


Subject: Analytical Chemistry / Instrumentation

Production of Courseware

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Paper No. : 01 Fundamentals of Analytical Chemistry

Module : 15 Titrimetric method of analysis



Principal Investigator: Dr. Nutan Kaushik, Senior Fellow
The Energy and Resources Institute (TERI), New Delhi

Co-Principal Investigator: Dr. Mohammad Amir, Professor of Pharm. Chemistry,
Jamia Hamdard University, New Delhi

Paper Coordinator: Prof. Rajeev Jain, Professor of Chemistry, Jiwaji
University, Gwalior

Content Writer: Dr. Nimisha Jadon, Assistant Professor, Jiwaji University,
Gwalior

Content Reviewer: Prof. Rajeev Jain, Professor of Chemistry, Jiwaji
University, Gwalior

Description of Module	
Subject Name	Analytical Chemistry / Instrumentation
Paper Name	Fundamentals of Analytical Chemistry
Module Name/Title	Titrimetric methods of analysis
Module Id	15
Pre-requisites	
Objectives	
Keywords	

Paper: Fundamentals of Analytical Chemistry

Module 15

Titrimetric methods of analysis

INTRODUCTION

Titrimetric or volumetric analysis is one of most important technique of analytical chemistry and its calculations involved are based on simple stoichiometric relationships. The term titration refers to process of measuring the volume of titrant required to reach equivalence point. However, from a rigorous standpoint the term titrimetric is preferable because volume measurements need not be confined to titrations.

TYPES OF TITRATIONS

Chemical reactions which may serve as the basis for titrimetric determinations are of four types:

1. Acid –base

If HA represents the acid to be determined and B the base, the reactions are



The titrants are generally standard solutions of strong electrolytes, such as sodium hydroxide and hydrochloric acid.

2. Oxidation-reduction (redox)

Chemical reactions involving oxidation-reduction are widely used in titrimetric analyses. For example, iron in the +2 oxidation state can be titrated with a standard solution of cerium(IV) sulfate:



3. Precipitation

The precipitation of silver cation with the halogen anions is a widely used titrimetric procedure. The reaction is



4. Complex formation

An example of a reaction in which a stable complex is formed is that between silver and cyanide ions:



This reaction is the basis of the so-called Liebig method for the determination of cyanide. Certain organic reagents, such as ethylene di amine tetra acetic acid (EDTA), form stable

complexes with a number of metal ions and are widely used for the titrimetric determination of these metals.

Conditions for Reactions Used in Titrimetric Analysis

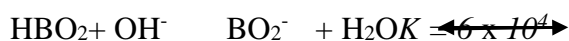
A reaction must satisfy following requirements:

1. It must proceed as per a definite chemical equation. There should be no side reactions.
2. The reaction should be almost complete at the equivalence point.
3. An indicator should be available, or some instrumental method may be used to tell the analyst to stop the addition of titrant.
4. It is desirable that the reaction should not be time consuming, so that the titration can be completed in a few minutes. Consider an example of a reaction well suited for titrations,



- The reaction goes to virtual completion. At the equivalence point the large change in pH of the solution takes place by a few drops of titrant, and a number of indicators are available which respond to this pH change by changing colour.

On the other hand, there are many reaction which are not sufficiently complete to satisfy requirement 2, for example the reaction between boric acid and sodium hydroxide



CONCENTRATION SYSTEMS

- The methods used by the analytical chemistry to express the concentration of a solution, viz., relative amounts of solute and solvent.

- The systems of molarity and normality are most commonly used since they are based on the volume of solution, the quantity of analyte measured in a titration.
- Formality and analytical concentration are useful in situations where dissociation or complex formation occurs.
- The percent -by -weight system is commonly used to express approximate concentrations of laboratory reagents.
- For very dilute solutions parts per million or parts per billion units are convenient.

