CHEM352: Physical Chemistry I — Exam III - 18^{th} of Dec, 2018

Name: _____

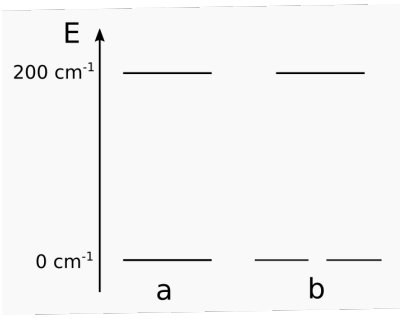
Answer all questions in the space provided. Show all work with ink, no white-outs, use back of the page when needed. Unexplained answers will not receive credit.

The exam consist of 5 questions, 25 points each. Only 4 highest score questions will make the final score.

Total - 100 Pts.

Problem I — 25 Pts

Imagine two systems, (a) a two-level system and (b) two-level system with a doubly-degenerate ground state, both separated from the excited state by 200 cm^{-1}:



1. Calculate the occupation of the excited state in both systems at 200K.
2. At what temperature, the occupation of the excited state in the ground-state degenerate system (b) equals occupation of the excited state in the non-degenerate system (a) at 200K?
3. What is the occupaion of the excited states in both systems at high temperature limits ($T \to +\infty$)

In calculations, use $k = 0.695$ cm^{-1}/K.

Problem II **25 Pts**

The partition function of a I_2 molecule in a gas phase is given by:

$$q^{I_2} = \left(\frac{V}{\Lambda^3}\right)\left(\frac{\bar{k}T}{2\bar{B}}\right)\left(\frac{1}{1-e^{\frac{\bar{\nu}}{\bar{k}T}}}\right) \tag{1}$$

Where $\bar{k} = 0.695$ cm^{-1}/K ($\bar{k} = \frac{k}{hc}$), $\bar{B} = 0.037$ cm^{-1} and $\bar{\nu} = 217$ cm^{-1}. Derive the expression for the molar heat capacity (you can derive contributions due to translations, rotations and vibrations separately) and sketch an approximate diagram of $C_{v,m}$ as a function of temperature.

Problem III **25 Pts**

Entropy of an ideal monoatomic gas is given by Sackur-Tetrode equation:

$$S = nR \ln \left[\frac{e^{5/2} V}{\Lambda^3 N} \right] \tag{2}$$

where $\Lambda^3 = \left(\frac{h^2}{2\pi m k T} \right)^{3/2}$. Please compute the difference in molar entropy between two noble gases, argon and krypton (molar mass 39.95 u and 83.8 u respectively). Explain the sign.

Problem IV **25 Pts**

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Consider the following sets of population for four equally spaced energy levels:

ϵ/k [K]	set A	set B	set C
300	5	3	4
200	7	9	8
100	15	17	16
300	33	31	32

1. Demonstrate that the sets have the same energy.
2. Determine which of the setcs is the most probable. (Don't compute 60!, rather use ratios or stirling approx)
3. Is the most probable set cosistent with a Boltzmann distribution?

Problem V **25 Pts**

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Discuss contributions from four energetic degrees of freedom to the total energy of NO molecule at 300K. The rotational cosnstant and vibrational frequency are $\bar{B} = 1.67$ cm^{-1} and $\bar{\nu} = 1904$ cm^{-1} respectively. Spacing between doubly degenerate electronic energy levels is 121 cm^{-1}). Molar mass of NO is 30 g/mol. (By discussing, I mean showing temperature limits, absolute contibutions to the total energy, you don't have to compute stuff(.