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BR—376—2016

FACULTY OF SCIENCES

M.Sc. (Second Year) (Third Semester) EXAMINATION

OCTOBER/NOVEMBER, 2016

(Revised Course)

PHYSICAL CHEMISTRY

Paper XVI (CH 534/3A)

(Statistical Thermodynamics)

(Wednesday, 23-11-2016) **Time : 2.00 p.m. to 5.00 p.m.**

Time—Three Hours *Maximum Marks*—50

N.B. :— (*i*) Attempt *All* questions.

(*ii*) Use of calculator is allowed.

1. Solve any *five* : 10

(*a*) Derive an expression for Lagrange method of undetermined multiples.

(*b*) Derive an expression $N_o/N_p = 0$.

(*c*) The Debye characteristic temperature for Al and Cu are 308 K and 315 K respectively. Calculate atomic specific heat of Al and Cu at one absolute temperature.

(*d*) Derive an expression for entropy for diatomic molecules.

(*e*) Give an account of residual entropies.

(*f*) Prove for a homonuclear diatomic molecule with spin I is (2I + 1)

(*g*) Explain Maxwell-Boltzmann statistics.

P.T.O.

(*h*) Derive an expression :

$$Z_v = \frac{\exp\ (-h\nu / 2kT)}{[1 - \exp\ (-h\nu / kT)]}$$

2. Solve any *four* : 10

(*a*) Explain thermodynamic characteristics of the crystalline solids.

(*b*) Explain relation between chemical potential pressure and partition function.

(*c*) What is ideal solution ? Derive equation of Raoult's law.

(*d*) Calculate the possible number of ways of distribution, 3 particles among 5 energy states, when :

(*i*) particles are fermions

(*ii*) particles are bosons.

(*e*) Derive an expression for entropy of an ideal gas molecule.

(*f*) Explain ortho and para nuclear states.

3. Solve any *two* : 10

(*a*) Derive an expression for Fermi-Dirac statistics.

(*b*) Calculate the ratio of number of particles at 25°C in energy levels separated by :

(*i*) 5 kcal mol^{-1}

(*ii*) 150 kJ mol^{-1}

(*c*) Deduce equation for Bose-Einstein Statistics.

4. Solve any *two* : 10

(*a*) Explain mean distribution and mean square deviation.

(*b*) Explain in brief nuclear spin statistics of deuterium.

(*c*) Show that :

$$E = \tfrac{1}{2} CN_{AA}W_{AA} + \tfrac{1}{2} CN_{BB}W_{BB} + CN_{AB}W'$$

for binary mixture of two liquids A and B.

5. (A) Select the *correct* alternative from the following : 5

(*i*) The group of states of higher nuclear spin degeneracy is called ..... .

(*a*) Ortho (*b*) Para

(*c*) Both (*a*) and (*b*) (*d*) None of these

(*ii*) Heat capacity is ..... characteristic of solid.

(*a*) Thermal (*b*) Physical

(*c*) Chemical (*d*) None of these

(*iii*) A boson is ..... .

(*a*) proton (*b*) $^{19}_{9}F$

(*c*) $^{4}_{2}H$ (*d*) $_{8}O^{18}$

(*iv*) The percent of ortho hydrogen at T = 0K is ..... .

(*a*) 50% (*b*) 25%

(*c*) 75% (*d*) 100%

P.T.O.

(*v*) The unit of molecular partition function is ..... .

(*a*) cm^{-1} (*b*) s^{-1}

(*c*) $JK^{-1}\ mol^{-1}$ (*d*) dimensionless

(B) Write short notes on any *two* : 5

(*a*) Brownian movement

(*b*) Stirling approximations

(*c*) Internal rotation of polyatomic molecules.