

[4]

- b) Find an expression for pressure and internal energy 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, $Q = B.e^{aT^3.V}$ (a and B : are constants).
- c) Estimate the Helmholtz free energy and internal energy of a system with a set of N localized particles at temperature, T . Consider that each of the particles can exist in three levels of energies, 0 , ϵ , and 2ϵ having degeneracies 1 , 2 and 1 respectively. 4+3+3

Ex/SC/CHEM/UG/DSE/TH/03/2023(S)

B. SC. CHEMISTRY (SPECIAL SUPPLEMENTARY)

EXAMINATION, 2023

(6th Semester)

CHEMISTRY (DSE)

PAPER: DSE/CHEM/TH/03

Time : Two Hours

Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each unit.

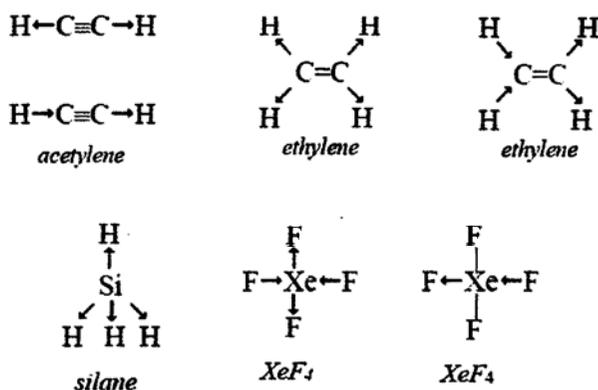
UNIT - 6031-P

1. Answer *all* questions:
- 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 diatomic molecule? 2+3
- b) What is transition moment integral? Explain briefly its significance for the spectroscopic selection rule. 3
- c) C-H stretching vibration in organic compounds occurs near 2900 cm^{-1} . Approximately what wave number would be the C-D stretching vibration? 2
- d) The rotational constant of diatomic AB molecule is 2 cm^{-1} . If the atom A has two isotopes while the atom B has three isotopes then how many absorption lines will be observed in $1-10\text{ cm}^{-1}$ region in the pure rotational spectrum of this molecule? 2

[Turn over

[2]

- e) Which of the following normal modes are infrared active and which are Raman active? The arrows indicate the movement of the exterior atoms. In the asymmetric stretches, the central atoms also move to maintain a fixed center of mass, but that movement is not shown. 3



- f) Explain various classification of photochemical reactions according to the nature of potential energy surface. 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. 2+3

[3]

UNIT - 6032-P

2. a) Mention briefly the basic limitations of Classical Thermodynamics.
- b) Define an ensemble and name the ensembles corresponding to an open and an isolated thermodynamic system. Write a short note on most commonly referred 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} vibrational 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,

$$q_{\text{vib}} = \frac{e^{-\theta_{\text{vib}}/2T}}{1 - e^{-\theta_{\text{vib}}/T}};$$

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