

Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
Comprehensive Examination, First Semester, AY: 2017-2018
CHEM G553: Advanced Physical Chemistry,

Time: 60 min. (Total: 180 min.) Part – A (Close Book) Marks: 45 (Max. Marks: 120)

Name: _____ ID: _____ Marks _____

There are 15 questions, each of 3 Marks. Attempt all the questions. Pencil should not be used. Don't scribble on the question paper.

Useful data: $h = 6.63 \times 10^{-34} \text{ J s}$; Velocity of light = $2.998 \times 10^8 \text{ ms}^{-1}$; Mass of the electron = $9.1 \times 10^{-31} \text{ kg}$,
 $1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$

- 1) Are the following function eigenfunctions of the operator $\frac{d^2}{dx^2}$ and if so, what is the corresponding eigen value? i) $\cos(3x+5)$ and ii) e^{3x+5}
- 2) What would be the outcome(s) of \widehat{L}_Z operator on the following hydrogen atom orbital. Determine the probability of each outcome(s).
$$\psi = \frac{1}{81\sqrt{2\pi}} \left(\frac{Z}{a_0}\right)^{3/2} (Zr/a_0)^2 \exp(-Zr/3a_0) \sin^2\theta \sin 2\phi$$
- 3) H_2O_2 may exist in three different conformations depending on the dihedral angle d_θ ($d_\theta = \angle \text{H-O-O-H}$). Those three conformers can be represented by (i) $d_\theta = 0^\circ$, (ii) $d_\theta = 90^\circ$, and (iii) $d_\theta = 180^\circ$. Comment on rotational activity of the individual conformers.
- 4) Write down the form of the Hamiltonian for a particle having mass m confined to move in one-dimensional box of length l .

- 5) Write down three main differences between the fluorescence and phosphorescence.
- 6) Determine the number of normal mode of vibration in C_2H_2 and D_2O_2 molecule.
- 7) If an electric motor produced 25 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings per seconds. Determine the change in the internal energy of the motor each second.
- 8) Obtain an expression for the entropy change of a sample of perfect gas when it expands isothermally from a volume V_i to a volume V_f .

9) "Change in entropy upon heating will be greater when the energy is transferred to a cold body than when it is transferred to a hot body" – Explain this statement in brief using the concept of statistical view of entropy.

10) Write down the expression for K_P^0 for: $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

11) Consider an ideal gas undergoes an isothermal change of state from pressure P_1 to P_2 . Fill in the blank: $\mu(T, P_2) = \dots + \dots$

12) The unit of the rate constant of a zero order reaction is

- 13) The rate of reaction for $2 \text{NO}(\text{g}) + \text{O}_2 (\text{g}) \rightarrow 2\text{NO}_2 (\text{g})$ is given by (in terms of all the components)
- 14) Determine f for a system consisting of solid glucose in equilibrium with an aqueous solution of glucose.
- 15) The chemical shift of the CH_3 protons in $\text{CH}_3\text{CH}_2\text{Y}$ is $\delta=1.26$ and that of the CH_2 protons is 3.46. What is the difference in local magnetic field between two regions of the molecule when the applied field is 19.5 T?

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