

Lecturer 1

First Year/ Analytical Chemistry

Some Important Statistical terms

Replicates are samples of the same size that are carried through an analysis.

The mean of two or more measurements is their average value. It is obtained by dividing the sum of the replicate measurements by the number of measurements in the set.

For example the mean of the set of replicates 1, 3, 7, 9 is

$$(1+3 + 7 + 9) / 4 = 5$$

The median is the middle result when replicate data arranged according to increasing or decreasing value. For even number of data, the average of the middle two results is the median.

The median of the set 1, 3, 7, 9 is $(3 + 7) / 2 = 5$

The mode describes how frequently happening a replicate is. There is no mode in the set 1, 3, 7, 9.

For example he set 7, 3, 7, 9, the mode is 7

A bimodal set means the set has two modes.

The set 1, 3,,7 , 9, 7, 1 the set is bimodal of 1 and 7.

and sometimes is a multimodal means some replicates are repeated the same number of times.

The set 1, 3,,7 , 9, 7, 1, 3 is trimodal

The term precision describes the reproducibility of the measurements. Three ways are used to describe the precision of a set of data viz. the standard deviation, the variance, and the coefficient of variation. These three are functions of the deviation from the mean, $d_i = |x_i - x_m|$ where x_m is the mean of x .

Accuracy describes the closeness of measurement to the true or accepted value and is expressed by the error; absolute or relative error;

$$x_i - \bar{x} \text{ and } |x_i - \bar{x}_m| / x_i \text{ or } |x_i - \bar{x}_m| / x_i \% \text{ where } \bar{x}_i \text{ is the mean of } x_i.$$

The standard error of the mean is given by $s_m = s/\sqrt{N}$ where s is the standard deviation and N is the number of replicates.

The standard deviation can be calculated from the square root of sum of the absolute error squared divided by the N or $N-1$ depending on the number of replicates. For $N \geq 30$ N is used.

Q TEST FOR AN OUTLINER

Q test for an outlier replicate is given by gap and w is the spread, range

$$Q = |x_o - x_c| / w \text{ where } x_c = \text{the nearest replicate to the suspected value or the outlier, i.e. the odd value, } x_o$$

This ratio is then compared with Q_{crit} found in standard tables which takes into account the number of observations and the confidence level e.g. 90%, 95% or 99%. If Q is greater than Q_{crit} then the questionable result can be rejected with the indicated degree of confidence.

Standard tables for Q_{crit} are used to determine the rejection of a replicate. These tables depend on the number of replicates and the sought degree of precision. Below is table of up to 10 replicates.

Table summarizes the limit, critical, values of Q- test

No. of Replicates	Confidence level %		
	90	95	99
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740

7	0.507	0.568	0.680
8	0.468	0.526	0.635
9	0.437	0.493	0.598
10	0.412	0.466	0.568

Example: Consider the data set below, Check for an outlier using Q test.

0.18, 0.15, 0.19, 0.17, 0.12, 0.19, 0.17, 0.16, 0.18, 0.18

$$Q = \text{Gap} / \text{range}$$

$$Q = (0.15-0.12) / (0.19 - 0.12) = 0.429$$

With 10 observations and at 90% confidence, $Q = 0.429 > 0.412 = Q_{\text{table}}$, so we conclude 0.12 is an outlier. However, at 95% or 99% confidence is not considered an outlier.

Practice Questions

Q1. Consider the data set below, Check for an outlier using Q test at 90% confidence.

0.18, 0.15, 0.19, 0.17, 0.12, 0.19, 0.17, 0.16, 0.18.

Q2. Carry out a Q test for the following data using the indicated confidence

a) 0.23, 0.27, 0.20, 0.29, 0.15, 0.19 at 99% confidence.

b) at 95% confidence for 1.1, 1.9, 1.6, 1.8

Q3: The following results were obtained in the replicate determination of drug content in blood samples: 0.70, 0.75, 0.65, 0.75, 0.79 ppm. Calculate

- a) The mean, mode and median
- b) The variance
- c) The Standard deviation
- d) The spread.
- e) The standard error of the mean
- f) Apply a Q test at 99% confidence.

Q4. Use your text book to write an account of 60 ± 20 words on the three types of errors in analytical chemistry.

