MODEL ANSWER

M. Sc. (First Semester) – 2013, CHEMISTRY (AS-2142)

Analytical Chemistry-I

SECTION: A (2 marks)

1. (i) UV-visible spectrophotometer (ii) Atomic absorption spectrometer (iii) Nuclear magnetic resonance spectrometer, (iv) Flame photometer (v) X-ray fluorescence spectrometer (vi) Fluorescence spectrometer

(ii) Sample processing: Preparation of sample for quantitative analysis that consists of (i) preparing a laboratory sample, (ii) defining replicate samples, (iii) preparing solutions

(iii) (a) 0.44 (2) (b) 0.0144 (3) (c) 7.93 (3) (d) 7.11 (3)

(iv) Random error (Indeterminate error): is error whose exact cause cannot be determined and thus it cannot be corrected. Indeterminate errors cannot be prevented or eliminated by corrections.

They can be considerably reduced by increased care in work, and increase of the number of replicate determinations.

(v) Activity: The effective concentration of an ion in the given solution is called activity of the ion. The activity can be used to describe quantitative the effects of salts on the equilibrium constant.
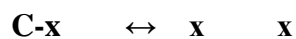
Activity of an ion a_i: $c_i f_i$

Where c_i is the concentration of the ion i and f_i is its activity coefficient

Activity coefficient: The ratio of activity of the ion to the concentration of the ith ion

$f_i = a_i/c_i$

(vi) Let x be the concentration after the ionization of H^+ and OAC^- and C-x is the concentration of HOAC; $K_a = 1.75 \times 10^{-5}$; $C = 1.2 \times 10^{-3}$ M

HOAC $\leftrightarrow$ H^+ + OAC^-

C-x $\leftrightarrow$ x x

$K_a = \dfrac{(x)\,(x)}{C-x}$, Value of x is negligible in c-x, $C_{HOAC} \gg K_a$

$x = \sqrt{Ka \times C}$, $\{x = [H^+]\}$

$[H^+] = \sqrt{1.75 \times 10^{-5} \times 1.2 \times 10^{-3}}$ $[H^+] = 1.4 \times 10^{-4}$

$pH = -\log(1.4 \times 10^{-4})$

$= 4 - \log 1.4 = 4 - 0.15;$ **pH = 3.85**

(vii) Structure of metal-EDTA complex
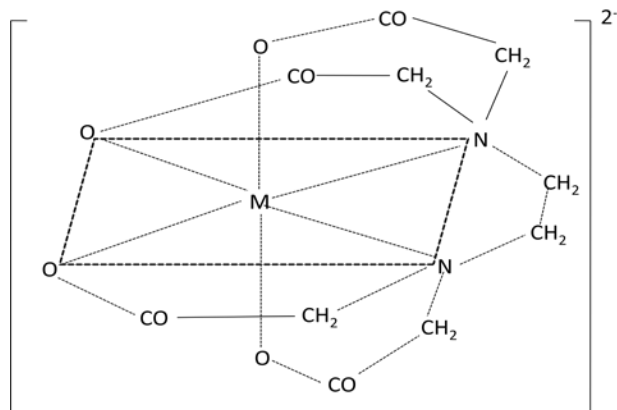
(viii)

| Mole ratio method	Slope ratio method
(a) One constituent is fixed constant (metal) and other is varied (ligand), and vice versa	(a) One constituent (metal) is taken in large excess in fixed amount and other is varied.
(b) Mole ratio of one constituent to other is considered	(b) Slope ratio of two sets of experiments are considered
(c) More than one complex may be observed	(c) Single complex

(ix) Principle of flow injection analysis: The sample solution is delivered in the flowing stream and mixes with chemical reagents to form colored complex and directed towards detector for measurement.
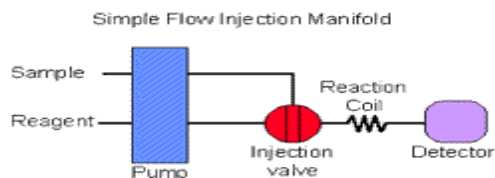
(x) Process Control instruments are operated by means of control loop, which consists of three parts:

