M.Sc. 1st Semester Examination, 2019

CHEMISTRY

(*Physical Chemistry*)

PAPER – CEM-101

Full Marks : 40

Time : 2 hours

The figures in the right hand margin indicate marks

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

Illustrate the answers wherever necessary

GROUP–A

Answer any **four** questions of the following : 2×4

1. Write down the dimension of wave function, $\psi(x, y, z)$. 2

2. If two operators $\hat{A}$ and $\hat{B}$ has same set of eigen-

functions, then which of the following relation is correct : 2

(*i*) $[A, B] \neq 0$

(*ii*) $[\hat{A}, \hat{B}] = 0$

(*iii*) $[\hat{A}, \hat{B}] = 1$

(*iv*) $\hat{A} = \hat{B} = 0$

3. In stretching of rubber band,

$$dG = Vdp - SdT + fdL$$

which of the following is true ? 2

(*a*) $\left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial f}{\partial V}\right)_{P,L}$

(*b*) $\left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial f}{\partial T}\right)_{P,L}$

(*c*) $\left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial V}{\partial T}\right)_{P,L}$

(*d*) $\left(\frac{\partial S}{\partial L}\right)_{P,T} = -\left(\frac{\partial f}{\partial P}\right)_{T,L}$

4. Which of the following statements is wrong ? 2

(*a*) UV absorption is attributed to electronic transitions

(*b*) UV absorption provide information about valence electron

(*c*) IR absorption is attributed to transition between rotational energy levels of whole molecules.

(*d*) NMR spectrometers use radiofrequency electromagnetic radiation

5. The letters 'CHEMISTRY' are written separately one on each card. The nine cards are shuffled. Calculate the probability of obtaining the word 'chemistry'. 2

6. When should we apply rational system of activity to determine the activity co-efficient of a system ? 2

7. Distinguish between identical distinguishable and indistinguishable particle. 2

8. Identify the molecule whose rotational constant cannot be determined by IR spectroscopy. 2

CH_4, H_2, CO_2, HCl.

GROUP–B

Answer any **four** questions of the following : 4×4

9. Find the constrained maxima of the function

$$f(x) = e^{-x^2-y^2}$$

subject to the condition $x + y = 1$. 4

10. Normalized state ϕ is constructed as a linear combination of ground state ψ_0 and first excited state ψ_1 with energies $\frac{1}{2}$ and $\frac{3}{2}$ respectively. If the average energy of the state ϕ is $\langle E \rangle = \frac{7}{6}$, then calculate the probability of finding ψ_1 in ϕ. 4

11. A non-ideal gas follows the equation

$$P = \frac{RT}{V}\left[1 + \frac{B}{V}\right]$$

where 'B' is a function of temperature only.

Show that deviation of internal energy from that of ideal gas,

$$U - U_{\text{ideal}} = -\frac{RT^2}{V}\left(\frac{\partial B}{\partial T}\right)_V$$ 4

12. Arrange the following in order of increasing wave number of stretching vibration :

(*i*) C–H (alkane)

(*ii*) –O–H (alcohol)

(*iii*) $\rangle$C=O (Ketone)

(*iv*) –C≡C– (alkyne)

Give proper justification. 4

13. What are the driving forces for the stabilization of nanoparticle synthesized in organic and aqueous medium ? What are organosol and hydrosol ? 2 + 2

14. Can β be negative ? 4

15. The energies and degeneracies of the two lowest electronic states of atomic iodine are listed below :

Energy/cm^{-1}	Degeneracy
0	4
7603·2	2

What temperature is required so the 2% of the atoms are excited in the excited state ? 4

16. Define fugacity co-efficient and hence derive the relation

$$\ln \phi = \int_0^p \frac{z-1}{p}\, dp$$

where symbols have their usual meanings. 4

GROUP–C

Answer any **two** questions of the following : 8×2

17. Show that time evolution of the expectation value of an operator $\hat{D}$ of a system is given by the following expression,

$$\frac{d\langle D\rangle}{dt} = \frac{1}{i\hbar}\langle [D, H]\rangle.$$

(All the symbols have their usual significances. Assume $\hat{D}$ has no explicit time dependence.) Hence, obtain the time evolution of the average value of momentum for a one-dimensional system. 4 + 4

18. (*a*) A particle in a state $\phi = \psi_1 + 3\psi_2$, where ψ_1 and ψ_2 are the eigenfunctions of the Hamiltonian of the particle with eigenvalues E_1 and E_2 respectively. Obtain the average energy of the particle in the state ϕ.

(*b*) Show that,

$$\left[x^2, p_x^2\right] = 4i\hbar p_x x - 2\hbar^2$$ 4 + 4

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

20. (*a*) Derive the expression of molar entropy of a rigid diatomic rotor.

(*b*) Calculate the translational partition function for benzene in a volume of $1 m^3$ at 25° C. 5 + 3