MOLECULAR AND FORMULA WEIGHTS

- The mole (or mol) is defined as the amount of a substance which contains as many entities. The entities may be atoms, molecules, ions, or electrons.
- If particles are molecules, weight in grams of a mole of substance is called the gram - molecular weight (usually molecular weight).
- If the particles are atoms, the weight in grams of 1 mol of the substance is called the gram atomic weight.
- The term gram formula weight (or formula weight) is the addition of the atomic weights of all the atoms in the chemical formula of a substance and is normally the same as the molecular weight.
- We shall use the term molecular weight as synonymous with formula weight in such cases.

MOLARITY

- Molar concentration, also called molarity, amount concentration or substance concentration is a measure of the concentration of a solute in a solution, or of any chemical species, in terms of amount of substance in a given volume.
- Unit for molar concentration is defined as the number of moles per litre.

WEIGHT PERCENT

- This system of concentration is commonly employed to express approximate concentrations of laboratory reagents.
- It specifies number of grams of solute per 100 g of solution:

$$P = \frac{w}{w + w_0} \times 100$$

$w + w_0$

Where, P is the percent by weight of solute,
 w the number of grams of solute, and
 w_0 the number of grams of solvent.

PARTS PER MILLION (PPM)

- PARTS PER MILLION is convenient for expressing the concentrations of very dilute solutions.
- It specifies the number of parts of solute in 1 million parts of solution and can be expressed mathematically as

$$\text{ppm} = \frac{w}{w + w_0} \times 10^6$$

$w + w_0$

Where,

w is the number of grams of solute

w_0 the number of grams of solvent.

STOICHIOMETRIC CALCULATIONS

Once the concentration of a solution determined, it can be employed as a titrant in the determination of purity of an unknown sample. The calculations involved, called *stoichiometric*, are based on the mole and mass relations between the elements and compounds as expressed by a chemical equation

STANDARDIZATION OF SOLUTIONS

The process by which the concentration of a solution is determined is called *standardization*. The few substances which are adequate in this regard are called *primary standards*. A solution is standardized by a titration in which it reacts with a weighed portion of a primary standard. A widely used primary standard for base solutions is the compound potassium hydrogen phthalate, abbreviated KHP, Sulfamic acid, HSO_3NH_2 , and potassium hydrogen iodate, $KH(IO_3)_2$, are both strong acids and are excellent primary standards. Sodium carbonate, Na_2CO_3 and tris(hydroxymethyl) aminomethane, known as TRIS or THAM, are common primary standards for strong acids.

ALIQUOTS

Analyst weighs the primary standard, dissolves it in a volumetric flask, and withdraws a portion of the solution using a pipette, the withdrawn portion is called an aliquot. *An aliquot is a known portion of the whole, usually some simple fraction.* This process of dilution to a known volume and removing a portion for titration is called *taking an aliquot*.

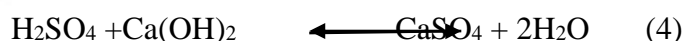
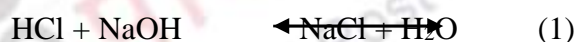
DILUTION

Take an aliquot of a standard solution and diluting it to a larger volume in a volumetric flask.

The number of moles of solute in the original solution must be the same as the number of moles in the final solution.

EQUIVALENT WEIGHTS AND THE NORMALITY SYSTEM OF CONCENTRATION

The term equivalent in an attempt to simplify stoichiometric calculations in titrimetry. A titration involves adding the titrant until an amount chemically equivalent to the analyte is reached and this point is called the equivalence point (EPt). The equivalent is defined so that at the EPt the equivalents of analyte and titrant are always equal. Examples:



NORMALITY

The normality system of concentration is based on the volume of solution.

Normality = number of equivalents per liter of solution

or $N = \frac{\text{eq}}{V}$

V

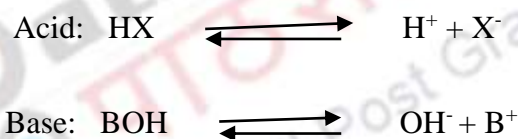
Where N is the normality, eq the number of equivalents, and V the volume of solution in liters.

ACID-BASE TITRATION

Titration involving acids and bases are widely employed in the analytical chemistry.