1. Sensor or measuring device that monitors the variable being controlled

2. A controller that compares the measured variable against reference value (set point) and feeds the information to an operator

3. An operator that activates some device such as a valve to bring the variable back to the set point.
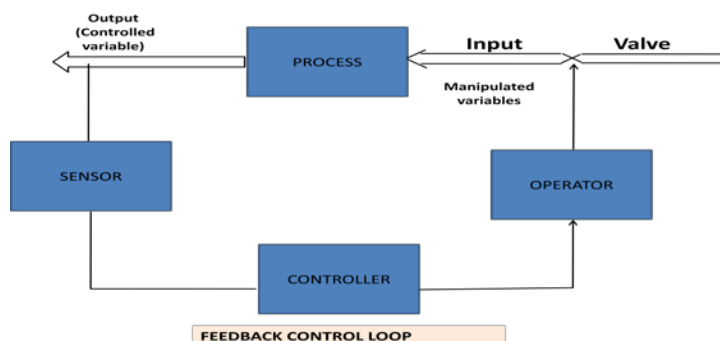
Section-B (8 marks)

2.

Scope of Analytical Chemistry:

1. Chemistry: Biochemistry, inorganic, organic and physical chemistry

2. Biology: Botany, zoology, microbiology and molecular biology

3. Geology: Geochemistry and paleontology

4. Environmental sciences: Ecology, meteorology and oceanography

5. Agriculture/agronomy: Agronomy, animal science, crop science, food science, horticulture and soil science

6. Social sciences: Archeology, anthropology and forensics

7. Material sciences: Metallurgy, polymers and solid state

8. Medicine: Clinical chemistry, medicinal chemistry, pharmacy and toxicology

9. Engineering: Civil, chemical and electrical and mechanical

10. Physics: Astronomy and biophysics

Objective of Analytical Chemistry:

1. Broaden your perception of the field of analytical chemistry

2. Distinguish between various analytical techniques

3. Classify the chemical, electrical, optical, nuclear, and thermal methods of analysis

4. Understand the utility of analytical techniques

5. Highlight the development of methods of chemical analysis

<u>**3.**</u>

2. Student t-test

* In this method, comparison is made between two sets of replicate measurements made by two different methods, one of them will be the test method and other will be an accepted method. A statistical t value is calculated and compared with a tabulated value for the given number of tests at the desired confidence level.

* If the calculated t value exceeds the tabulated t value, then there is a significant difference between the results by the two methods at that confidence level. If it does not exceed the tabulated value, then we can predict that there is no significant difference between the methods.

1. t-test when an accepted value is known:

$$\pm\, t = (\bar{x} - \mu)\,\frac{\sqrt{N}}{S}$$

Where, t is statistical value, x average mean value, N number of observations and S is standard deviation and μ is true mean value

ii. Comparison of the two mean of two samples: When the t test is applied two sets of data

$$\pm\, t = (x - \bar{\mu})\,\frac{\sqrt{N}}{S}$$

$$= \frac{(\bar{x}_1 - \bar{x}_2)}{S_p}\,\frac{\sqrt{N1\,N2}}{N1 + N2}$$

$$S_p = \sqrt{\frac{\sum(x_{i1} - \bar{x}_1)^2 + \sum(x_{i2} - \bar{x}_2)^2 + \ldots\ldots + \sum(x_{ik} - \bar{x}_k)^2}{N - k}}$$

Where $\bar{x}_1$, $\bar{x}_2$, …..$\bar{x}_k$ are the means of each k sets of analysis and xi_1, xi_2…xi_k are the individual values. N is total number of measurement and equal to ($N_1 + N_2 + N_3…N_k$)

iii. Paired t-test

In the chemical laboratory, a new method is frequently tested against an accepted method by analyzing several different samples of slightly varying composition. In this case, the t value is calculated in slightly different form. The difference between each of the paired measurements on each sample is completed.