Q5. Differentiate between; a) accuracy and precision b) quantitative and qualitative analysis.

Gravimetric Analysis

Gravimetric analysis is concerned about finding the mass of a certain substance in a sample, the analyte or the sought substance.

For example, the determination of calcium in natural waters involves the conversion to calcium oxalate. Excess oxalic acid is added to the sample followed by neutralization with ammonia. The latter converts the acid into oxalate ions which precipitates calcium ions from solution.

Calcium oxalate is then filtered and washed, dried and ignited to produce the stable material substance, calcium oxide. After cooling the crucible, calcium oxide is weighed and the mass of calcium oxide is determined by subtracting the known mass of the empty crucible from the combined mass.

The crucible with the lid on have to be cooled and weighted. The heating, cooling and reweighing process has to be repeated until a constant weight is achieved. The safety measures for handling hot equipment must be followed.

The mass of calcium is then calculated from the balanced chemical equations.

Types of Gravimetric Analysis;

GA is based on mass measurements. It is of three types;

1. Volatilization gravimetry, the analyte is separated from other constituents of the sample by conversion to a gas of known chemical composition. The weight of the gas then serves as a measure of the analyte concentration.

2. Electrogravimetry, the analyte is separated by deposition on an electrode by electrical current. The mass of this product then provides a measure of the analyte concentration.

3. In precipitation gravimetry, the analyte is converted to sparingly soluble precipitate. The later is then filtered, washed, heated to produce a precipitate of known composition and weighed.

Q6. Sketch the following equipments;

Equipment	Sketch
a) A conical flask,	
b) A volumetric flask	
c) Burette with a stand and a clamp.	
d) Tong	
e) A crucible a lid on.	
f) A Busen burner	

g) a pipestem tringle	
h) a gauze	

The Gravimetric Factor

The gravimetric factor denoted by G_f is the ratio of the (atomic, molecular or formula mass of the analyte) in g/mol divided by the (atomic, molecular or formula mass of the precipitate) multiplied by the ratio of number of moles required to balance the two substances. For example the gravimetric factor of iron ore precipitated as iron(III)oxide is $2 \times 56/160$, because there are two Fe^{3+} in the oxide.

Q: What is the gravimetric factor of Fe_3O_4 to be precipitated as

A) Fe_2O_3 ?

B) FeO ?

Q: What is the gravimetric factor of Ca^{2+} to be precipitated as calcium oxide?

Properties of precipitates

It is easily filtered and washed.

It has low solubility to reduce loss of mass during filtration and washing.

It does not react with constituents of the atmosphere.

It has known chemical composition after it is dried or ignited.

Factors affecting the Precipitate particle size

In gravimetry, the main concern is how to obtain easily filtered and pure solids of known composition.

The particles of a precipitate vary widely in particle size. Small particles, invisible to naked eye (0.1-100 μ m in diameter) form colloidal precipitates. The later do not settle from solution and are not easily filtered. On the other hand, particles of in the liquid phase of diameters greater than 0.1 mm tend to settle spontaneously forming crystals that can be filtered easily.

The main factors affecting the particle size of a precipitate

The main factors are;

1. Solubility,
2. Temperature
3. Reactant concentrations
4. Rate of mixing reactants

The Control of Particle Size

The particle size of a precipitate is directly proportional to the relative supersaturation given by $(Q-S)/S$ where Q is the concentration of the solute at any instant and S is the equilibrium solubility.

A combination of nucleation and particle size determines the particle size. High relative supersaturation favors nucleation leading to smaller particle sizes. Particle growth predominates and precipitation on existing particles leading to larger particles at low supersaturation.

Therefore, larger particle size of a precipitate can be enhanced by increasing S and minimizing Q. This goal can be achieved by increasing temperature, using dilute solutions, slow mixing with continuous stirring and controlling pH.

Precipitating Agents

Inorganic Precipitating Agents

Inorganic reducing agents form slightly soluble salts or hydrous oxides.

They include ammonium hydroxide, hydrogen sulphide, diammonium sulphide, diammonium hydrogen phosphate, sulphuric acid, oxalic acid, silver nitrate and barium chloride

Organic Precipitating Agents

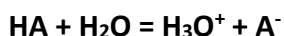
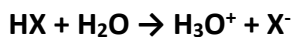
Several reagents can react selectively with certain organic functional groups. These reagents can be used for the determination of compounds containing these functional groups.

