CHEM352: Physical Chemistry I / Fall 2020
Problem Set IV - due 15^{th} of Dec, 5.00 pm

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20 points total/2 points per problem

1. According to the latest basic rules of the PowerBall® lottery game (https://en.wikipedia.org/wiki/Powerball), winning the lottery requires selecting correctly both 5 of 69 (white balls) and 1 of 26 balls (red Powerball).
   (a) Calculate the odds of winning the lottery.
   (b) Calculate the odds of predcicting correctly 3 white balls and 1 powerball.
   (c) If one bet is 2$, what is a minimum prize pool that justifies playing the game? (Disregard 'powerplay'.)

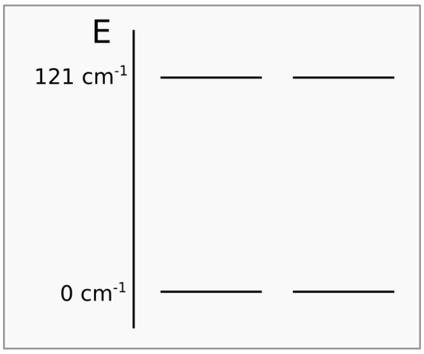
2. Consider Maxwell-Boltzmann velocity distribution in one dimentsion:

$$P(v)dv = C \cdot v^2 \cdot e^{-mv^2/2kT} dv$$

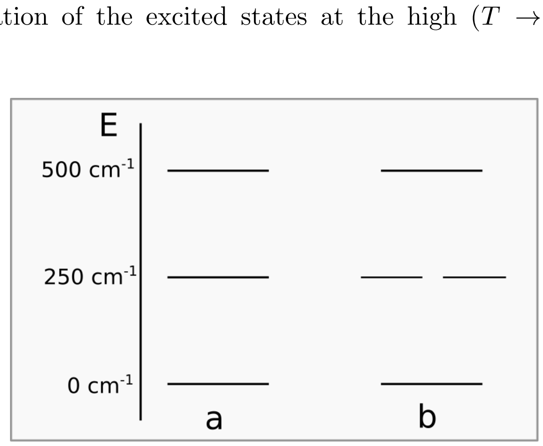
   (a) Determine the normalization constant C
   (b) Deteremine $< v >$, $< v^2 >$ and the variance $< \sigma >^2 = < v^2 > - < v >^2$.
   (c) Determine the most probable velocity.

   Solutions to respective integrals you can find in your favorite pchem/calculus book, web-search engine, or social-media channel.

3. Simplified electronic energy diagram for radical ·N=O molecule is shown below. Determine the occupation of the excited state at 100, 298 and 3000 K.



4. The figure below shows energy diagram for two model systems: (a) the system has three non-degenerate energy states available and (b) the system has three states available,one of them being doubly degenerate.
   (a) At what temeprature the occupation of the second energy level is equal to 0.25?
   (b) What is the population of the excited states at the high ($T \to +\infty$) and low ($T \to 0$) temperature limits



5. Discuss the molecular interpretation of the 3^{rd} law of thermodynamics.

6. A gas absorbed on a surface can sometimes be modelled as a two-dimensional ideal gas which partition fuction is given by:

$$Q(N, A, T) = \frac{1}{N!} \left(\frac{2\pi m k_B T}{h^2} \right)^N A^N \tag{2}$$

where A is the area of the surface.

   (a) Derive the expression for $< E >$ and compare with the three-dimensional result. Next, calculate the heat capacity of 2-dimensional gas.
   (b) Derive the entropy of 2-dimensional ideal gas. Compare it to the entropy of 3-dimensional ideal gas.

7. The vibrational energy of a molecule can be written as:

$$E_{vib} = N k_b \sum_{j=1}^{\alpha} \left(\frac{\Theta_{vib,j}}{2} + \frac{\Theta_{vib,j} e^{-\Theta_{vib,j}/T}}{1 - e^{-\Theta_{vib,j}/T}} \right) \tag{3}$$

Where Θ_{vib} is a vibrational temperature ($\frac{h\nu}{T}$), α is total number of vibration and k_b is a Boltzmann constant ($k_b = 0.695$ cm^{-1}/K).

Starting from this equation:

   (a) Discuss the temperature-dependence of the heat capacity C_v of a diatomic molecule.
   (b) Derive a relation for the heat capacity $C_v = \left(\frac{\partial E_{vib}}{\partial T}\right)_v$ and show that the vibrational heat capacity goes to R for $T \to +\infty$

8. Calculate the conribution of each component (translational, rotational and vibrational, neglect electronic) to the partition energy funcion of CO_2 at 500K in volume of 8 nm^3. The vibrations energies are 1388, 667.4 (doubly degenerate) and 2349 cm^{-1}. The rotational constant is 0.39 cm^{-1}. (Use excel to manage this calculations).

9. Using the answer from the previous problem, calculate energy and heat capacity and Gibbs energy of CO_2 at 500K in cavity of 8 nm^3. Show the individual contributions to the Gibbs energy. Which vibrations contribute the most to the heat capacity and how it compares to translational and vibrational contributions?

10. Detertmine the equilibrium constant for the sodium dissociation at 500K (again, use excel to manage the calculations):

$$Na_{2(g)} \rightleftarrows 2Na_{(g)} \tag{4}$$

where B=0.155 cm^{-1}, $\bar{\nu} = 159$ cm^{-1} and dissociation energy is 70.4 kJ/mol, and ground-state energy-degeneracy of sodium atom is 2.