An average difference $\bar{D}$ is calculated and the individual deviation of each from $\bar{D}$ are used to compute a standard deviation (S_d).

The test is calculated for

$$t = \frac{\bar{D}}{S_d}\sqrt{N}$$

$$S_d = \sqrt{\frac{\sum(D_i - \bar{D})^2}{N-1}}$$

Di is the individual difference between two methods for each sample, with regard to sign; $\bar{D}$ is the mean of all the individual differences.

<u>**4.**</u>

(a) **Standard deviation and relative standard** deviations are used express the precision of analytical measurements.

Precision in a common way is expressed in terms of standard deviation (S). Less the deviation more precise the result is. Deviation is defined as the difference between the measured value and the mean (average) of the series of measurements.

When the number of observations (N) is very large, the standard deviation known as population standard deviation, S, which is used to express the precision of a population of data is given by the square root of the average of squares of deviations,

Thus,

$$\text{Std. dev. (S)} = \sqrt{\frac{D_1^2 + D_2^2 + D_3^2 + \ldots\ldots D_n^2}{N}} = \sqrt{\frac{\sum D_i^2}{N}} = \sqrt{\frac{\sum(xi - \mu)^2}{N}}$$

$$S = \sqrt{\frac{\sum(xi - \bar{x})^2}{N-1}}$$

Where, xi represents the individual observations, Di the individual deviations, the population mean, N the number of observations, and the symbol $\sum$ denotes the summation for $i = 1$ to $I = N$ values.

Relative standard deviation (RSD), %: The RSD, % will tells about the deviation of measurement in percentage (100%), which can be better understandable than standard deviation. The value less than 20% RSD is acceptable in analytical chemistry.

$$RSD = \frac{S}{mean} \times 100\%$$

(b)

x_i	$x_i - \bar{x}$	$(x_i - \bar{x})^2$
13.22	-0.12	0.0144
13.37	0.03	0.0009
13.34	0	0
13.23	-0.11	0.0121
14.00	0.66	0.4356
12.90	-0.44	0.1936
$\bar{x}$= 13.34		$\Sigma(x_i - \bar{x})^2$=0.6566

Std. dev. (s) = $\frac{\sqrt{\Sigma(x_i - \bar{x})^2}}{N-1}$ =$\sqrt{0.657/5}$ = 0.36g

RSD,%=$\frac{s}{x}$x100%

=0.0.36/13.34x100%= 2.7%

* The obtained value tells that a good reproducible value is obtained in terms of standard deviation and relative standard deviation.

5.

Precipitation Reaction:

The process of conversion of an analyte into its insoluble compound by adding precipitating agent (precipitant) is called precipitation.

* When two aqueous solutions of ionic compounds are combined a solid precipitate is formed. This occurs when a positive cation from one solution and negative ions from other solution form a soluble compound. The attraction between the oppositely charged ions is stronger than the attraction between individual ions to the polar water molecules. Thus the solid precipitate comes out of the solution.

$AgNO_3$ (Aq)+ NaCl (Aq) $\rightarrow$ AgCl (s)$\downarrow$ + $NaNO_3$ (Aq)
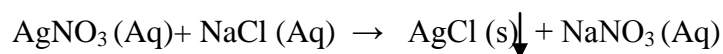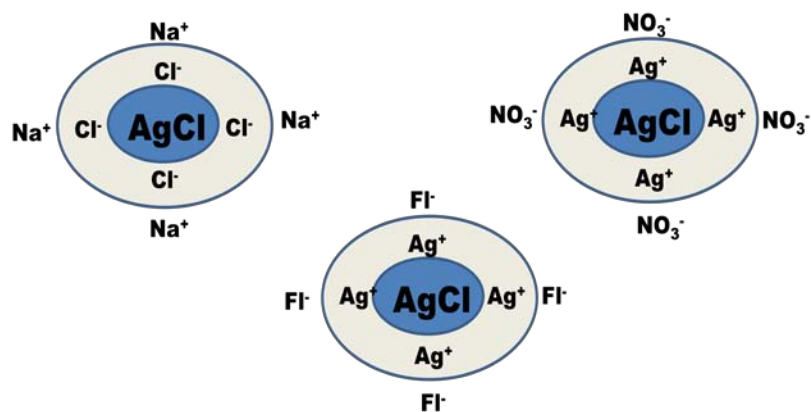
Precipitation titration:

Volumetric methods based upon the formation of slightly soluble precipitate and endpoint is determined in the presence of indicator is called precipitation titration. The use of precipitation titration with silver ions (Ag^+) are for determination of chloride, bromide, iodide and thiocyanate from the sample solution or other applicable sample is also called Argentometry titration.

Adsorption Indicator: For precipitation titration, adsorption indicators are the most satisfactory organic dyes which can indicate the endpoint of precipitation titration by change of the color of the precipitation due to their adsorption on the surface of precipitate are called adsorption indicators.

Theory of adsorption Indicator (Fajan's method):

A colloidal precipitate adsorbs its own ions from solution. Thus, silver chloride, precipitate from a solution of NaCl by treatment with $AgNO_3$ solution, will tend to adsorb Cl^- ions primary layer and Na^+ ions a secondary layer. After, the equivalence point, when excess of $AgNO_3$ is added, the precipitate of AgCl, adsorb as the primary layer and NO_3^- as a secondary layer. The indicator then gets preferentially adsorbed on the surface of AgCl precipitate by substituting color of AgCl precipitate changes to pink to red.


Adsorption indicators do not give a color change in solution but a color change of the precipitate. Ions like Br^-, I^- and SCN^- can titrated with standard AgCl solution in acetic acid medium (pH 1-2) in the presence of eosin (tetrabromo-(R)-fluorescein) as an indicator, the end point is marked by a change in color from pink to reddish-violet.

6.

Mole ratio method for the determination of composition of the complex:

The mole ratio method is popular method for the investigation of colored complex, which is worked out by Yoe and Jones. For this method a series of solution are prepared containing a constant amount of the one constituent but with increasing ratio of the concentration of other constituent, i.e. metal ion (M) and ligand (L) with constant amount of other.

   A plot of absorbance as a function of ratio of moles of ligand to moles of metal ion at a particular wavelength gives a straight line passing through origin with inflation at point of equivalence and then it becomes horizontal as all the metal cations are consumed and addition of excess of ligand produces no more color. The interaction of the extra plotted linear segments determines the ratio of moles of ligand/mole of metal from which the composition can be determined.
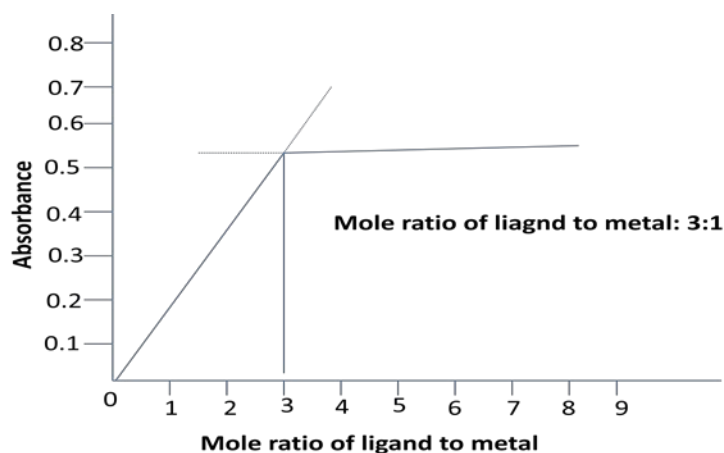
Slope ratio method for the determination of composition of the complex:

This method is also use for the determination of the single colored complex which is spectrophotometrically determined. In this method, two sets of solutions are prepared.