Examples are; 2,4-dinitrophenylhydrazine for carbonyl quinoline for aromatic carbonyl,

mass of barium phosphate for phosphates and mass loss of Cu for azo compounds.

Lecture 3: Complex systems in Acid- Base volumetric analysis

Mixtures of Strong Acids and Weak Acids



Example 1:

Calculate the pH of a solution containing 25.0ml of 0.12M HCl and 0.10M HA when titrated with 0.10M KOH at (i) start (ii) after addition of 10.0 ml (iii) 29.0ml and (iv) after addition of 30.0ml KOH solution.

At start, the hydronium ions come from the complete dissociation of HCl and the partial dissociation of the weak acid HA.

As a valid approximation, the amount of H_3O^+ from HA is very small as compared to that from HCl. Hence,

$$\text{H}_3\text{O}^+ = 0.12 \text{ M and the pH}$$

$$= -\log \text{H}_3\text{O}^+ = 0.92$$

After addition of 10.0ml 0.10M KOH, the strong acid will react with an equivalent amount of KOH according to the equation:



The remaining HCl will be:

$$(25 \times 0.12 - 10 \times 0.1) / (25 + 10) = 0.057 \text{ M}$$

Still the concentration of H_3O^+ from HCl is greater than that from HA, hence the $[\text{H}_3\text{O}^+]$ will be = 0.057 and the $\text{pH} = -\log 0.057 = 1.24$

$$\text{HCl}_{\text{left}} = (25 \times 0.12 - 29.5 \times 0.1) / (25 + 29.5) = 9.17 \times 10^{-4} \text{ M}$$

$$\text{and } [\text{HA}] = 0.1 \times 25 / 54.5 = 0.046 \text{ M}$$

From the dissociation constant of the weak acid we write,

$$1 \times 10^{-4} = [\text{H}_3\text{O}^+][\text{A}^-] / [\text{HA}]$$

On rearranging this equation gives,

$$[\text{HA}] = [\text{H}_3\text{O}^+][\text{A}^-] / 1 \times 10^{-4}$$

$$\text{Since } [\text{HA}] + [\text{A}^-] = 0.046$$

$$[\text{H}_3\text{O}^+][\text{A}^-] / 1 \times 10^{-4} + [\text{A}^-] = 0.046$$

Making [A] the subject of the equation gives;

$$[\text{A}^-] = 0.046 \times 1 \times 10^{-4} / ([\text{H}_3\text{O}^+] + 1 \times 10^{-4})$$

$$\text{Since } [\text{H}_3\text{O}^+] = \text{HCl}_{\text{left}} + [\text{A}^-]$$

$$[\text{A}^-] = 4.6 \times 10^{-5} / ([\text{H}_3\text{O}^+] + 1 \times 10^{-4})$$

$$\text{and } [\text{H}_3\text{O}^+]_{\text{total}} = [\text{H}_3\text{O}^+]_{\text{HCl}} + [\text{H}_3\text{O}^+]_{\text{HA}}$$

$$[\text{H}_3\text{O}^+] = 9.17 \times 10^{-4} + 4.6 \times 10^{-5} / ([\text{H}_3\text{O}^+] + 1 \times 10^{-4})$$

Multiplying by the denominator and solving the quadratic equation, using the formulae, for $[\text{H}_3\text{O}^+]$ gives;

$$[\text{H}_3\text{O}^+]^2 - 8.17 \times 10^{-4} [\text{H}_3\text{O}^+] - 4.609 \times 10^{-5} = 0$$

$$[\text{H}_3\text{O}^+] = 7.21 \times 10^{-3} \text{ and } \text{pH} = 2.14$$

Q: Calculate the pH at the equivalence point and after addition of 5.0ml after the equivalence point.

H/W: Write an account o the calculation of pH of Salt solutions with an example.

Polyfunctional Acids

Phosphoric Acid with K_{a1} , K_{a2} and K_{a3} as 7.11×10^{-3} , 6.32×10^{-8} and 4.5×10^{-11} respectively.

K for the dissociation of phosphoric acid equals the product of the constants of the three steps.

Q3: Write expression for the dissociation constants of sulphuric acids.

Q4: Comment on their relative magnitudes.

