FIRST B.SC. EXAMINATION, 2018

(2nd Semester, Old Syllabus)

CHEMISTRY (HONOURS)

PAPER - IV

Time : Two hours Full Marks : 50

Use a separate answerscript for each group.

GROUP - A

1. Answer ***any four*** questions : 2×4

   a) State and explain Hess's law of constant heat summation.

   b) 'The enthalpy of neutralisation of a strong acid by a weak base or of a weak acid by a strong base is always much less than that of a strong acid by a strong base' – explain.

   c) Calculate the enthalpy change for the reaction,

   $$H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g).$$

   The bond energies are : $\in_{H-H} = 103$ KCal mol^{-1}

   $\in_{C=C} = 145$ KCal mol^{-1}, $\in_{C-C} = 80$ KCal mol^{-1} & $\in_{C-H} = 99$ KCal mol^{-1}

   d) Given the standard molar enthalpy of formation at 298 K for $CO_2(g)$ and $H_2O(l)$ are –394 kJ mol^{-1} and –286 kJ mol^{-1}, respectively and the standard molar enthalpy of

combustion of $C_6H_6(l)$ at 298 K is –3268 kJ mol^{-1}. Calculate the standard enthalpy of formation of liquid benzene, $C_6H_6(l)$.

e) The standard molar enthalpy of formation of gaseous ammonia is –46 kJ mol^{-1} at 25°C. Using the heat capacity data given below, calculate the standard molar enthalpy of formation of gaseous ammonia at 227°C

$$C^o_{p,m}(H_2, g) = 29\cdot0 - (8\cdot4\times10^{-4}K^{-1})T \ (JK^{-1}\,mol^{-1})$$

$$C^o_{p,m}(N_2, g) = 27\cdot0 + (5\cdot9\times10^{-3}K^{-1})T \ (JK^{-1}\,mol^{-1})$$

$$C^o_{p,m}(NH_3, g) = 26\cdot0 + (3\cdot26\times10^{-2}K^{-1})T \ (JK^{-1}\,mol^{-1})$$

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

a) Show that five-fold rotational axis of symmetry is absent in crystals.

b) Prove, $\lambda = 2d_{hkl}\sin\theta$, where the terms bear usual significance.

c) Compute the limiting ratio of radius of cation and anion in triangular arrangement of an ionic crystal.

d) The first order reflection from (200) planes of NaCl using X-rays of wavelength 58 pm occurs at an angle of 5·9°. Calculate (i) edge length of the unit cell (ii) density of solid NaCl. Given molar mass of NaCl = 58·443 gm.

GROUP - C

5. a) Calculate the pH of 100 mL 0·1 (N) acetic acid solution when (i) 00 mL, (ii) 99 mL, (iii) 100 mL and (iv) 101 mL of 0·1 (N) KOH is added to it. [Given : $k_a = 1\cdot8 \times 10^{-5}$] 6

b) Second acid dissociation constant of a polyfunctional acid is smaller than its first acid dissociation constant – Explain. 2

c) What do you mean by buffer solution ? Derive Henderson-Hasselbalch equation for the determination of pH of a buffer solution. 3

d) pH of a very dilute acid (strong) solution is less than 7 – Explain. 1

e) Discuss about the relationship between hydronium ion concentration and sulfide ion concentration and also the role of hydronium ion concentration in separation of Group II and Group IIIB metal ions of qualitative group analysis. 4

Given : K_{a1} of $H_2S = 9\cdot60 \times 10^{-8}$

K_{a2} of $H_2S = 1\cdot30 \times 10^{-14}$

GROUP - B

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

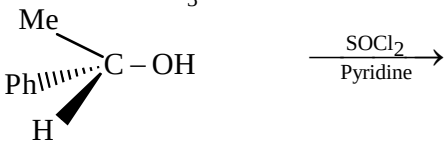
a) i) Write the IUPAC names of the following compounds.

A) $CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-CH_2-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

B) $CH_2=CH-C\equiv C-CH_3$

ii) Write the structures of the products of the following reactions (mechanism not required)

A) $CH_2=CH-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH_2 \xrightarrow{Na\,/\,hq\ NH_3}$

B) 

b) Write the mechanism of acid-catalyzed polymerization of isobutene.

c) How would you carry out the following transformation ? Give mechanism (s) of the reaction step(s)

$$Me_2C=CMe_2 \rightarrow Me_2C=C=CMe_2$$

d) Predict the product(s) of the following reaction and give appropriate mechanism.

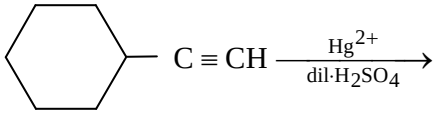
$$Me_3CH + SO_2Cl_2 \xrightarrow[(PhCOO)_2\,(trace)]{h\nu}$$

e) What do you mean by E1cB mechanism for elimination reactions ? Explain by taking a suitable example where this mechanism operates.

4. Attempt ***any three*** of the following questions : 3×3

a) How would you carry out the conversion of 1-butyne to 2-butyne and vice-versa ?

b) With appropriate mechanism show the outcome of the following reactions.

i) 

ii) $Me_3C-CH_2OH \xrightarrow{HBr}$

c) Predict the products of the following reactions and give plausible mechanism in each case -

i) $Me_2\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CH_2 \quad \dfrac{PhSNa}{EtOH}$

ii) $E-CH_3CH=CH-CH_3 \xrightarrow[\text{of } Me_2C=O]{O_3 \text{ in presence}}$

d) Predict the product of the following reactions and give plausible mechanism in each case.

i) $Me_2CHCH_2OH \xrightarrow[\text{iii) } \Delta,\ 200^oC]{\text{i) } CS_2\,/\,NaOH,\ \text{ii) MeI}}$

ii) *meso* – CHDBr – CHDBr $\xrightarrow{I^{\ominus}}$