Birla Institute of Technology & Science, Pilani, Rajasthan 333 031
First Semester 2022-2023

Course Number: CHEM G553 **Course Title: Advanced Physical Chemistry** **Marks: 25**
Comprehensive Examination **Date: 26th December, 2022** **Time: 120 mins.**
(CLOSED BOOK)

Useful Data: *Given are commonly used values, notations have usual meanings;* $m_e = 9.109\times10^{-31}$ *kg, , h =* 6.626×10^{-34} *Js, e =* 1.602×10^{-19} *C,* $R_H =$ 109680 cm^{-1} c = 2.998 x 10^8 ms^{-1}, I J = 1 kg m^2 s^{-2}, $m_H =$ 1.008 amu ; $R = 8.314\, JK^{-1}mol^{-1}$; $0\,K = -273\ ^oC$; $Boltzmann\ constant, k = 1.381\times10^{-23} JK^{-1}$; $1\ amu = 1.6605\times10^{-27} kg$; $c = 3.0\times10^8\ ms^{-1}$; 1 eV = $1.602\times10^{-19} J$

Q. 1. (a) A photochemical reaction, $A \rightarrow B + C$, the quantum efficiency with 550 nm light is $1.2\times10^2\,mol$ $einstein^{-1}$. After exposure of 180 *mmol A* to the light, 1.5 *mmol B* is formed. The number of *moles of photons* absorbed by *A* is, **[3M]**

(A) 1.5×10^{-5} einstein **(B)** 1.25×10^{-5} einstein

(C) 1.5 einstein **(D)** 80000 einstein

(b) Suppose the reaction $A \rightarrow B$ is driven by light absorption and that its rate is I_a, but the reverse reaction $B \rightarrow A$ is bimolecular and second-order with a rate $k[B]^2$. So, for the 'photostationary state' find which of the following statement is correct? **[2M]**

(A) $[B] = \left(\frac{k}{I_a}\right)^{1/2}$ **(B)** $[B] = \left(\frac{k}{I_a}\right)^2$ **(C)** $[B] \propto A^{1/2}$ **(D)** $[B] \propto A^{-1/2}$

(c) Which one of the following statements is correct regarding the kinetic chain length (λ) in chain polymerization? **[2M]**

(A) $\lambda = \frac{number\ of\ activated\ centres\ produced}{number\ of\ monomer\ units\ consumed}$ **(B)** $\lambda = \frac{rate\ of\ propagation\ of\ chains}{number\ of\ monomer\ units\ consumed}$

(C) $\lambda = \frac{rate\ of\ production\ of\ radicals}{number\ of\ activated\ centres\ produced}$ **(D)** $\lambda = \frac{rate\ of\ propagation\ of\ chains}{rate\ of\ production\ of\ radicals}$

Q.2. (a) Show that two sp^2 orbitals on the same atom are orthogonal. Given the expressions of the two sp^2 orbitals are $\Psi_I = s + (3/2)^{1/2} P_x - (1/2)^{1/2} P_y$ and $\Psi_{II} = S - (3/2)^{1/2} P_x - (1/2)^{1/2} P_y$ (where the terms have usual meaning). **[3M]**

(b) Write all possible terms for ground state and first excited state of magnesium (At. No = 12).

[3M]

(c) Fill up the table below predicting the electronic configuration of Na, N and O atoms in $NaNO_2$ and $NaNO_3$. Briefly comment on your result. **[2+1=3M]**

Molecule/atoms	Na	N	O
$NaNO_2$			
$NaNO_3$			

(d) When ultraviolet radiation of wavelength 58.4 nm from a helium lamp is directed to a sample of krypton, electrons are ejected with a speed of 1.59×10^6 m/s. Calculate the ionization energy of krypton (in eV). **[3M]**

Q.3. Isotopic substitution changes the rotational energy levels of a molecule. This phenomenon can be used for precise evaluation of the atomic weight of isotopes. The first line (J = 0) in the pure rotational spectrum of $^{12}C^{16}O$ and $^{13}C^{16}O$ are found to be 3.84235 and 3.67337 cm^{-1}, respectively. Calculate the precise atomic weight of ^{13}C given that the precise atomic weight of ^{16}O is 15.9994 and that of ^{12}C is 12.011. (Consider the molecules as rigid rotor and isotopic substitution does not affect the bond length).

[6M]

END

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First Semester 2022-2023

Course Number: CHEM G553 **Course Title: Advanced Physical Chemistry** **Marks: 15**
Comprehensive Examination **Date: 26th December, 2022** **Time: 60 mins.**
(OPEN BOOK)

Useful Data: *Given are commonly used values, notations have usual meanings; m_e = 9.109×10^{-31} kg, , h = 6.626×10^{-34} Js, e = 1.602×10^{-19} C, R_H =* 109680 cm^{-1} c = 3 x 10^8 ms^{-1}, I J = 1 kg m^2 s^{-2}, m_H = 1.008 amu ; $R = 8.314\ JK^{-1}mol^{-1}$; $0\ K = -273\ ^oC$; $Boltzmann\ constant\ , k = 1.381 \times 10^{-23} JK^{-1}$; $1\ amu = 1.6605 \times 10^{-27} kg$; $c = 3.0 \times 10^8\ ms^{-1}$

Q.1. (a) The molecule A has two conformations (A_I and A_{II}) separated by an energy difference of 5 kJmol^{-1} with A_{II} being the high energy conformation. Calculate the relative population of A_I and A_{II} (i.e., $N_{A_{II}}/N_{A_I}$) at (i) 100 K (ii) 200 K and (iii) 300 K, and comment on the variation in the relative population with temperature in one sentence. **[3M]**

(b) Calculate the two possible energies of the ^{1}H nuclear spin in a uniform magnetic field of 5.50 T. Also calculate the ratio of populations of these two states in equilibrium at 300 K. (Given the ^{1}H nuclear g factor g_N = 5.5854 and nuclear magneton μ_N = 5.051 x 10^{-27} JT^{-1}). **[3M]**

Q.2. (a) Consider the chemical reaction for the formation of 1 mole of H_2O. Complete the following thermodynamic table, and with the help of the table predict whether the reaction is spontaneous at T = 298 K. Explain the physical significance of the 'TΔS^0' product in one sentence. At T= 298 K, the thermodynamic quantities are: **[2M]**

Thermodynamic Quantity	**H_2**	**0.5 O_2**	**H_2O**	**ΔH^0 and ΔS^0**
Enthalpy (H^0/kJ)	------	------	-285.83	------
Entropy (S^0/JK^{-1})	130.68	102.57	69.91	------

(b) One mole of He is mixed with 2 moles of Ne, both at the same temperature and pressure. Calculate ΔS for the process if the total volume remains constant. **[3M]**

(c) A compound having molecular formula $C_4H_8O_2$ gives the following spectral data and respond to iodoform test.

(i) IR Absorption peaks

(a) Sharp peak at 1720 cm^{-1}

(b) Broad peak at 3300 cm^{-1}

(ii) ^{1}HNMR data when dissolved in $CDCl_3$

(a) A doublet at δ 1.35

(b) A sharp singlet at δ 2.15

(c) A broad singlet at δ 3.75

(d) A quartet at δ 4.25.

From the above information, propose a structure for the compound and assign all the spectral data given.
[0.5x6 + 1 = 4M]

END