2019

M.Sc.

2nd Semester Examination

CHEMISTRY

Paper - CEM 201

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.

Group A (a)

Answer any *one* question from the following.

1. Define autocatalytic reaction with a suitable example. 2

2. The standard Gibb's energy change of reaction for

$$2H_2(g)+O_2(g)\rightarrow 2H_2O(g)$$

is –457.2 kJ at 298K. At room temperature, however, this reaction does not occur and mixtures of gaseous hydrogen and oxygen are stable. Explain why this is so ? Is such a mixture indefinitely stable ? 1+1

[Turn Over]

Group A (b)

Answer any *one* question from the following.

3. Why Transition State Theory is called Absolute Reaction Rate Theory ? 2

4. How would you expect the intensity of Rayleigh scattered lines to vary with increasing wavelength of the light ? 2

Group A (c)

Answer any *one* question from the following.

5. What would be the speacing between the two Raman spectral lines around the Rayleigh scattered lines in case of Rotational Raman spectra ? 2

6. What is Born-Oppenheimer approximation ? 2

Group A (d)

Answer any *one* question from the following.

7. How does a quantum Harmonic Oscillator differ from a classical Harmonic Oscillator ? 2

8. In a rigid rotator problem L^2 is measured and the value $20\hbar^2$ is obtained. If L_z is measured, what possible values can be found. 2

Group B (a)

Answer any *one* question from the following.

9. Derive the expression for relaxation time of the reaction.

$A \rightleftharpoons B + C$ 4

10. The turnover number for acetylcholinestearase, an enzyme with a single active site that metabolizes acetylcholine, is $1.4\times10^{4}s^{-1}$. How many grams of acetylcholine can 2.16×10^{-6} g of acetycholinestearase metabolize in one hour ? (Assume the molecular mass of the enzyme to be 4.2×10^{4} $gmol^{-1}$; acetylcholine has the molecular formula $C_7NO_2H_{16}^{+}$) 4

Group B (b)

Answer any *one* question from the following.

11. Taking a suitable example discuss the mechanism of a redox reaction proceed through bridged activated complex mechanism. 4

[Turn Over]

12. For N_2O following are the spectral data :

ν (cm^{-1})	Infrared	Raman
580	Three peaks, temperature dependent, medium	Single peak, medium
589	Three peaks, strong	Single peak, very weak
1167	Two peaks, medium	Single peak, very weak
1285	Two peaks, very strong	Single peak, very strong
2233	Two peaks, very strong	Single peak, strong

Assign the different peaks with proper justification. Also comment on the structure of the molecule on the basis of the spectral data. 4

Group B (c)

Answer any *one* question from the following :

13. The following three solutions are obtained from the time independent Schrödinger equation of H-atom.

$$\psi_{2p_0} = R_{2,1}(r)\left(\frac{3}{4\pi}\right)^{1/2}\cos\theta$$

$$\psi_{2p_{+1}} = R_{2,1}(r)\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{i\phi}$$

$$\psi_{2p_{-1}} = R_{2,1}(r)\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{-i\phi}$$

Write down the expression of ψ_{2p_x}, ψ_{2p_y} and ψ_{2p_z}. 4

14. The trial wave function of a system is given as

$\psi = c_1\phi_1 + c_2\phi_2$, where ϕ_1 and ϕ_2 are the orthonormal basis in a two dimensional linear function space. Find the approximate ground state energy of the system using linear variational principle.

The matrix elements of the Hamiltonian are given below,

$H_{11} = 0;\ H_{12} = H_{21} = 4;\ H_{22} = 6$ 4

Group B (d)

Answer any *one* question from the following :

15. At a given instant of time a rigid rotator is described by the following superposition of state.

$$Y(\theta,\phi)=\frac{1}{\sqrt{2}}\left(Y_{1,1}+Y_{1,-1}\right)$$

Find the value of L_z and L^2 for the above state. 4

16. Write short notes on Coherent Antistokes Raman spectroscopy. 4

Group C (a)

Answer any *one* question from the following :

17. (a) Find out the expression for rate equation of a kinetic reaction occurring through 'plug flow' technique.

(b) The reaction

$$SO_2Cl_2(g)\rightarrow SO_2(g)+Cl_2(g)$$

is first order and has a rate constant of $2.24\times10^{-5}s^{-1}$ at 320°C. Calculate half-lilfe of the reaction. What fraction of a sample of $SO_2Cl_2(g)$ remains after being heated for 5.00 hours at 320°C ? How long will a sample of $SO_2Cl_2(g)$ need to be maintained at 320°C to decompose 92% of the initial amount present ? 4+4

18. (a) What do you mean by competitive and uncompetitive ezyme inhibition reaction ?

(b) Obtain the Lineweaver-Burk plot for competitive and uncompetitive enzyme inhibition reaction. 2+6

Group C (b)

Answer any *one* question from the following :

19. Wave function of rigid rotator is described by the spherical Harmonics, $Y_J^M(\theta, \phi)$. Use the rigid rotator as model system to show that the molecule showing microwave activity must follow the following criteria.

(i) $\mu \neq 0$ (ii) $\Delta M = 0$ and (iii) $\Delta J = \pm 1$

(where symbols have their usual significances)

Recurssion formula for the Associated Legendre function is given by,

$$(2J+1)xP_J^M(x) = (J-|M|+1)P_{J+1}^M(x) + (J+|M|)P_{J-1}^M(x)$$

8

20. (a) If $|n\rangle$ is the eigen function of Hamiltonian operator, H of a linear Harmonic Oscillator with eigen value E_n, then show that $a^+|n\rangle$ is an eigen function of H with eigen value $E_n + \hbar w$.

[Turn Over]

(b) Use operator method to deduce the following for a linear Harmonic Oscillator.

(i) $a^{+}|n\rangle = \sqrt{n+1}\,|n+1\rangle$

(ii) $|n\rangle = \dfrac{(a^{+})^{n}}{\sqrt{n!}}|0\rangle$

(Symbols have their usual significances)

3+(3+2)=8