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(*University of Choice*)

MASINDE MULIRO UNIVERSITY OF SCIENCE AND TECHNOLOGY (MMUST)

MAIN CAMPUS

UNIVERSITY EXAMINATIONS

2021/2022 ACADEMIC YEAR

FOURTH YEAR SECOND SEMESTER EXAMINATIONS

FOR THE DEGREE

OF

BACHELOR OF SCIENCE (CHEMISTRY)

COURSE CODE: SCH 441

COURSE TITLE: STATISTICAL THERMODYNAMICS

DATE: 26/4/2022 **TIME: 12-2P.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

$e^{-x^2}dx = \sqrt{\pi}/2$

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

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

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

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

$\int_0^\infty e^{-u}du = \left[-e^{-u}\right]_0^\infty$ $K_p = \frac{qB^b}{qA^a} N_A{}^{-\Delta n_e} e^{-\Delta U0/RT}$

QUESTION ONE (20 MARKS)

a. What is the significance of studying statistical thermodynamics? (4 marks)

b. Calculate the number of microstates when 10 molecules are equally distributed among five energy levels. What will be the value of the microstate when one molecule is removed from one state and added to the other? (4 marks)

c. Distinguish between equally likely cases and mutually exclusive cases giving relevant examples in each case (4 marks)

d. Write down the expression for the equilibrium constant of the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ in terms of the molecular partition functions of the reactants and products (4 marks)

e. Evaluate the translational partition function of gaseous CS_2 (76) at 298 K in a container of volume 10.0 cm^3. (4 marks)

QUESTION TWO (15 MARKS)

a. Apply the Boltzmann distribution to deduce the ratio of number of particles in two adjacent degenerate energy states (5 marks)

b. Suppose you have four identical, non-interacting molecules distributed over energy levels and the total energy of the system is restricted to five units.

i) How many macrostates and microstates are present in the system?

ii) What is the relationship between the macrostates in terms of probability?

Illustrate your answer with clear diagrams (10 marks)

QUESTION THREE (20 MARKS)

a. Consider the HCl with a bond length of 1.275Å and frequency of vibration in wavenumbers of 2886 cm-1. Calculate the vibrational contribution to entropy at 298K and 1 bar given that the masses of H and Cl are 1.008 amu and 34.97 amu respectively (5 marks)

b. Given that $qrot = \int_0^{\infty}(2J+1)e^{-J(J+1)h^2}/8\pi^{2IkT\,dJ}$, Show that $qrot = 8\pi^2\,IkT/h^2$

(10 arks)

c. Evaluate the rotational partition function at 298K of $^1H^{35}Cl$ for which the rotational constant is 318 GHz (5 marks)

QUESTION FOUR (15 MARKS)

a. A system consists of three energy levels (ε_0 =0, g_o =4); a first excited level (ε_1=kT, g_1 = 2) and a second excited level (ε_2=4kT, g_2 =2). Calculate the partition function of the system. What is the probability for the second energy level?

(7 marks)

b. Starting from the first law of thermodynamics, show that dG= -SdT +VdP (8 marks)