

CH352 Assignment 3: Due Thursday, 27 April 2017

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Q1 Adiabatic quasi-static volume and temperature changes in ideal gases

In the last assignment you showed that the internal energy of a mono-atomic ideal gas sample containing N particles was proportional to the temperature, T and N , so that $U = \frac{3}{2}Nk_B T$. Since the heat capacity at constant volume is $C_V = (\partial U / \partial T)_{V,N}$, $C_V = \frac{3}{2}Nk_B$ for an ideal gas. Thus, in this system, we find $dU = C_V dT$.

- (i) Use the above result and the differential form of the fundamental energy equation, $dU = T dS - p dV$, (assuming fixed N) to obtain an expression for the differential entropy change dS in a general, constant- N , ideal gas process.
- (ii) Consider a quasi-static transformation of an N -particle sample of ideal gas, and re-express your result for dS from (i) for this special case ideal gas process.
- (iii) Integrate your result from (ii) to obtain a general expression for the entropy change $\Delta S = S_2 - S_1$ accompanying the quasi-static, fixed- N transformation from (T_1, V_1) , to (T_2, V_2) .
- (iv) In an adiabatic quasi-static expansion of an ideal gas, how do you reconcile the following two facts: (1) the increase in volume should lead to an increase in entropy, but (2) in an adiabatic process $\delta q = 0$ so there should be no change in entropy (since $dS = \delta q / T = 0$)?

Q2 The work of compression

One mole of a van der Waals gas is compressed quasi-statically and isothermally from V_1 to V_2 . For a van der Waals gas the equation of state is

$$p = \frac{RT}{(V-b)} - \frac{a}{V^2} \quad (\text{Q2.1})$$

where a and b are positive constants of the gas, V is the volume, and RT is the gas constant times temperature. The constant b is related to the excluded volume of each gas molecule, and a is related to the strength of intermolecular attraction between molecules.

- (i) Write an expression for the work done.
- (ii) Compared to compression of an ideal gas, is more or less work required in the low density limit? What about the high density limit? Why?

Q3 Ideal efficiency of a car engine

Suppose the compression ratio in your car engine is $V_2/V_1 = 8$. For a diatomic gas, $C_V = (5/2)Nk_B$ and for ethane $C_V \sim 5Nk_B$.

- (i) What is the efficiency of your engine if the working fluid is a diatomic gas?
- (ii) Which is more efficient: a diatomic gas or ethane?
- (iii) Would your engine be more or less efficient with a higher compression ratio?

Q4 Computing enthalpy and entropy with a temperature dependent heat capacity

The heat capacity of liquid *n*-butane depends on temperature:

$$C_p(T) = a + bT \quad (\text{Q4.1})$$

where $a = 100 \text{ J K}^{-1} \text{ mol}^{-1}$ and $b = 0.1067 \text{ J K}^{-2} \text{ mol}^{-1}$ from its freezing temperature $T_f = 140 \text{ K}$ to $T_b = 270 \text{ K}$, its boiling temperature.

- (i) Compute ΔH for heating liquid butane from $T_A = 170 \text{ K}$ to $T_B = 270 \text{ K}$ at constant pressure.
- (ii) Compute ΔS for the same process.

Q5 Objects in thermal contact and enthalpy of vaporization of water at $T = 473 \text{ K}$

- (i) Suppose two objects *A* and *B* with heat capacities C_A and C_B and initial temperatures T_A and T_B , are brought into thermal contact. If $C_A \gg C_B$ is the equilibrium temperature closer to T_A or T_B or is not enough information given? What about if $c_A \gg c_B$? Show some math to support your argument.
- (ii) Suppose you want to know how much heat it would take to boil water at $p = 1 \text{ atm}$ and $T = 473 \text{ K}$, rather than at $T = 373 \text{ K}$. At $T = 373 \text{ K}$ the enthalpy of vaporization is $\Delta H_{\text{boil}}(T = 373 \text{ K}) = 40.7 \text{ kJ mol}^{-1}$. Assuming that the heat capacities of the liquid ($C_{p,\text{liquid}} = 75 \text{ J K}^{-1} \text{ mol}^{-1}$) and the vapor ($C_{p,\text{vapor}} = 3.5 \text{ J K}^{-1} \text{ mol}^{-1}$) are constant over this temperature range, calculate the enthalpy of vaporization at $T = 473 \text{ K}$, $\Delta H_{\text{boil}}(T = 473 \text{ K})$.

Q6 Oxygen gas at room temperature

Consider a gas phase system of N identical, indistinguishable, independent oxygen atoms, with partition function Q . Suppose the single particle partition function is the product of a translational partition function q_t and an electronic partition function q_e , so

$$q = q_t q_e. \quad (\text{Q6.1})$$

The nine electronic states of the lowest energy 3P electronic level are split due to spin-orbit coupling. Table 1 lists various characteristics of these states as well as some of the higher energy levels. Data are reported for $T = 300$ K, and for convenience energies are given in Kelvin units.

Table 1: Atomic oxygen electronic energy level characteristics

$^{2S+1}L_J$	$g = 2J + 1$	$(\Delta\epsilon_n/k_B)/\text{K}$	$\beta\Delta\epsilon_n$	$(\beta\Delta\epsilon_n)^2$
3P_2	5	0	0	0
3P_1	3	232	0.7733	0.5980
3P_0	1	348	1.16	1.3456
1D_2	5	22 860	76.2	
1S_0	1	48 621	162.1	

- (i) Use the fact that the internal energy is

$$U = -\frac{1}{Q} \frac{\partial Q}{\partial \beta} \quad (\text{Q6.2})$$

to show that

$$U = -N \left(\frac{1}{q_t} \frac{\partial q_t}{\partial \beta} + \frac{1}{q_e} \frac{\partial q_e}{\partial \beta} \right) = U_t + U_e \quad (\text{Q6.3})$$

- (ii) Calculate (a) the translational component of the internal energy U_t and (b) the translational component of the constant volume heat capacity:

$$C_V^t = \left(\frac{\partial U_t}{\partial T} \right)_{N,V}. \quad (\text{Q6.4})$$

- (iii) (a) Comment on why we can neglect the contributions from the states 1D_2 and 1S_0 at room temperature and calculate the general expression in this case for (b) the electronic component of the internal energy U_e and (c) the electronic heat capacity

$$C_V^e = \left(\frac{\partial U_e}{\partial T} \right)_{N,V} = -k_B \beta^2 \left(\frac{\partial U_e}{\partial \beta} \right)_{N,V}. \quad (\text{Q6.5})$$

- (iv) You should be able to write your results from (ii) and (iii) in the form $C_V = Nk_B \times x$ where x is some dimensionless number. Compute these dimensionless numbers for C_V^t and, using the data in table 1 for $T = 300$ K, C_V^e at this temperature. From this, you can get an idea of how big the spin-orbit contribution to the heat capacity is compared to the translational heat capacity for atomic oxygen at room temperature.