E–307

M. Sc. (First Semester)
EXAMINATION, Dec.-Jan., 2020-21

CHEMISTRY

Paper Third

(Quantum Chemistry, Thermodynamics and
Chemical Dynamics—I)

Time : Three Hours]   [*Maximum Marks : 80*

[*Minimum Pass Marks : 16*

Note : Attempt all Sections as directed.

Section—A   1 each
(Objective/Multiple Choice Questions)

Note : Attempt all questions.

Choose the correct answer :

1. For a box with infinitely hard walls, the potential is maximum at ....

   (a)   L

   (b)   2L

   (c)   L/2

   (d)   3L

2. If $y = e^{-2x}$, then find the value of dy/dx is :

   (a) $2e^{2x}$

   (b) $-2e^{-2x}$

   (c) $\dfrac{e^{2x}}{2}$

   (d) e^{-4x}

3. Which of the following is not a characteristics of wave function ?

   (a)   Continuous

   (b)   Single valued

   (c)   Differentiable

   (d)   Physically Significance

4. Any wave function can be written as a linear combination of ....

   (a)   Eigen Vectors

   (b)   Eigen Values

   (c)   Eigen Functions

   (d)   Operators

5. Which of the following can be a wave function ?

   (a) $\tan x$

   (b) $\sin x$

   (c) $\cot x$

   (d) $\sec x$

6. For an ideal gas, the fugacity by pressure ratio is ....
   (a) $f/p = 1$
   (b) $f/p = 0$
   (c) f/p varies
   (d) $f/p > 1$

7. The ratio of chemical potential to free energy of a pure substance at constant temperature and pressure is :
   (a) Zero
   (b) 1
   (c) ∞
   (d) None of these

8. The four properties of a system viz. P, V, T, S are related by .... equation.
   (a) Gibbs-Helmholtz
   (b) Gibbs-Duhem
   (c) Maxwell's
   (d) Vant-Hoff

9. Partial molar free energy of an element A in solution is same as its :
   (a) Fugacity
   (b) Activity
   (c) Activity coefficient
   (d) Chemical potential

10. In an ideal solution, the activity of a component is equal to its :
   (a) Mole fraction
   (b) Partial pressure
   (c) Fugacity at the same temperature and pressure
   (d) None of these

11. The ionic strength of 2M KCl solution is :

    (a)   1

    (b)   2

    (c)   3

    (d)   4

12. The activity coefficient of 'm' modal $CuSO_4$ solution can be expressed in terms of its mean activity coefficient $(\gamma\pm)$ as :

    (a) $m^2\gamma\pm^2$

    (b) $4m^3\gamma\pm^3$

    (c) $16m^2\gamma\pm^4$

    (d) $108m^5\gamma\pm^5$

13. Consider the statements S1 and S2 :

    S1 : Conductivity always increases with decreases in the concentration of electrolyte.

    S2 : Molar conductivity always increases with decreases in the concentration of electrolyte.

    (a)   Both S1 and S2 are correct

    (b)   S1 is correct and S2 is wrong

    (c)   Both S1 and S2 are wrong

    (d)   S1 is wrong and S2 is correct

14. The Debye-Huckel equation provides a means to estimate the activity coefficients of single ions in solution, but requires knowledge of :

    (a)   The ionic strengths of solution and the hydrated radius of the ion of interest

(b) Ions most influence the total ionic strength and charges on these ions

(c) Ionic strength of the solution, size of the hydrated ion for which the activity coefficient is being calculated and its change

(d) Sizes of the hydrated ionic species

15. The effect that tends to retard the mobilities of ions in solution is :

(a) Relaxation effect

(b) Asymmetry effect

(c) Electrophoretic effect

(d) All of the above

16. Consider the following statements, the correct statement is :

(A) increase in concentration of the reactant increases the rate of a zero order reaction

(B) A plot of $\ln(k)$ vs. t is a straight line

(C) A pot of $in(k)$ vs. $1/t$ is a straight line with a positive slope

(D) Rate constant k is equal to collision frequency a if $Ea = 0$

17. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first order reaction. it is because the :

(A) Rate is proportional to the surface coveragbe

(B) Rate is inversely proportional to the surface coverage

(C) Rate is independent of the surface coverage

(D) Rate is decomposition is slow

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18. Which method is used, for determining the order of reaction ?

    (a) Refractometric method

    (b) Half-life method

    (c) Dilatometric method

    (d) Optical activity method

19. The unit of slope in Arrhenius plot to calculate the energy of activation is :

    (a) K^{-1}

    (b) F

    (c) K

    (d) C

20. Activate complex if formed due to :

    (a) Effective collision

    (b) Pressure

    (c) Ineffective collisions

    (d) Temperature

Section—B   2 each

(Very Short Answer Type Questions)

Note : Attempt all questions.

1. Integrate $\int_{10}^{100} R T \dfrac{dV}{V}$.

2. What is eigen function and eigen values.

3. Write the Maxwell relation for the following fundamental equation :

    (i) $dA = {}^{-}S\,dT - P\,dV$

    (ii) $dH = T\,dS - V\,dP$

4. Define activity. How is it related to pressure and fugacity ?
5. Write the Lippmann's equation.
6. Define Relaxation effect.
7. What is Steric factor ?
8. Define oscillatory reaction with example.

Section—C   3 each

(Short Answer Type Questions)

Note : Attempt all questions.

1. What are operators ? Derive Schrödinger wave equation in terms of Hamiltonian operator.

2. What is the ΔE between the $n = 4$ and $n = 5$ states for an F_2 molecule trapped within in a one dimension well of length 2.0 ? (Given : $h = 6.626 \times 10^{-34}$ J-s, $m = 6.309 \times 10^{-26}$ kg.

3. Derive the Gibbs-Duhem equation.

4. Determine the partial molar heat content of a system.

5. What is thickness of ionic atmosphere ? Write the equation for it and explain how it varies with concentration of ion, valency of ion and temperature of solution.

6. Briefly discuss various aspects of ion-solvent interaction.

7. Write a note on salt effect.

8. Derive the rate equation for hydrogen-bromine reaction.

Section—D   5 each

(Long Answer Type Questions)

Note : Attempt all questions.

1. Describe briefly the various postulates of quantum mechanics.

Or

Discuss the application of Schrödinger wave equation for the hydrogen atom.

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2. Define the term Fugacity. Discuss any *two* methods for the determination of fugacity.

Or

Explain the term chemical potential. How does chemical potential vary with temperature and pressure ? Derive the value of chemical of a mixture of ideal gases.

3. Write a note ionic strength. Give the explanation of the following statements :

    (i)   How the mean acitivity coefficient of an electrolyte determined ?

    (ii) How does it affect ?

    (iii) Calculate the ionic strength of 1.00 m-mol. kg^{-1} $CaCl_2$ at 25°C.

Or

Briefly discuss Debye-Huckel's theory of activity coefficient of electrolytic solutions. Derive the Debye-Huckel-Onsager equation.

4. Discuss the different methods for the determination of rate law. Derive the rate equation and obtain the value of A, B and C for the consecutive reaction :

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$
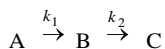
Or

Bring out clearly the main features of collision theory of reaction rates. What do you mean by effective collision ? Derive the rate equation for unimolecular reaction.