of a gaseous system of volume V at temperature, T containing N particles of individual mass, m. The canonical partition function for the system is given as, $Q = e^{aT^3.V}$; (a is constant).

c) Estimate the Helmholtz free energy of a system with a set of N localized particles at temperature, T. Consider that each of the particles can exist in four levels of energies, 0, ε, 2ε and 3ε having degeneracies 1, 3, 3, and 1 respectively. 4+3+3

B. Sc. (Chemistry) Examination, 2022

(3rd Year, 6th Semester, CBCS Syllabus)

Chemistry (DSE)

Paper – DSE/Chem/Th/03

Time : Two hours Full Marks : 40

(20 marks for each unit)

(Write answers for each unit separately)

UNIT: 6031-P

1. a) Distinguish between harmonic and anharmonic oscillator with respect to energy, selection rule, and zero point energy. What is the effect of isotopic substitution on microwave spectra of linear diatomic molecules? $2+2\frac{1}{2}$

b) The molecule AB_3 is not active in the microwave region, i.e. no absorption lines are observable. How many absorption lines will be observed in the vibrational and Raman spectra? 2

c) In vibration-rotation spectrum $(v = 0 \rightarrow 1)$ of HF, the rotational constants are found to be slightly differnt, $B_{v=0} = 20{\cdot}6$ cm^{-1} and $B_{v=1} = 19{\cdot}8$ cm^{-1}. Calculate the percentage increase of bond length on going from v = 0 to 1. What effect does this

lengthening of the bond have on the spacing of the lines for the P- and R-branch spectra? $2\frac{1}{2}+2$

d) Explain the rule of mutual exclusion in spectroscopy. "Pure rotational Raman spectrum of linear molecule exhibits first line at 6B cm^{-1} but remaining at 4B cm^{-1}." Justify with proper reasoning. $1\frac{1}{2}+1\frac{1}{2}$

e) The molecule $^{12}C^{32}S$ has been detected in interstellar clouds using microwave spectroscopy. Predict which rotational level in $^{12}C^{32}S$ will have the greatest population at a temperature of 70 K. The masses of the two atoms are $m_C = 12{\cdot}00$ u and $m_S = 31{\cdot}972$ u and the equilibrium bond length of the molecule is 1.534 Å. Note: The Boltzmann constant, k, has a value of $0{\cdot}69503$ cm^{-1} and absolute mass of hydrogen atom $1{\cdot}67343\times10^{-27}$ kg. 3

f) Show that the rate constant of a unimolecular photochemical reaction can be simply expressed by the inverse of lifetime of the reactive species when the reaction with unit quantum yield occurs entirely from the state reached by the absorption. 3

UNIT: 6032-P

2. a) Describe briefly the basic limitations of Classical Thermodynamics.

   b) Define an ensemble and name the ensembles corresponding to a closed and an isolated thermodynamic system. Write a short note on Gamma-phase space and comment on its significance.

   c) The distribution function of classical thermodynamic system of non-interacting diatomic gas is given by, $P_j = \frac{e^{-\beta E_j}}{Q}$. Establish the expression for distribution function associated with the probability that a given molecule in the system is in its k^{th} rotational state. [E_j is the energy of the system in its j^{th} state, Q is the canonical ensemble partition function and $\beta = 1/k_B T$.] 2+4+4

3. a) The vibrational partition function of a diatomic molecule (with vibrational temperature, θ_{vib}) is given as, $q_{vib} = \frac{e^{-\theta_{vib}/2T}}{1-e^{-\theta_{vib}/T}}$.

   Derive an expression for the vibrational contribution to molar specific heat for a gaseous system of such diatomic molecules.

   b) Find an expression for pressure and internal energy