \ln \frac{P_1}{P_2} = -nRT \cdot 0.7 = -1.75 \text{ kJ}$$

The reversible work is larger in that the irreversible work in that it is a larger negative number, so $-w_{Iso-T}^{Rev} > -w_{Iso-T}^{Irr-Rev} = -\frac{1}{2} nRT$

- c) Compare the heat transferred for this process and that in question 1a.

The heat is transferred into the system in both cases (endothermic process), but the heat under the reversible path is larger, because to do more work you need more heat. No energy comes from the gas in the container.

- d) Compare the energy change for the system for this process and that in question 1a.

There is no energy change for either process because the temperature is held constant.

- e) Comment on which parameters are different and which are the same and why.

The work and heat are both different because they depend on path. The energy change depends only on the start and final state of the system, which are the same for these two processes. Even if ΔU had not been zero, which will be the case for a real gas, it would have to be the same because the two processes connect the same two states of the system.

Q4) Now consider one mole of an ideal gas for which $C_{v,m} = \frac{3}{2}R$. From an initial state of the gas described by $T = 28^\circ\text{C}$ and $P = 2.0 \cdot 10^4 \text{ Pa}$, the gas undergoes an adiabatic expansion against a constant external pressure of $1.0 \cdot 10^4 \text{ Pa}$ until internal pressure equals the external pressure. In an adiabatic expansion $q = 0$ because no heat is transferred either in or out of the system.

- a) Write down the equation of state, the general equations for Law 1A (the first law) and Law 1B (the relation of the energy to the thermodynamic parameters), and the work. This represents your starting point.

$$\text{EoS: } PV = nRT$$

$$\text{Law 1A: } \Delta U = w + q$$

$$\text{Law 1B: } \Delta U = C_v \Delta T$$

$$\text{Work: } w = -P_{\text{ext}} \Delta V$$

- b) Develop a general expression that relates the temperature change ($\Delta T = T_2 - T_1$) and the pressure change, which can include the start and end pressures and temperatures (and the heat capacity) but not the volumes. [You have enough expressions to equate the work and the internal energy change and using the EoS remove the volume dependence.] This gives you an equation for the temperature drop, and you should know everything else.

$$PV = nRT$$

$$C_v \Delta T = \Delta U = w = -P_2 \Delta V = -(P_2 V_2 - P_2 V_1)$$

$$\frac{C_v}{nR} \Delta T = -\left(T_2 - \frac{P_2}{P_1} T_1\right) = -\left(T_2 - T_1 - \left(\frac{P_2}{P_1} T_1 - T_1\right)\right)$$

$$\frac{3}{2} \Delta T = -\left(\Delta T - \frac{\Delta P}{P_1} T_1\right)$$

$$\left(\frac{3}{2} + 1\right) \Delta T = \frac{\Delta P}{P_1} T_1$$

- c) Determine the final temperature and comment on why you expect the temperature to go up or down.

$$\left(\frac{3}{2}+1\right)\Delta T = \frac{\Delta P}{P_1}T_1 = -\frac{1}{2}T_1$$

$$\Delta T = -\frac{1}{5}T_1$$

$$T_2 = \frac{4}{5}T_1 = 240K$$

- d) Determine the new volume. Compare the volume change to the result in question 1a in which the volume doubled. Did you expect the final volume to be larger or smaller than that in 1a?

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

$$V_2 = V_1 \frac{P_1}{P_2} \frac{T_2}{T_1} = V_1 \cdot 2 \cdot \frac{4}{5} = 1.6 \cdot V_1$$

Because the temperature dropped, from the I.G. EoS then the volume will not double: In this case the volume increased by 60% not 100%, because the temperature dropped by 20%.

- e) Compare the amount of work done in this (adiabatic) process with that in 1a (the isothermal process). [As a hint: The ratio of these two works is 5/3, not specifying which is which.] In both cases the work is one-step against the same constant pressure.

Both cases start at the same state and use the same final pressure, but the final volume is different as well as the final temperature.

$$w = -P_{ext}\Delta V$$

| | |
|-------------------|------------------|
| <i>Isothermal</i> | <i>Adiabatic</i> |
|-------------------|------------------|

| | |
|-----------------------|-----------------------|
| $w = -P_2(V_2 - V_1)$ | $w = -P_2(V_2 - V_1)$ |
|-----------------------|-----------------------|

| | |
|---------------|------------------|
| $w = -P_2V_1$ | $w = -0.6P_2V_1$ |
|---------------|------------------|

| | |
|-------------------------|------------------------|
| $w = -\frac{1}{2}nRT_1$ | $w = -0.3 \cdot nRT_1$ |
|-------------------------|------------------------|

The isothermal process can do more work, $-w_{IsoT} > -w_{Adia}$, because it can garner heat energy from the environment and use that to do productive work ($w=-q$). Whereas the adiabatic case must use the internal energy of the gas to do all the work. ($w=DU$).