

Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031  
Comprehensive Examination (make-up), 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)

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Name: \_\_\_\_\_ ID: \_\_\_\_\_ Marks \_\_\_\_\_

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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 =  $9.1 \times 10^{-31} \text{ kg}$ ,  
 $1 \text{ amu} = 1.66054 \times 10^{-27} \text{ kg}$

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- 1) Are the following function eigenfunctions of the operator  $\frac{d^2}{dx^2}$  and if so, what is the corresponding eigen value? i)  $\sin(8x+5)$  and ii)  $e^{8x+5}$
  
- 2) What would be the outcome(s) of  $\widehat{L}_z$  &  $\widehat{S}_z$  operators on the hydrogen atom  $2p_y$  orbital. Determine the probability of each outcome(s).
  
- 3) 1,4-dihydroxybenzene may exist in three different conformations depending on the dihedral angle  $d_\theta$  ( $d_\theta = \angle \text{H-O-O-H}$ ). 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) What would be the magnitude of momentum of a particle 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 vibrations in  $X_2Y_2$  molecule. Also predict the number of stretching mode vibrations in the same molecule.
- 7) Determine  $\Delta_{rxn}G^\circ$  and  $\Delta_{rxn}G$  for the following reaction at  $25^\circ\text{C}$ .  
 $2\text{CO}(\text{g}, 0.650 \text{ bar}) + \text{O}_2(\text{g}, 34 \text{ bar}) \leftrightarrow 2\text{CO}_2(\text{g}, 0.0250 \text{ bar})$   
( $\Delta_f G^\circ(\text{CO}_2 \text{ at } 25^\circ\text{C}) = -394.35\text{kJ/mol}$ ;  $\Delta_f G^\circ(\text{CO at } 25^\circ\text{C}) = -137.16\text{kJ/mol}$ )
- 8) What is the change in entropy when 1 g of benzene,  $\text{C}_6\text{H}_6$ , boils reversibly at its boiling point of  $80.1^\circ\text{C}$  and a constant pressure of 1 atm. The heat of vaporization of benzene is 395 J/g.

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  $P_i$  to  $P_f$ . Fill in the blank:  $\mu(T, P_f) = \dots + \dots$

12) The integrated rate law for a 2nd order reaction of the type  $A \rightarrow P$  is

- 13) The rate of reaction for  $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$  is given by (in terms of all the components)
- 14) Determine  $f$  for a system consisting of solid 1,4-dihydroxybenzene in equilibrium with an aqueous solution of 1,4-dihydroxybenzene.
- 15) The chemical shift of the  $\text{CH}_3$  protons in  $\text{CH}_3\text{CH}_2\text{Y}$  is  $\delta=1.56$  and that of the  $\text{CH}_2$  protons is 3.76. What is the difference in local magnetic field between two regions of the molecule when the applied field is 16.5 T?

\*\*\*\*\*End\*\*\*\*\*