MAASAI MARA UNIVERSITY

REGULAR UNIVERSITY EXAMINATIONS

2021/2022 ACADEMIC YEAR

FOURTH YEAR FIRST SEMESTER

SCHOOL OF PURE APPLIED AND HEALTH SCIENCES

BACHELOR OF SCIENCE IN CHEMISTRY

COURSE CODE: CHE 4144

COURSE TITLE: STATISTICAL THERMODYNAMICS

DATE: 1ST APRIL, 2022 TIME: 1430-1630

INSTRUCTIONS TO CANDIDATES

1. Answer Question **ONE** and any other **TWO** questions.
2. All Examination Rules Apply.
3. Avogardro's costant= 6.022×10^{23} mol^{-1}
4. Gas constant R = 8.314JK^{-1}mol^{-1} = 0.0821 L atm K^{-1} mol^{-1}
5. Plank constant, h, = 6.626×10^{-34} Js
6. Speed of light, c, = c = 2.99×10^{8} Ms^{-1}
7. Mass of an electron = 9.11×10^{-31}Kg
8. Mass of a proton = 1.7×10^{-27} Kg
9. Boltzmann constant = 1.38×10^{-23} JK^{-1}
10. $\pi = 22/7$
11. 1 u = 1.6605×10^{-27} Kg
12. $P^{\theta} = 10^5$ Pa
13. Speed of light, c, = 3.0×10^{8} Ms^{-1}

SECTION A

Question One (30mks)

a) What is the temperature of a two-level system of energy separation equivalent to 300 cm^{-1} when the population of the upper state is one-half that of the lower state **(3mks)**

b) Derive the expression for the partition function of a two-state system with one state at zero and another state at energy E, given that q = $\Sigma e^{-\beta E_i}$ **(3mks)**

c) Explain the following terms;

i) Optical trapping **(2mks)**

ii) Adiabatic demagnetization **(2mks)**

d) Calculate the translational partition function of a hydrogen molecule confined to a 100 cm^3 vessel at 25 ^{o}C. Mass of Hydrogen = 2.016 u. **(4mks)**

e) From $E = \Sigma_i n_i E_i$, show that $E = - Ndq/qd\beta$ **(4mks)**

f) Calculate the translational partition function at 300 K of a molecule of molar mass 120 g mol^{-1} in a container of volume 2.00 cm^3 **(3mks)**

g) Calculate (a) the thermal wavelength, (b) the translational partition function of an Argon atom in a cubic box of side 1.00 cm at 300 K. Mass of argon = 39.948 u. **(5mks)**

h) The mean energy for any mode of motion is given by $\langle \epsilon^m \rangle = -\frac{1}{q^m}\left(\frac{\partial q^m}{\partial \beta}\right)_V$, If the translational partition function is given by; $q^T = \frac{X}{\Lambda}$ where $\Lambda = h(\frac{1}{2\pi m})^{\frac{1}{2}}(\beta)^{\frac{1}{2}}$. Show that $\langle \epsilon^m \rangle = \frac{1}{2}kT$ **(4mks)**

SECTION B

Answer any TWO questions from this section, each question carries 20 marks

Question Two (20mks)

a) Define a canonical ensemble **(1mk)**

b) Evaluate the rotational partition function of H-Cl at 25 ^{o}C given that B = 10.59 cm^{-1}, KT/hC = 207.22cm^{-1} **(3mks)**

c) Calculate the standard molar entropy of Neon gas at 200 K Mass of Neon = 20.1797 u **(5mks)**

d) Define the following terms as used in statistical thermodynamics;

i) A configuration **(1mk)**

ii) The weight of a configuration **(1mk)**

e) Use the equipartition theorem to estimate the constant-volume molar heat capacity of O_3 **(2mks)**

f) Calculate the rotational partition function of SO_2 at 298 K from its rotational constants 2.027 36 cm^{-1}, 0.344 17 cm^{-1}, and 0.293 535 cm^{-1}. σ = 2 **(3mks)**

g) Estimate the molar constant-volume heat capacity of water vapour at 100 °C. Vibrational wave numbers are $3656.7cm^{-1}$, $1594cm^{-1}$ and $3755.8cm^{-1}$. The rotational constants of a water molecule are 27.9, 14.5 and $9.3cm^{-1}$. **(4mks)**

Question Three (20mks)

a) Calculate the rotational partition function of H_2O at 298 K from its rotational constants 27.878 cm^{-1}, 14.509 cm^{-1}, and 9.287 cm^{-1}. $\sigma = 2$ **(3mks)**

b) Calculate the value of $G^{\theta}_m - G^{\theta}_m(0)$ for $H_2O_{(g)}$ at 1500K given that, $q^v = 1.352$, $q^R = 486.7$ and mass of water = 18.015 u. Density of water = $1gcm^{-3}$. **(7mks)**

c) Evaluate the equilibrium constant for the dissociation $Na_{2(g)} \rightleftarrows 2Na_{(g)}$ at 1000K from the following data. $D_o = 70.4$ $Kjmol^{-1}$.

The sodium atoms have doublet ground terms. $P^{\theta} = 1.0 \times 10^5$ Pa **(4mks)**

Λ $(Na_2) = 8.14$ pm Λ $(Na) = 11.5$ pm
q^R $(Na_2) = 2246$ q^V $(Na) = 4.885$
g $(Na_2) = 1$ g $(Na) = 2$

d) Given that $3/2nRT = 3N/2\beta$, show that $\beta = 1/KT$ **(3mks)**

e) Calculate the proportion of I_2 molecules in their second and third vibrational states at 25 ^{O} C. The vibration wave number is 214.6 cm^{-1} **(3mks)**

Question Four (20mks)

a) Calculate the standard molar entropy of xenon gas at 100 K. Mass of Xenon = 131.293 u **(2mks)**

b) Calculate the standard molar entropy of gaseous Argon at 25 $^{\circ}$C. Let $P^{\theta} = 1.0 \times 10^5$ Pa. Mass of Argon = 39.948 u **(3mks)**

c) Given that $p = NKT/q(dq/dV)$, show that $P = nRT/V$ **(3mks)**

d) Determine the expression for proportions of molecules in the ground state, first excited state for a two-level system given that the partition function for a two-level system is given by $q = 1+e^{-\beta E}$ **(3mks)**

e) The wave numbers of three modes of CO_2 modes of vibration are 1388 cm^{-1}, 667 cm^{-1}, and 2349 cm^{-1}. Calculate the Vibrational partition function given that $kT/hC = 1050.42$ cm^{-1}. **(4mks)**

f) Explain the origin of residual entropy **(2mks)**

g) Estimate the rotational partition function of O_2 at 25°C, given that B = . **(3mks)**

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