BRONSTED TREATMENT OF ACIDS AND BASES

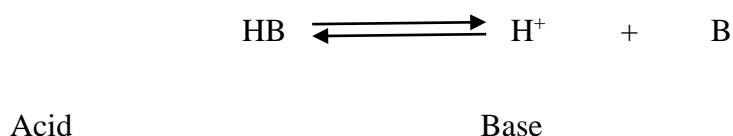
The quantitative treatment of acid-base equilibria became possible after 1887, when Arrhenius presented his theory of electrolytic dissociation in water solution, according to Arrhenius, acids dissociate into hydrogen ions and anions, and bases dissociate into hydroxide ions and cations:



The Debye-Huckel theory (1923) permitted a refined treatment that was even better.

The Bronsted Theory

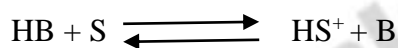
In 1923, Bronsted presented a new view of acid-base behaviour. In Bronsted terms, an acid is any substance that can donate a proton, and a base is a substance that can receive a proton. The hydroxide ion, to be sure is such a proton acceptor and hence a Bronsted base. When an acid yields a proton, the deficient species must have some proton affinity and hence it is a base. Thus in the Bronsted treatment we encounter conjugate acid-base pairs:



The acid HB may be electrically neutral, anionic, or cationic (e.g., HCl, H₂SO₄, NH₄⁺), and thus we have not specified the charge on either HB or B.

LEVELING EFFECT

If HB is inherently a stronger acid than HS⁺, it will transfer its proton to the solvent



A series of acids, all of which are very much stronger than the solvated proton, will dissociate completely; such solutions will be brought to a level of acidity governed by the acid strength of HS⁺. This is known as the *leveling effect*. According to Bronsted terms, the dissociation of bases is treated in a similar fashion, except that here the process is promoted by the *acidity of the solvent*. The interaction of two conjugate pairs can be:



TITRATION CURVES

To know about a reaction to determine whether or not it can be used for a titration, it is of interest to construct a titration curve. For acid-base reactions a titration curve consists of a plot of pH or pOH vs. milliliters of titrant. We shall examine two cases, titration of a strong acid with a strong base and titration of a weak acid with a strong base.

Strong Acid-Strong Base Titration

Strong acids and bases (Fig 1) are completely dissociated in aqueous solution. At the equivalence point the pH is determined by the extent to which water dissociates at 25°C the pH of pure water is 7.00.

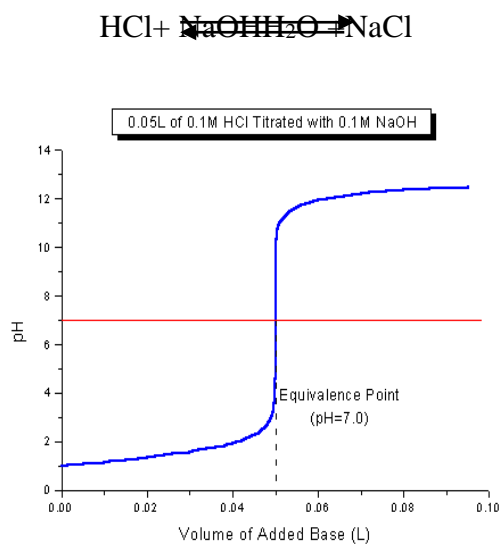


Figure-1

Weak Acid vs Strong Base Titration

Titration of a weak Acid with a strong base (fig 2) at the equivalence point, all of the weak acid is neutralized and converted to its conjugate base (the number of moles of H^+ is equal to added number of moles of OH^-). However, the pH at the equivalence point does not equal 7.