The first set consists of large excess with fixed concentration of ligand (L) with variable concentration of metal ion (M). If the complex formation proceeds according to the reaction

$nM + pL \leftrightarrow M_nL_p$

The concentration of the formed is proportional to C_M as given below

$M_nL_p = C_M/n$

Thus, the absorbance of the solution will be equal to

$A = \varepsilon . C_M/n$

* The plot of absorbance against C_M will be straight line with slope equal to ε/n

Similarly, second set of solution is prepared with large excess with fixed concentration of metal (M) with variable concentration of ligand (L).

The concentration of the formed is proportional to C_L as given below

$M_nL_p = C_L/n$

Thus, the absorbance of the solution will be equal to

$A = \varepsilon.C_L/p$

* The plot of absorbance against CM will be straight line with slope equal to ε/p.

* Since the ratio of the slopes in these two cases is $1/n:1/p$, i.e. p/n, then ratio of M/L complex can be evaluated.

7.

Equalibria of acetic acid in water:

When acetic acid ionizes, it dissociates to equal proportions of H^+ and OAC^-. If the original concentration of acetic acid is C and concentration of ionized acetic acid species (H^+ and OAC^-) is x and final concentration for species at equilibrium:
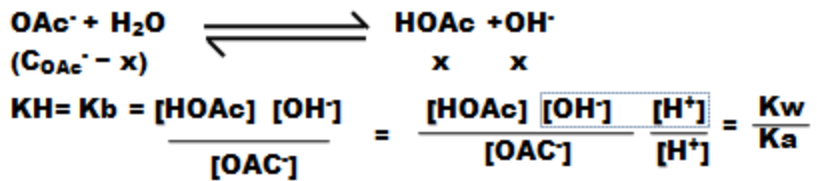
$$HOAC \rightleftharpoons H^+ + OAC^- \quad \text{(Ionization)}$$
$$C - x \qquad\qquad x \quad\; x$$
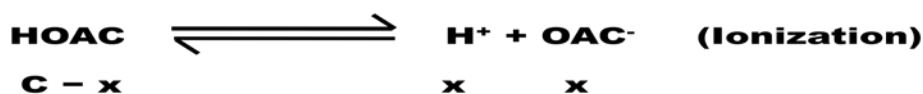
$$K_a = \frac{[H^+]\,[OAC^-]}{[HOAC]} \qquad K_a \text{ Acidity constant} = 1.75 \times 10^{-5}$$

$$K_a = \frac{(x)\,(x)}{C_{HOAC} - x}$$

$$x = \sqrt{K_a \times C}$$
$$H^+ = \sqrt{K_a \times C}$$
$$pH = -\log[H^+]$$

Equalibria of Sodium acetate in water:

Sodium acetate is salt of weak acid and the anion of the salt of weak acid is Bronstead base, which will accept protons. It partially hydrolyses in water to form hydroxide ion and the corresponding undissocaited acid.

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$$
$$(C_{OAc^-} - x) \qquad\qquad x \qquad x$$

$$KH = K_b = \frac{[HOAc]\,[OH^-]}{[OAC^-]} = \frac{[HOAc]\,[OH^-]}{[OAC^-]}\cdot\frac{[H^+]}{[H^+]} = \frac{K_w}{K_a}$$

$$\boxed{K_w = K_a \cdot K_b} \qquad \boxed{K_b = 1.0\times10^{-14}/1.75\times10^{-5} = 5.7\times10^{-10}}$$

$$K_b = \frac{(x)(x)}{C_A^- - x}$$

The value of x in denominator is negligible, if $C_{OAC^-} \gg K_a$

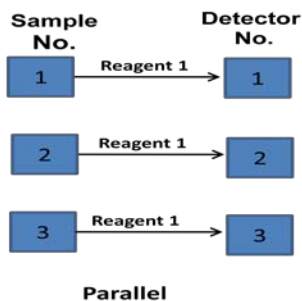$$x\,[OH^-] = \sqrt{K_b \times C_A^-}$$

$$pOH = -\log[OH^-]$$

8.

