(University of Choice)

MASINDE MULIRO UNIVERSITY OF SCIENCE AND TECHNOLOGY (MMUST)

MAIN CAMPUS

UNIVERSITY EXAMINATIONS

2022/2023 ACADEMIC YEAR

FOURTH YEAR SECOND SEMESTER EXAMINATIONS

FOR THE DEGREE OF BACHELOR OF SCIENCE (CHEMISTRY)

COURSE CODE: SCH 441

COURSE TITLE: STATISTICAL THERMODYNAMICS

DATE: 11-4-2023 **TIME:** 3-5 P.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

$$W = \frac{N!}{n_1!n_2!....} \bar{S}_{trans} = Rln\left[\frac{(2\pi m k_B T)^{3/2}}{h^3}\frac{k_B T}{P}e^{5/2}\right],$$

$$\bar{S}_{rot} = Rlnq_{rot} + R, \; q_{rot} = \frac{8\pi^2 I k_B T}{\sigma h^2}$$

$$\frac{n_2}{n_1} = \frac{g_2 e^{\varepsilon_2/k_B T}}{g_1 e^{\varepsilon_1/k_B T}} \; E_{rot} = \frac{J(J+1)h^2}{8\pi^2 I} \; J=0,1,2...$$

$$\bar{S}_{vib} = -Rln(1 - e^{-hv/k_B T}) + R\frac{hv}{k_B T}\frac{1}{e^{hv/k_B T} - 1}$$

$$\int_0^\infty e^{-x^2}dx = \sqrt{\pi}/2, \; q = \sum_i g_i e^{\varepsilon_i/k_B T}$$

$$q_{vib} = \frac{1}{1-e^{-\frac{hv}{k_B T}}}, \; q_{trans} = \frac{(2\pi m k_B T)^{3/2}V}{h^3} \; q_{trans} = \int_0^\infty e^{-(\frac{n^2h^2}{8mL^2k_BT})}dn$$

$$lnx! = xlnx - x$$

B=h/$8\pi^2$I, 1GHz = 10^9Hz

QUESTION ONE (20 MARKS)

a. What is the relationship between Quantum chemistry, chemical thermodynamics and statistical thermodynamics? (3 marks)

b. Calculate the number of ways of distributing 20 identical objects with the arrangement 1,0,3,5,10,1. (2 marks)

c. The typical energy difference between successive electronic energy level is 1.0×10^{-17} J. Calculate the ratios of the number of molecules in the two adjacent energy levels. (4 marks)

d. What is the definition of temperature in relation to statistical thermodynamics (4 marks)

e. Explain the difference in entropy values for an element with molar mass of 20.18 $gmol^{-1}$ and 39.95g mol^{-1}. (4 marks)

f. Estimate the q_{vib} for carbon monoxide at 300K given that the fundamental frequency of vibration for CO is 6.4×10^{13} s^{-1} (3 marks)

QUESTION TWO (15 MARKS)

a. Given that $-\ln n_i + \alpha + \beta \varepsilon_i = 0$. Apply the Boltzmann definition of entropy, Second law of thermodynamics and Stirling's approximation to evaluate α and β (10 marks)

b. Consider the equilibrium between A and B as per the equation $A \leftrightarrow B$, deduce an expression for the equilibrium constant when the lowest and higher energy levels are available

(5 marks)

QUESTION THREE (20 MARKS)

a. Consider the following equilibrium system at 1000 K $Na_2(g) \leftrightarrow 2Na(g)$, q_{elec} for Na is 2 and q_{elec} for Na_2 is 1, $P° = 10^5$ N m^{-2}, m=22.99 amu, The reduced mass of Na_2 is 1.1×10^{-26} kg, the moment of inertia is 1.81×10^{-45} kg m^2, the wave number of f Na_2 is 159.1 cm^{-1}. Calculate $\frac{q^2 Na}{qNa_2}$ for the system. (10 marks)

b. Given that $E_n = \frac{n^2 h^2}{8mL^2}$ $n = 1, 2, 3 \ldots$, Show that $q_{trans} = \frac{(2\pi m k_B T)^{3/2} V}{h^3}$

(10 marks)

QUESTION FOUR (15 MARKS)

a. Calculate the rotational contribution to entropy for HCl at 298K and 1 bar, given that the bond length is 1.275Å and the masses of ^1H and ^{35}Cl are 1.0008 and 34.97 amu?

(6 marks)

b. Starting from the first law of thermodynamics, show that dA= -SdT -PdV (5 marks)

c. N_2O and CO_2 have similar rotational constants but strikingly different rotational partition functions. Provide an explanation for this observation (4 marks)