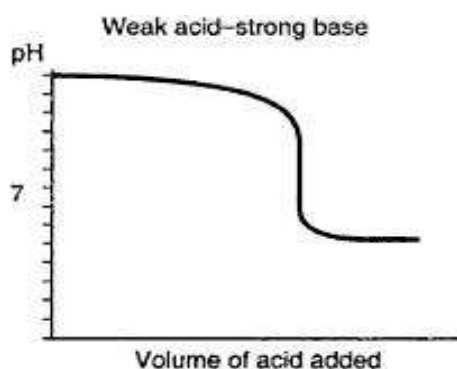
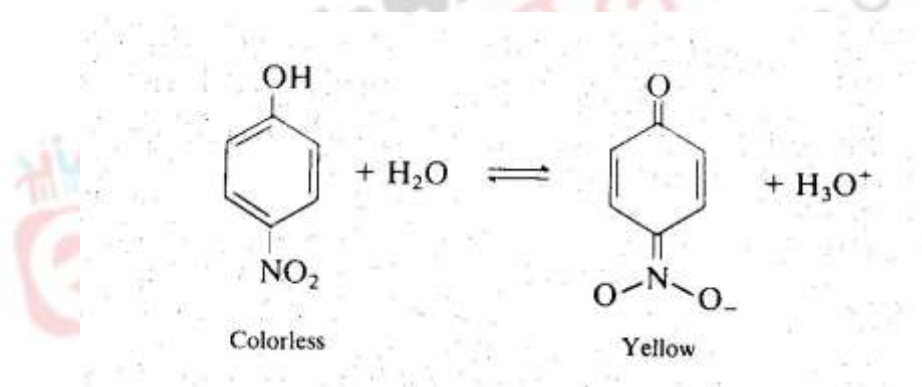


Fig: 2 Weak Acid vs Strong Base Titration curve

INDICATORS FOR ACID BASE TITRATION

Principle of indicator Behaviour

There are many weak organic acids and bases in which the undissociated and ionic forms show different colors. Such molecules may be used to determine when sufficient titrant has been added and are termed visual indicators. A simple example is p-nitrophenol, which is a weak acid, dissociating as follows:



The undissociated form is colorless, but anion, which has single and double bonds is yellow. Phenolphthalein is a diprotic acid and is colorless. It dissociates first to a colorless form and then, on losing the second proton, to an ion with a conjugated system; a red color results. Methyl orange indicator, is a base and is yellow in the molecular form. Addition of a proton gives a cation which is pink in color. Fig 3: shows the reactions

