[110]

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SARDAR PATEL UNIVERSITY

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

November-**2019, Date:** 22.11.2019

Friday, **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) CCl_4 (FW=154) to be sought is weighed gravimetrically as AgCl(s) (FW=143). The value of gravimetric factor will be...
a) 1.08 **b)** 0.269
c) 4.31 **d)** 0.929

ii) Method(s) dealing with substance weight-loss is/are
a) DTA **b)** DSC
c) Both a) and b) **d)** TG

iii) Lux-Flood theory for '$CO_2(g)+CaO(s)\rightarrow CaCO_3(s)$' states that
a) CO_2 acts as a base and CaO an acid
b) CaO acts as a neutral and CO_2 a base
c) CO_2 acts as a neutral CaO an acid
d) CO_2 acts as an acid and CaO a base

iv) Amphiprotic solvent is
a) Ethanol **b)** Diethyl ether
c) Chloroform **d)** Carbon tetrachloride

v) A $1X10^{-8}$ M solution of HCl in water has pH...
a) Slightly more than 7 **b)** 8
c) Slightly less than 7 **d)** 6

vi) Volhard titrimetry at end point involves the formation of..
a) $Ag_2CrO_4(s)$ **b)** $Fe(SCN)^{2+}$
c) Starch-I_3^- complex **d)** $Fe(SCN)_3$

vii) Lie-big titrimetric method leads to form...
a) Soluble $Ag(CN)_2^-$ at equivalence point
b) Insoluble $Ag(CN)_2^-$ at end point
c) Insoluble $Ag[Ag(CN)_2]$ at equivalence point
d) Soluble $Ag[Ag(CN)_2]$ at end point

viii) $KMnO_4$ and K_2CrO_4 are colored, due to
a) Cations are colored **b)** Anions are colored
c) Both a) and b) are correct **d)** None

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

i) List the thermal events that a substance undergoes to show when being heated

ii) Distinguish between 'lyophilic' and 'lyophobic' precipitates giving suitable examples

iii) List the requirements of the reaction in titrimety. Why strong acid–base titrations show the reaction equilibrium constant larger? Explain

iv) State the term 'leveling effect' with suitable examples

v) A 100 mL, O.1N HCl soln is titrated partially with 30 mL, 0.2N NaOH Soln. Calculate volume of 0.25 N KOH soln to complete the remaining titration.

vi) State the pH range of an indicator. Calculate theoretical pH range of an indicator HIn($Ka=1X10^{-6}$)

vii) If $9.0X10^{-12}$, $2X10^{-8}$ and $1.1X10^{-10}$ are Ksp values of $Ag_2CrO_4(s)$, $AgIO_3(s)$ and $BaSO_4(s)$ respectively, then arrange them in increasing order of their solubilities.

viii) Illustrate the terms 'stability' and 'over all stability' constants

ix) 1.8 g of a weak acid (FW = 60) is dissolved in 300 mL of water. Calculate Ka of this acid, if the resulting pH is 2.88.

Q.3. **a)** Classify thermal techniques. State working principle of any of them with schematic diagram [06]

b) Outline i) Applications of DSC, ii) Steps in precipitate formation. [06]

OR

b) Describe various co-precipitation processes. It is desirable to add NaCl soln to that of $AgNO_3$, and not the reverse, to receive gravimetric precipitates of AgCl(s)! Explain

Q.4 **a)** Define buffer solution. Give examples of acidic and basic buffer solutions. Derive the equation of pH for any of them. [06]

b) Calculate $[H_3O^+]$ values of 1M, 0.01M, and 0.001M HOAC solutions, using simple and quadratic equations. Comment on errors introduced in considering these values [$Ka=1.76X10^{-5}$] [06]

OR

b) Distinguish between 'autoprotolysis' and 'dissociation' constants. Derive the equation of $[EtOH_2^+]$ for benzoic acid in pure ethanol.

Q.5. **a)** Derive the equation of pH for Na_2A salt solution in water. Calculate 2nd equivalence point pH of 50 mL, 0.1M acid H_2A titration with 0.1M NaOH soln. [$Ka_1=1.2X10^{-2}$, $Ka_2= 6X10^{-7}$] [06]

b) State general principle of redox-titrimetric methods. Classify them. Describe ways of end point detection. [06]

OR

b) State Nearnst equation and its significance. Equal (50 mL) volumes of 0.1 F Fe^{2+} and 0.1 N MnO_4^{1-} solutions were mixed together. Calculate pE of the resulted solution [$E^o_{MnO4-} = 1.51$ V, $E^o_{Fe3+} = 0.77$ V].

Q.6 **a)** Derive pMg range for the color-shift of a metallochromic (H_3In) indicator EBT at pH 10, if $K_3(H_3In) = 2.5X10^{-12}$ and $Kf(MgIn) = 1.0X10^7$ at pH 10. [06]

b) State apparent stability constant with a suitable example. For Ca-EDTA complex, this value is $1.8X10^{10}$ at pH 10. Calculate its formation constant, if EDTA fraction α_4 value is 0.35. [06]

OR

b) Outline

i) Types of EDTA titrations

ii) Metallochromaic Indicators

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