(*University of Choice*)

MASINDE MULIRO UNIVERSITY OF SCIENCE AND TECHNOLOGY (MMUST)

MAIN CAMPUS

UNIVERSITY EXAMINATIONS

2021/2022 ACADEMIC YEAR

FOURTH YEAR SECOND SEMESTER SPECIAL/SUPPLEMENTARY EXAMINATIONS

FOR THE DEGREE OF BACHELOR OF SCIENCE (CHEMISTRY)

COURSE CODE: **SCH 441**

COURSE TITLE: **STATISTICAL THERMODYNAMICS**

DATE: 03/08/2022 **TIME:** 8-10 a.m .

INSTRUCTIONS TO CANDIDATES

- Answer all the Questions

TIME: 2 Hours

MMUST observes ZERO tolerance to examination cheating

This Paper Consists of 4 Printed Pages. Please Turn Over.

Useful information

h= 6.626 x 10^{-34} Js dS=dq/T, S= klnW I = μr^2 k_B = 1.381 x 10^{-23} JK^{-1} R= 8.314 $JK^{-1}mol^{-1}$

Atomic mass unit = 1.661 x 10^{-27} kg dU=dq+dw $\int_0^\infty e - u\, dU$ =[-e^u]

$$W = \frac{N!}{n1!n2!...} \quad S = R\, In[\frac{(2\pi mkBT)}{h^3}^{3/2} \frac{kBT}{P} e^{5/2}] \quad S = R\, Inq + R \quad q = \frac{8\pi^2 IkBT}{\sigma h^2}$$

$$\frac{n_2}{n_1} = \frac{g_2 e^{-\varepsilon_2/k_B T}}{g_1 e^{-\varepsilon_1/k_B T}} \qquad q_{trans} = \left[\frac{(2\pi m k_B T)^{1/2} L}{h}\right]^3 = \frac{(2\pi m k_B T)^{3/2} V}{h^3} \qquad q = \sum_i g_i e^{-\varepsilon_i/k_B T}$$

$$S = -R\ln(1 - e^{-hv/kBT}) + R\frac{hv}{kBT}\frac{1}{e^{hv}/kBT-1} \qquad q_{vib} = \frac{1}{1 - e^{-hv/k_B T}}$$

E_{rot} =J(J+1)$h^2/8\pi^2 I$ J=0, 1, 2,... B=h/$8\pi^2$I, 1GHz = 10^9Hz

QUESTION ONE (20 MARKS)

a. Distinguish between mutually exclusive and mutually inclusive cases giving a relevant example in each case (4 marks)

b. Describe the significance of the molecular partition function.

(4 marks)

c. Calculate the partition translational partition function of N_2 at 298 K in a container of volume 10.0 cm^3. (N_2 28.02 amu) (4 marks)

d. Explain the difference in entropy values for neon and argon at the same temperature.

(4 marks)

e. Explain whether temperature is a macroscopic or microscopic concept (4 marks)

QUESTION TWO (15 MARKS)

a. Given that the bond length is 1.128 Å, calculate the ratio of J = 1to J= 0 populations for carbon monoxide as $T \rightarrow \infty$ ($I=1.46 \times 10^{-46} kgm^2$) (8 marks)

b. Consider a Nitrogen molecule. The frequency for Nitrogen is 7.08 x 1013s-1. For 1 mole of the molecules, calculate the number of Nitrogen molecules in the $\upsilon=0$ and $\upsilon=1$ at 298K (7 marks)

QUESTION THREE (20 MARKS)

a. The rotational energy of a linear rotor is hBJ (J+1) and the degeneracy of each level is 2J+1. For HCl, B=318 GHz at 25°C . Calculate the relative numbers of molecules with J=2 and J=1. Provide a detailed explanation for the values obtained. (10 marks)

b. A hypothetical system consists of quantum states with energies of 0, ε, 2ε,...., with the populations of the states determined by the Boltzmann distribution.

i) Show that, at a temperature of T=ε/k, the populations of the first four excited states relative to that of the lowest state are 37%, 14%, 5%, and 1%, with the population of all higher states being negligible (6 marks)

ii) What is the total energy of a quantum system described in i) above that consists of 100 molecules (4 marks)

QUESTION FOUR (15 MARKS)

a. The translational partition function of helium at at 1 bar in a 1.00 m^3 is 7.75 x 10^{30}

i) Explain whether this motion can be treated classically or quantum mechanically (1 mark)

ii) What happens to the motion when translational partition function is equals to ten (1 mark)

iii) Calculate the temperature when the motion changes from classical mechanics to quantum mechanics (6 marks)

b. Show that $C_{V\ trans} = [\frac{\partial(U-U_0)}{\partial T}]_V = \frac{3}{2}$ R for a monoatomic gas (7 marks)