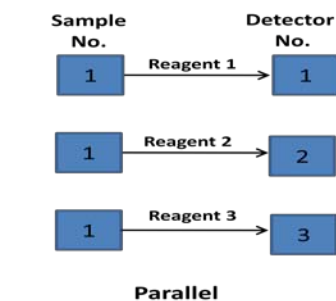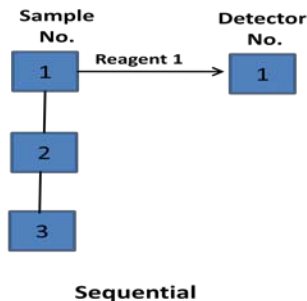### Discrete/Batch Type Analyzers

* Sample reactions are kept discrete through the use of separate reaction cuvettes, cells, slides, or wells that are disposed of following chemical analysis.

* This keeps sample and reaction carryover to a minimum but increases the cost per test due to disposable products.

1. Discrete Analyzers
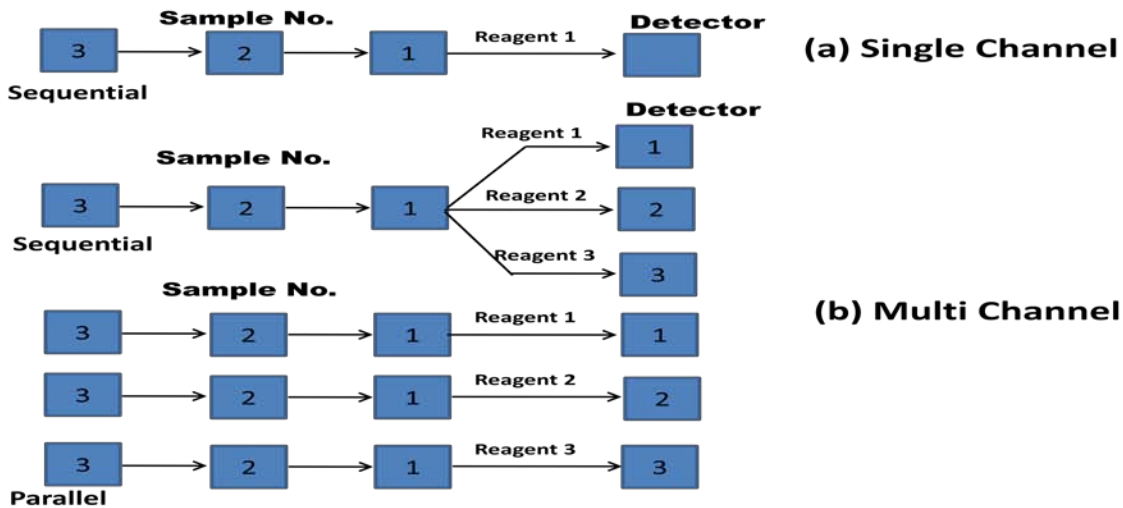

(a) Single Channel   (b) Multi Channel

* Discrete instruments may be designed to analyze samples for one analyte at a time. These are also called single channel analyzers. This may parallel or sequential type. In parallel, many samples can be analyzed and in sequential, samples are analyzed one-by-one.

* In multichannel analyzer, several numbers of analyte can analyzed at a time very quickly parallel.

2. Continuous Flow Analyzers:

Continuous-process control instruments may make measurement directly in a flowing stream. The samples flow sequentially and continuously in tube, perhaps being separated by air bubbles. They are each sequentially mixed with reagents in the same tube at the same point downstream and then flow sequentially in to a detector.

* Continuous-flow sampling, there is single and multichannel analyzers. In single channel instrument that analyze a continuous series of sample sequentially for single analyte.

* In multichannel instruments in which the samples are split one or more points downstream in to separate stream for different analyses, or separate aliquots of sample may be taken with separate stream in parallel.