2018

M.Sc.

1st Semester Examination

CHEMISTRY

PAPER—CEM-101 (Old)

Full Marks : 40

Time : 2 Hours

The figures in the margin indicate full marks.

Candidates are required to give their answers in their own words as far as practicable.

Illustrate the answers wherever necessary.

(Physical Chemistry)

Group—A

Answer *four* questions taking
one question from each of these pairs
(Q1, Q2), (Q3, Q4), (Q5, Q6), (Q7, Q8) 4×2

1. If $\left[\hat{A},\hat{B}\right]=0$ and $\left[\hat{A},\hat{C}\right]=0$ then which of the following necessarily holds

(a) $[\hat{B},\hat{C}]=0$ (b) $[\hat{A},\hat{B}\hat{C}]=0$

(c) $[\hat{B},\hat{A}\hat{C}]=0$ (c) $[\hat{C},\hat{A}\hat{B}]=0$

2. Which of the following is not a suitable un-normalized wave function for the excited 1s'2s' electronic configuration of the Helium atom ?

(a) $[1s(1)\ 2s(2)-2s(1)\ 1s(2)]\ \beta(1)\ \beta(2)$

(b) $[1s(1)\ 2s(2)+2s(1)\ 1s(2)]\ [\alpha(1)\ \beta(2)-\beta(1)\ \alpha(2)]$

(c) $[1s(1)\ 2s(2)+2s(1)\ 1s(2)]\ [\alpha(1)\ \beta(2)]$

(d) $[1s(1)\ 2s(2)-2s(1)\ 1s(2)]\ [\alpha(1)\ \beta(2)+\beta(1)\ \alpha(2)]$

3. The letters 'PHILOSOPHY' are written separately one on each card. The ten cards are shuffled. Calculate the probability of obtaining the word 'Philosophy'.

4. Give one example each of Boson and Fermion.

5. What is fugacity co-effiicient? What is it's utility?

6. What is the degeneracy of the rotational energy level with $J=4$ for a heteronuclear diatomic molecule?

7. Define grand canonical ensemble.

8. State the basic principle of cyclic voltametry.

Group—B

Answer *four* questions taking
one question from each of these pairs
(Q9, Q10), (Q11, Q12), (Q13, Q14), (Q15, Q16) 4×4

9. Find the expression for angular momentum operators $\left(\hat{L}_x, \hat{L}_y, \hat{L}_z\right)$ in terms of linear momentum operators $\left(\hat{p}_x, \hat{p}_y, \hat{p}_z\right)$ and co-ordinator (x,y,z).

Evaluate the commutator, $[L_z, L_+]$.

10. A freely moving particle of mass, 'm' is confined in a one-dimensional box extending from $x = -2L$ to $x = 2L$. Write down the expression of energy and wave function for its ground state. Find the value of $\langle x \rangle$ in its ground state.

11. Show that time evolution of the expectation value of an operator, $\hat{D}$ of a system is given by the following expression, $\frac{d}{dt}\langle \hat{D} \rangle = \frac{1}{ih}\left\langle \left[\hat{D}, \hat{H}\right] \right\rangle$

    Assume, $\hat{D}$ has no explicit time dependence.

12. Calculate the translational partition function for $H_2(g)$ at $1000K$ and $1 atm.$ pressure.

13. Define partial molar quantity. Describe a suitable method to estimate partial molar volume for a binary system. 1+3

14. Calculate the force constant for a *Br–Br* bond, given that the harmonic vibrational wave number of the $^{79}Br^{81}Br$ isotopomer of the bromine molecule is $323{\cdot}2 cm^{-1}$.

15. Write down the order of increasing wave number of the stretching vibrations of (1) $C - H$ (Alkane), (2) $O - H$ (Alcohol), (3) $C = O$ (Ketone), and (4) $C \equiv C$ (Alkyne) 4

16. Obtain an expression for association constant of an ion pair following Fuoss model. 4

Group—C

Answer *two* questions taking either odd (Q17, Q19) or even (Q18, Q20) pair of question. 2×8

17. Deduce Schwartz inequality relation. Use this relation to obtain Heisenburg Uncertainty relation for two non-commutating operator.

18. (a) Derive Sackur-Tetrode equation for entropy.

(b) The rotational constant of gaseous *HCl*, determined from micro wave spectroscopy, is 10·59 cm^{-1}. Calculate the rotational partition function of *HCl* at 500*K*. 5+3

19. Obtain an expression for the thermodynamic probability distribution of particles described by antisymmetric wave functions and arrive at the appropriate quantum statistical distribution law. 8

20. (a) How many normal modes of vibrational are possible for a benzene molecule ? The A, rotational constant of a phosphorus pentafluoride, PF_5, molecule is 3·566 *Hz*. Calculate the lengths of the equational $P-F$ bonds. 1+3

(b) A free particle of mass 'm' is moving in a two dimensional square box having length in each side 'a'. How does the energy of its first excited state charge upon small charge (da) in the Y-direction. Comment on your result. 4