FIRST B. SC. EXAMINATION, 2017

(1st Semester)

CHEMISTRY (HONOURS)

PAPER - I

Time : Two hours Full Marks : 50

Use a separate answerscript for each group.

GROUP - A

1. Answer ***any two*** questions :

   a) Find the units (in SI system) with reasons-

      i) 'B' and 'C' in $Z = 1\frac{B}{V_m} + \frac{C}{V_m^2}$

      ii) 'a' & 'b' in $\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$

      iii) 'M' in $M = \rho_o RT$; where is *limiting density.*

      2+2+1

   b) Write down Maxwell-Boltzmann speed distribution equation with symbolic meanings. Draw its representative plots at two different temperatures and mention any two differences and one similarity. 2+3

   c) State the ***'Principle of Equipartition of Energy'***. With the help of this, show that 'γ' of an ideal gas decreases with increase in atomicity of the molecule. 2+3

2. Answer ***any two*** questions : $3\frac{1}{2}\times 2$

   a) Draw the one dimensional velocity distribution curve at two different temperatures and mention one difference and two similarities.

   b) Average energy contribution per degree of freedom of translational & rotational motion is $\frac{1}{2}k_BT$ whereas of vibrational motion is k_BT. Explain why.

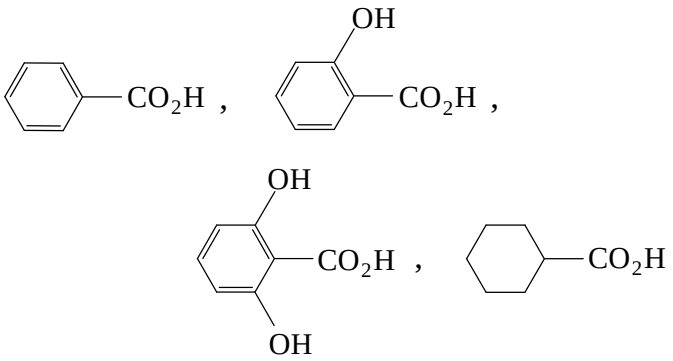
   c) At a particular state, a gas contains 10^{15} molecules L^{-1} and the mean free path of the molecule is $\frac{1}{\sqrt{2}\pi}m$. Calculate the diameter of the hard sphere molecule in pm.

7. Prove that the frequency of rotations of the electron in Bohr orbit of the hydrogen atom is given by $v = 4\pi^2z^2e^4m/n^3h^3$ Now prove that whenever quantum numbers are very high the frequency of radiation for the transition $(n + 1) \rightarrow n$ is equal to the frequency of rotation of the electron. What is the principle associated with such a result ? $1\frac{1}{2}+1+\frac{1}{2}$

8. Describe the Stern Gerlach experiment to show how aspects of electron spin and the spin quantum number were understood from it. 3

9. Considering the Schrodinger equation discuss the particle in a box experiment. What significance does the final expression for kinetic energy E obtained from it have on such sub atomic particles ? 3

g) Arrange the following acids in the increasing order of acid strength and give proper explanation for your answer.



h) Potassium can liberate hydrogen from cyclopentadiene. – Account for the observation.

4. Attempt ***any four*** of the following questions : 2×4

a) What most significant observation one can get from the following heat of hydrogenation data ?

Cyclohexene + H_2 → Cyclohexane ($\Delta H = -120$ kJ mol^{-1})

Benzene + $3H_2$ → Cyclohexane ($\Delta H = -208$ kJ mol^{-1})

Cyclooctene + H_2 → Cyclooctane ($\Delta H = -96$ kJ mol^{-1})

Cyclooctatetraene + $4H_2$ → Cyclooctane ($\Delta H = -410$ kJ mol^{-1})

b) N, N-Dimethylaniline readily couples with benzene diazonium choride but N, N, 2, 6-tetramethylaniline fails. – Account for the observation.

c) What do you mean by polarizability ? Arrange the halide ions in the increasing order of polarisability. What would be the effect of addition of a small amount of KI to a reaction mixture containing methyl chloride and aq. NaOH ?

d) Show one method for generation of radicals. How do $\dot{C}H_3$ and $\dot{C}H_3$ differ in their geometries ? What explanation(s) could be given for the difference ?

e) The order of base strength of n-$BuNH_2$, n-Bu_2NH and n-Bu_3N are not same in water and chlorobenzene. Show the order in these two solvents and give proper explanation for your answer.

GROUP - C

Answer question no. ***5*** and ***any two*** other questions.

5. a) Calculate the Rydberg constant values for the three isotopes of hydrogen and hence justify why, although small, there would be differences in all the energy levels in the corresponding hydrogen isotopes.

[given $R_\infty = 109677\ cm^{-1}$] $1\frac{1}{2}$

b) Considering elliptical orbits Sommerfeld suggested the Bohr quantum number (n) required a replacement by n_r and n_ϕ where the radial quantum number (n_r) is a non-

negative integer and the azimuthal quantum number (n_ϕ) is a positive integer. Present a discussion on the outcome of this assumption by Sommerfeld. $2\frac{1}{2}$

c) Discuss the selection rules for electronic transitions for both $\Delta 1$ and Δm_1 [symbols have their usual meanings]. $1\frac{1}{2}$

d) An electron in the n = 1 level of the H atom travels at $2{\cdot}2 \times 10^6$ m/sec. What is the wavelength associated with the motion of the electron ? How many such wavelengths fit in the first Bohr orbit of the H atom (radius = 0·529 Å).

[Given : h $6{\cdot}626 \times 10^{-34}$ J. sec & $m_e = 9{\cdot}11 \times 10^{-11}$ kg.] 2

e) What are the pairs of properties for which there is an uncertainty in determination of their precise values simultaneously as enunciated by Heisenberg. $1\frac{1}{2}$

f) Mention two experiments that utilized the Bragg equation for advancing our understanding of sub-atomic particles or the structure of the atom in general. 1

6. Utilizing the concept of the reduced mass of the system show that

$$m_H / m_e = R_H - 1/4R_{He} - R_H$$

[terms have their usual meanings] 3

GROUP - B

3. Attempt ***any six*** of the following questions : $1\frac{1}{2} \times 6$

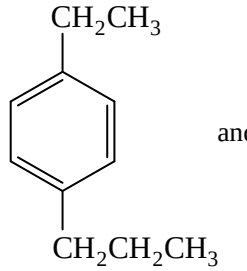
a) Construct the π-MOs of butadiene by combining the π-MOs of two ethylene molecules.

b) What are clathrates ? Give one suitable example.

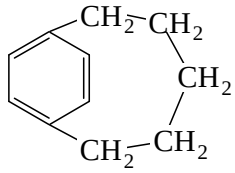
c) What do you mean by $\pi - \pi$ interaction ? Show the sandwich and T-shaped interactions between two arene systems.

d) What is the origin of vander Waals forces ? How does it vary among the isomeric alkanes ?

e) Compare the stabilities of the following two compounds :



and



Give appropriate reason(s) for your answer.

f) Show appropriate examples to show the following :

i) a C-H bond is involved in intermolecular hydrogen bond.

ii) A C = C bond is involved in intramolecular N-H ... π hydrogen bond.