7. What do you mean by covalent radii and how it is related to the electronegativity of constituent atoms ? Compare covalent radii and van der Waal's radii and how these two are related to the bond distance ? 1+2+2

FIRST B. SC. EXAMINATION, 2018

(1st Semester, Old Syllabus)

CHEMISTRY (HONOURS)

PAPER - II

Time : Two hours Full Marks : 50

Use a separate answerscript for each group.

GROUP - A

1. Answer ***any three*** questions : 3×3

   a) Define compressibility factor (Z). What is its unit ? Name the factors which can influence it.

   b) Define critical temperature (T_C), critical pressure (P_C) and critical volume (V_C) of a non-ideal gas. Out of these which one depends on the mass of the gas ?

   c) A gas obeys the equation of state, $PV_m = RT(1+b/V_m)$:

      i) Would it be possible to liquefy the gas ?

      ii) Would it have a critical temperature ? Give reasons in support of your explanation.

   d) Derive the reduced equation of state for Van der Waals gas. What is its significance ?

2. Answer ***any two*** questions : 4×2

a) Why does *saturated vapor pressure* depend on temperature ? Find out an empirical relation between *saturated vapor pressure* and *temperature.*

b) Why is difference in pressure observed between liquid and gas phases which are separated by a curved surface ? Explain how such pressure difference is connected with capillary rise or depression.

c) What is force of cohesion and force of adhesion ? At 20^oC, the interfacial tension between water and benzene is 35 $mN.m^{-1}$. If the surface tension $\gamma = 28.85$ $mN.m^{-1}$ for water, calculate : i) the work of adhesion between water and benzene, ii) the work of cohesion for benzene and water, iii) spreading coefficient for benzene on water.

GROUP - C

Answer question no. ***4*** and ***any two*** from the rest.

4. i) Why the alkali metals have very low ionization enthalpy value ? 1×6

ii) Why the electron affinity of chlorine is greater than fluorine?

iii) What is the basis of *Allred and Rochow* scale of electronegativity ?

iv) What is the major difference between electron affinity and electronegativity ?

v) Why copper has greater ionization enthalpy than potassium?

vi) What is collision radius of a diatomic molecule ?

5. Comment on the vertical periodic trends of ionization enthalpy. What are the factors that control the value of ionization enthalpy ? 1+4

6. What is partial ionic character ? How it is related to Pauling scale of electronegativity and the stability of a molecule ? Why the noble gases have very high positive value of electron affinity ? What does it signify ? 1+2+2

d) Predict the sign of ΔG^o for an endothermic reaction where entropy is decreased and comment on its spontaneity. 1

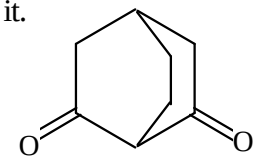
e) With the help of π-MO pictures of ethylene and formaldehyde molecules, explain that the π-bond in ethylene is more reactive towards electrophiles than the π-bond in formaldehyde. 3

GROUP - B

3. a) Justify the following statements :

i) Intramolecular hydrogen bonding is preferred rather than intermolecular hydrogen bonding in 1, 2-diols. 3

ii) While pentan- 2, 4-dione is readily soluble in aqueous NaOH, the formally similar 1, 3 - diketone A is insoluble in it. 3



A

b) B and C can react at a certain temperature to give the major product D (the kinetically controlled product). But, at a higher temperature they give the predominant product E (the thermodynamically controlled product). Use standard free energy diagram to explain this behaviour. 3

c) 2-Methylpropene reacts with hydrogen chloride to form 2-chloro-2-methylpropane following a two-step mechanism which involves slow formation of a carbocation intermediate. The reaction does not produce significant amount of 1-chloro-2-methylpropane. Use Hammond's postulate and appropriate energy profile diagrams to explain this experimental fact. 4