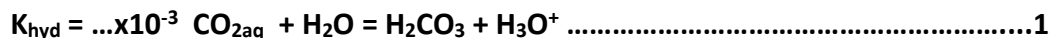
Buffer Solutions Involving Polyprotic Acids

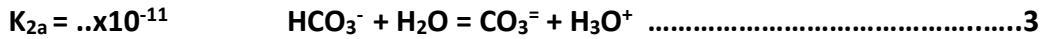
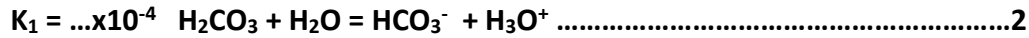
In such systems, the pH increases as dissociation continues. Approximations involving neglecting the acidity from the dissociation of the acid are common.

Q1 Find the pH of a buffer solution that is 1.0M in phosphoric acid and 0.5M in potassium dihydrogen phosphate.

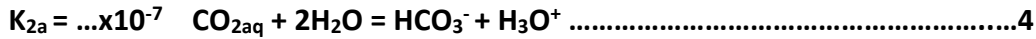
Q2 Find the pH of a buffer that is 0.02M in potassium hydrogen phthalate, KHP, and 0.4M in in potassium phthalate, K_2P .

Solutions Containing Carbon Dioxide





By addition of eq. 1 to eq. 2 implies;



By approximation, $\text{CO}_{2(aq)}$ is the main form as others can be neglected by they are so small in concentration and

$$[\text{H}_3\text{O}^+] = [\text{HCO}_3^-]$$

$$1 \times 10^{-7} = [\text{HCO}_3^-][\text{H}_3\text{O}^+] / [\text{CO}_{2(aq)}]$$

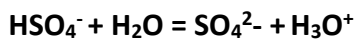
$$[\text{H}_3\text{O}^+] = \sqrt{1 \times 10^{-7} [\text{CO}_{2(aq)}]}$$

And the $\text{pH} = -\log \sqrt{1 \times 10^{-7} [\text{CO}_{2(aq)}]}$

Solutions Containing Sulphuric Acid

Finding the pH of sulphuric acid solutions is complicated as the first ionization of this dibasic acid is complete while the second is partial with a K_{2a} of 1.02×10^{-2} .

Example: Calculate the Hydronium ion in 0.04M sulphuric acid.



As a first approximation, the dissociation of the hydrogen sulphate ion is neglected;

$$[\text{H}_3\text{O}^+] \approx [\text{HSO}_4^-] = 0.04 \text{ M}$$

This leads to $1.02 \times 10^{-2} = 0.04 [\text{SO}_4^{2-}] / 0.04$

$[\text{SO}_4^{2-}] = 1.02 \times 10^{-2}$ or 0.0102 which is not small as compared with to $[\text{HSO}_4^-]$ of 0.04 and the approximation is not valid.

$$[\text{H}_3\text{O}^+] = 0.04 + [\text{SO}_4^{2-}] \text{ or } [\text{SO}_4^{2-}] = [\text{H}_3\text{O}^+] - 0.04 \text{ M}$$

Also, $0.04 = [\text{HSO}_4^-] + [\text{SO}_4^{2-}]$

Hence; $[\text{HSO}_4^-] = 0.04 - [\text{SO}_4^{2-}]$

From the expression for K_{2a}

$$1.02 \times 10^{-2} = \frac{[H_3O^+][H_3O^+] - 0.04}{0.08 - [H_3O^+]}$$

$$[H_3O^+]^2 - (0.0298) [H_3O^+] - 8.16 \times 10^{-4} = 0$$

Solving using the formulae gives

$$[H_3O^+] = 0.0471M$$

Acid Base Behaviour of Amino Acids

Neutral aa = Zwitterion, eq.

Zwitter as an acid,eq.1

Zwitter as a base,eq.2

Some amino acids are acidic while others are basic. However glycine is acidic.

At the isoelectric point there is no net migration of amino acid.

Writing expressions and dividing K_a by K_b gives;

At the isoelectric point $-ve$ ions = $+ve$ ions, hence

$$[H_3O^+] = \sqrt{K_a K_w / K_b} \quad K_a / K_b = [H_3O^+] / [OH^-], \text{ therefore,}$$

For glycine the isoelectric point occurs at 6.