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SEAT No.

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[161] ( ) SARDAR PATEL UNIVERSITY

M.Sc. Semester-III: Analytical Chemistry **Examination** (CBCS)

October-**2018, Date:** 27.10.2018, Saturday

Saturday, **Time:** 2.00 p.m. to 5.00 p.m.

Paper code: PS03CANC23

Subject: Classical and thermal methods of analysis, **Total marks:** 70

N.B.: i) Figure to the right indicate marks.
ii) Assume the suitable data if necessary and indicate clearly.

Q.1. Attempt MCQs with correct answer highlighted [08]

i) Phenomena that DTA technique able to detect include(s)
a) Endothermic **b)** Exothermic
c) Both a) and b) **d)** None

ii) A precipitate for successful gravimetry must have
a) Known chemical formulae **b)** Filterability
c) Chemical purity **d)** All

iii) Identify autoprotolysis process
a) $OAC^- + H_2O \leftrightarrow HOAC + OH^-$
b) $EtOH + EtOH \leftrightarrow EtOH_2^+ + EtO^-$
c) $NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$
d) $HOAC + H_2O \leftrightarrow OAC^- + H_3O^+$

iv) Factor(s) affecting feasibility of acid base titration is/are
a) Medium of solvent **b)** Concentration
c) Dissociation of acid/base **d)** All

v) Isoelectronic point of an amino acid (pKa=9.7,pKb=11.7) in water will be
a) 2 pH **b)** 4 pH
c) 6 pH **d)** None

vi) If 1.19V, 1.65V and 1.74 V are reduction potential (E^o) values of ClO_4^-, IO_4^- and BrO_4^- respectively, then correct order of them in oxidizing power will be
a) $ClO_4^- > IO_4^- > BrO_4^-$ **b)** $IO_4^- > BrO_4^- > ClO_4^-$
c) $BrO_4^- > IO_4^- > ClO_4^-$ **d)** $BrO_4^- > ClO_4^- > IO_4^-$

vii) At pH 10, 26.37 mL of 0.0741M EDTA forms complex with
a) 1.95 mmol of Mg^{2+} **b)** 1.95 mmol of Ca^{2+}
c) 78 mg of Ca^{2+} **d)** All

viii) Identify the indicator suitably used in FAJANS method
a) Phenolphthalein **b)** Fe^{3+} ion solution
c) Potassium chromate **d)** Fluorescein

Q.2. Answer any ***Seven*** [14]

i) Define specific surface area (SSA) A solid cube weighing 3 g has volume 1 cm^3. Prove that SSA gets increased when it is divided into 1000 small parts

ii) State principle of TG analysis. Discuss in brief nature and shape of thermogram of $BaC_2O_4H_2O$

iii) Calculate pH of 50 mL, 0.1M weak acid H_2A in water. [$Ka_1=1.3X10^{-2}$, $Ka_2=5.9X10^{-7}$]

iv) What is Pearson rule? Comment on reaction $HgCl_2 + H_2S = HgS + 2HCl$

v) State principle of gravimetric titrimetry and its advantages

vi) Describe ways of detecting end point in the complexometry

vii) State acid-base indicators. Derive pKa±1 for pH range of an acid-base indicator

viii) State formation and effective stability constants, (Kf) and (K_{eff}) respectively, of metal complex with suitable example.

ix) Calculate pH of an aqueous solution of a sparingly soluble MOH [$K_{sp}=1X10^{-10}$]

Q.3. **a)** State 'co-precipitation'. Write a short note on types of co-precipitation process [06]

b) What is significance of relative super saturation (RSS) in precipitation process? List ways of controlling magnitude of RSS during precipitation process [06]

OR

b) Write a note on factors affecting TG analysis results

Q.4 **a)** State buffer solution. Compare pH value before and after addition of 10 mmol of NaOH to 1 liter buffer solution which is 0.1F in HOAC and 0.1 M in NaOAC [$K_a = 1.75X10^{-5}$] [06]

b) List non-aqueous solvents. A weak acid HA has Ka value $6.4X10^{-5}$ in water and Ka' value $1.0X10^{-10}$ in pure ethanol. Compare '$-\log_{10}[H_3O^+]$' and $-\log_{10}[EtOH_2^+]$, pH values, which 0.1M salt (NaA) of the acid gives in respective solvents. [$pK_{(auto)}$ values of water and ethanol are 14 and 19.10 respectively] [06]

OR

b) Derive an equation of $[H_3O^+]$ for a weak dibasic acid monosodium salt NaHA in water.

Q.5. **a)** Give significance of theoretical titration curves. A 50.0 mL of 0.1M HCl is titrated against 0.1M NaOH solution. Derive titration curve – pOH Vs volume of titrant – and comment on the titration considering pOH 0.05 mL before and after the equivalence point (EP) and at EP, at least [$K_w=1.0X10^{-14}$] [06]

b) Answer the following [06]

i) Derive a balanced chemical reaction for a redox reaction $MnO_4^- + VO^{2+} \leftrightarrow Mn^{2+} + V(OH)_4^{1+}$ in acidic medium

ii) State 'formal potential' with suitable example

OR

b) State general principle of redox titrimetry. 50.0 mL aqueous solution of $FeSO_4$ required 12.0 mL of 0.02M $KMnO_4$ in acidic media for complete oxidation. Calculate molarity of ferrous sulfate solution.

Q.6 **a)** Describe principle of precipitation titrations. A 50 mL of 0.1M NaI solution was titrated against 0.1 M $AgNO_3$ solution in water. Derive titration curve– 'pI Vs Volume of titrant– [$K_{sp(AgI(s))}= 8.3X10^{-17}$] [06]

b) State masking and de-masking strategies, in complexometry. How will you determine metal ions Zn^{2+}, Pb^{2+} and Cu^{2+} present in mixture by complexometry. Describe the strategy. [06]

OR

b) Discuss 'auxiliary reagent' and 'metallochromic indicators', along with their significant roles in the complexometry.

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