Chemistry 456A (10:30AM Bagley 154)

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Problem Set 3B (due 9PM Wednesday, 1/25/12)

Q1) In the previous homework we compared isothermal one-step, irreversible work with reversible isothermal work. We also compared a one-step isothermal process and a one-step adiabatic process. Now we compare a one-step adiabatic, irreversible process with a reversible, adiabatic process. Let's consider that both of these processes start from the same P,V,T, called $P_1 V_1 T_1$, for both processes and end at the new pressure is $P_2 = \frac{1}{3} P_1$ for both the reversible and irreversible adiabatic expansions.

. Consider this gas to be an ideal gas with heat capacity $C_V = \frac{3}{2} nR$. [As a practice of your algebraic skills you might try leaving all the quantities in terms of $c = \frac{C_V}{nR}$ before you evaluate final answers.] The questions we consider are will the two systems end up at the same final state? And will the processes give us different amounts of heat, work and energy change?

Q1a) To help organize thinking about this we want to compare the equations: EoS, First Law (Part A), Energy Change (First Law part B), Work. These expression are fundamental to all problems and are very general, and are the same as done for the isothermal case, or any other problem involving the ideal gas.

Relation	
EoS	
First Law (Part A)	
Work	
Internal Energy Change (First Law Part B)	

Q1b) Now adapt the general rules to the specific cases of adiabatic expansion:

Relation	Reversible Adiabatic	Irreversible (1Step) Adiabatic
EoS		
First Law (Part A)		
Work		
Heat		
Internal Energy Change (First Law Part B)		
Relation of T to V		

Q1c) Of the above relations, for the reversible and irreversible processes which one is the key one that distinguishes between reversible and irreversible adiabatic process?

Q1d) Explain why the work cannot be greater than an upper bound: $|w| < C_V T_1$.

Q1e) Using the fact that $P_2 < P$, which means the pressure along the reversible path is always greater than the one on the irreversible path, to explain, qualitatively, why one will get more work from one case than the other.

Q1f) Use the premise that the work obtained from the system following the reversible path is greater than that from the irreversible path (i.e. $-w_{Adiabatic}^{Reversible} > -w_{Adiabatic}^{Irreversible}$) to explain qualitatively why the final temperature of the irreversible expansion must be larger than that of the reversible expansion.

Q1g) Qualitatively explain why the volume of the irreversible expansion will be different from that of the reversible expansion. Will the volume expansion for the reversible process be larger than that of the irreversible process? [You might check with the quantitative results below.] Hint: To reason through this assume the reversible path does more work so that the temperature drop must be larger for the reversible process and use the EoS to tell you whether this means the final volume of the irreversible process must be larger or smaller than that of the reversible process.

Q1h) Quantitatively determine the temperature ratio ${T_2}/{T_1}$ and the volume ratio ${V_2}/{V_1}$ for the reversible case. It is always true that for the I.G.: $\frac{P_2}{P_1}\frac{V_2}{V_1} = \frac{T_2}{T_1}$

Q1i) Quantitatively determine the temperature ratio ${T_2}/{T_1}$ and the volume ratio ${V_2}/{V_1}$ for the irreversible case.

Q1j) Summarize the quantitative results and discuss in qualitative terms what you expected for the relative temperature and volume ratios for the two processes. Use the temperature ratios to qualitatively describe the relative amount of work done by both processes.

Q1k) Draw a P-V diagram (which may require redoing your old one) for these two cases, taking into account what you learned above. Label V2 for the reversible and irreversible cases and compare with V2 for isothermal expansion. Block out the areas under the curves that correspond to the work in both adiabatic cases.

Q2) Compare the irreversible (one-step) adiabatic expansion with the reversible adiabatic expansion. Assume the system starts at pressure P_1 and drops to pressure P_2 in both processes and that $P_2 = \frac{1}{3}P_1$ and that the gas is an ideal monatomic gas $C_V = \frac{3}{2}nR$. To show that the irreversible work is less than the reversible work prove that $\frac{w_{one-step}}{w_{reversible}} = \frac{3}{4}$ for these two processes independent of the values of T_1 or V_1, or n. The work ratio only depends on the pressure ratio and no other quantity (excluding the fraction from the heat capacity).

Q3) We stated a general relation between $\left(\frac{\partial U}{\partial V}\right)_T$ and the state variables, called the T.EoS (Thermodynamic Equation of State) $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$. (Eqn 3.19 in Text)

Q3a) Evaluate $\left(\frac{\partial U}{\partial V}\right)_T$ For the van der Waal's gas in terms of P,V and T.

Q3b) Compare this result with that of the ideal gas.

Q4) a) Starting with the two parts of the first law of thermodynamics show that $\left(\frac{\partial U}{\partial T}\right)_V = C_V$ for a gas or any other system where the work done is only PdV work.

b) Using the relation in part A and assuming Cv is independent of temperature show that we recover the result of the ideal gas expression that, for a constant volume process, relates ΔU and ΔT. [For the I.G. is this relation restricted to just isochoric processes?]

c) If C_V depends on temperature, how do you in general find ΔU for a constant volume process?

d) Consider another form of energy, H=U+PV, and again assume only PdV work, then show that the heat transferred under constant pressure conditions must be q sub p and it must be dH, and therefore $\left(\frac{\partial H}{\partial T}\right)_P = C_p = \frac{q_P}{\Delta T}$.

Q5) This problem is closely related to problem P3.20 of your text. Because U is a state function we know Euler's test for a state function (also called a Maxwell Relation):

$$\left(\frac{\partial\left(\frac{\partial U}{\partial T}\right)_V}{\partial V}\right)_T = \left(\frac{\partial\left(\frac{\partial U}{\partial V}\right)_T}{\partial T}\right)_V$$

a) Using this relationship, show that the heat capacity, C_V, is independent of volume for an ideal gas; that is show that $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$.

b) Using the same relation, show that $\left(\frac{\partial C_V}{\partial V}\right)_T = 0$ for a van der Waals gas.

c) Can you suggest (from your text) another type of non-ideal gas where it is not the case that the heat capacity is independent of the volume of the gas?