University of Washington
Department of Chemistry
Chemistry 453
Winter Quarter 2015

Homework Assignment 2

Due at midnight on Monday 01/19/15. Show calculations as well as answers.

1) Multiple integrals are used to determine the average properties of a particle moving in three dimensions. The average kinetic energy of a monatomic ideal gas molecule moving in three dimensions is:

$$\langle E\rangle = \frac{m\langle v^2\rangle}{2} = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{mv^2}{2}f(v)\,dv_x dv_y dv_z = \left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\frac{mv^2}{2}e^{-mv^2/2k_BT}dv_x dv_y dv_z$$

a) Evaluate this integral in spherical coordinates and calculate the average energy of helium gas at T=1000K. Hint: Use the transformations $v^2 = v_x^2 + v_y^2 + v_z^2$ and $dv_x dv_y dv_z = v^2 \sin\theta dv d\theta d\varphi$, and the standard integral $\int_0^\infty x^{2n}e^{-ax^2}dx = \frac{1\times3\times5\cdots(2n-1)}{2^{n+1}a^n}\sqrt{\frac{\pi}{a}}$. See Lecture 1 for details.

b) Using you result in part a, calculate the root mean square velocity of helium gas at T=1000K. Using the standard integral form $\int_0^\infty x^{2n+1}e^{-ax^2}dx = \frac{n!}{2a^{n+1}}$ calculate the average velocity $\langle v\rangle$ for helium gas at T=1000K. Hint: Calculate the integral using spherical coordinates.

c) The most probable velocity is the velocity at the maximum of the distribution curve which in spherical coordinates is $4\pi v^2 f(v)$ where $f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}$.

Determine the most probable velocity of helium at T=1000K by solving the equation $\frac{d}{dv}\left(4\pi v^2 f(v)\right) = 0$.

2) Consider a system composed of 4 energy levels. Consider the following 4 distributions of 10 particles amidst these energy levels:

Distributions	N_1	N_2	N_3	N_4	W	S(JK^{-1})
1	10	0	0	0		
2	8	1	1	0		
3	6	2	1	1		
4	4	3	2	1		

a) Calculate the degeneracy W for each of these distributions and insert your answer in the column marked W.. Based on these calculations, which distribution is the most probable?
b) Using your values for W, calculate the entropy per molecule for each of these distributions.
c) Calculate the difference in entropy ΔS between the most probable and least probable distributions.

3) A system is composed of six particles. Each particle can have one of two energy values: $E_1 = 0J$ or $E_2 = 1.00\times10^{-20} J$.

a) Assuming the two energy values given above, list all the possible energies that result when you distribute six particles into a two energy level system. Hint: You can figure out the number of such energies using a Pascal triangle.

b) For each energy listed in part a, calculate the number of microstates. Hint: Again, a Pascal triangle is useful for this task.

c) Calculate the corresponding entropy S/Nk_B for each state.

4) A two level system again has energy level values $E_1 = 0J$ and $E_2 = \varepsilon = 5.00\times10^{-22} J$. Assume there is one microstate with energy E_1 and four microstates with energy E_2.

a). Using your expression for the single particle partition function q for a two level system calculate the internal energy U per mole for T=1000.K

b) Suppose the temperature changes from T=1000.K to T=5000.K. Calculate the change in internal energy ΔU .

c) Using the formula $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ and the expression for U in terms of q, and your expression for q in part a, obtain an expression for the heat capacity for a two level system. Using this expression calculate the value of the heat capacity of a two level system composed of one mole of particles, $\varepsilon = 5.00\times10^{-22} J$, and T=1000.K.

d) Assume the particles are distinguishable such that $Q = q^N$. Calculate the entropy for one mole of particles in this two level system again for $\varepsilon = 5.00\times10^{-22} J$, and T=1000.K. Assume the temperature changes to T=5000K. Calculate the change in entropy ΔS per mole.

5) Repeat the calculations in problem 4 for an energy ladder. Assume the ground state E_0=0J and the energy spacing of the ladder is ΔE= $\varepsilon = 5.00\times10^{-22} J$.