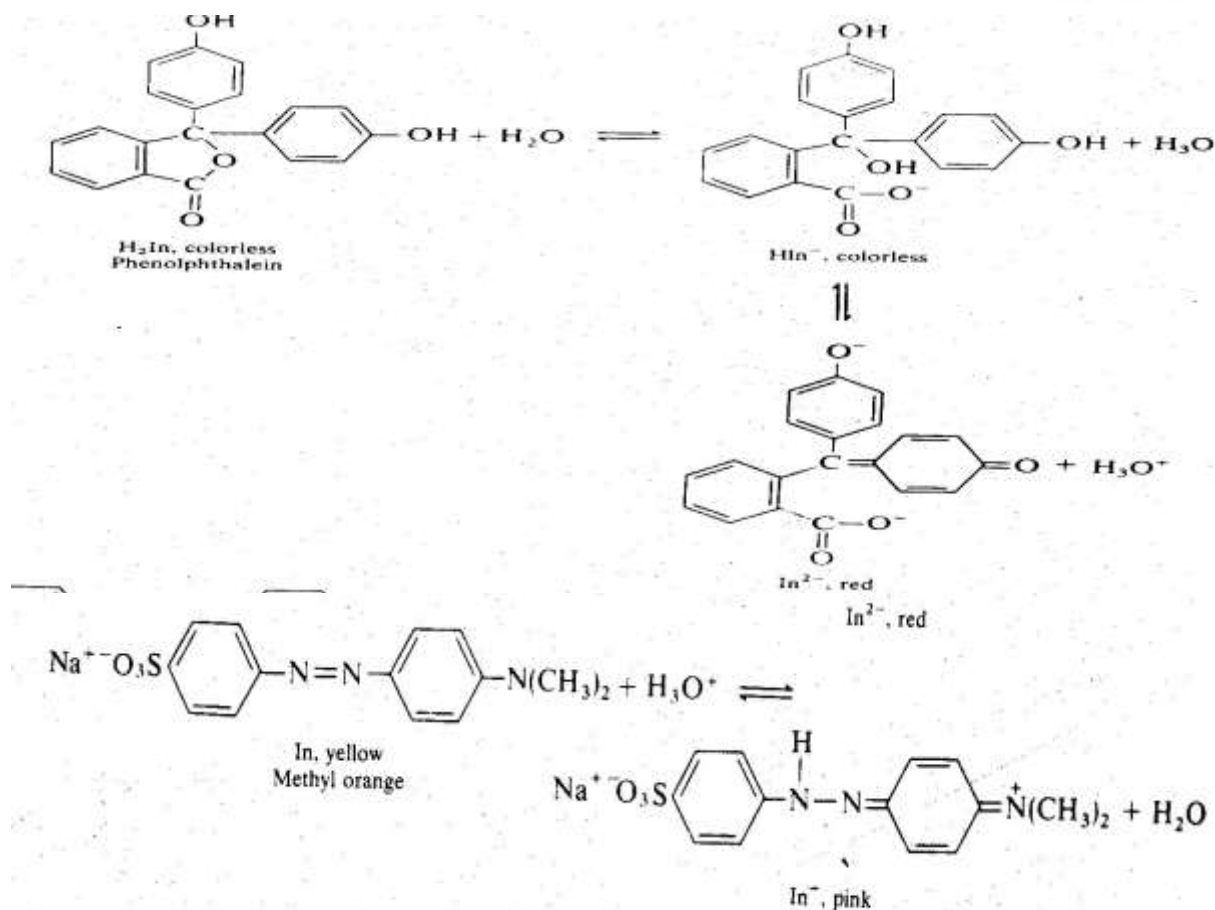


Fig 3: visual indicators

INDICATOR ERRORS

There are two chances of error in determination of the end point of a titration using visual indicators. One occurs when the indicator does not change its colour at the proper pH. This is a determinate error and can be corrected by the running an indicator blank. The indicator blank is usually determined experimentally. A second error occurs in case of weak acids (or bases) when we plot the curve where slope of the titration curve is not great and hence color change at the end point is not sharp.

SELECTION OF PROPER INDICATOR

TABLE-1

Name of Indicator	Indicator range
Methyl orange	3.1 to 4.4
Bromthymol blue	6.0 to 7.6
Phenolphthalein	8.0 to 9.6

A strong acid is titrated, large change in pH at *equivalence* point is sufficient to span the ranges of all three indicators. Hence anyone of these indicators would change colour within one or two drops of the equivalence point, as would any other indicator' changing colour between pH 4 and 10. In titration of weaker acids, choice of indicators is much more limited. *Phenolphthalein* changes colour at approximately the equivalence point and is a suitable indicator.

MAGNITUDE OF THE EQUILIBRIUM CONSTANT

The concentrations of the substance titrated and the titrant influence the magnitude of ΔpH , and under certain circumstances. All of the substance titrated be converted into product at or near the equivalence point and *conversion of the analyte into product at the equivalence point*. It is also desirable that the pH change by 1 or 2 units on the addition of a few drops of titrant at the equivalence point if a visual indicator is to be employed.

Effect of Concentration

The magnitude of ΔpH at the equivalence point also depends upon the concentrations (fig 4) of the analyte and the titrant.

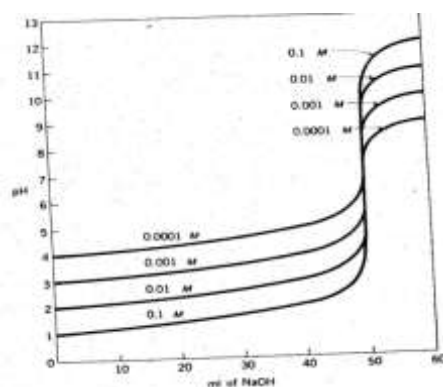


Fig 4: Effect of concentration on titration curves of strong acids with strong bases.
50 L acid titrated with base of same molarity as that of the acid

APPLICATIONS OF ACID-BASE TITRATIONS

Acid-base titrations are widely used for chemical analyses.

✓ *Acid-Base Reagents*

- In laboratory practice, to prepare and standardize one solution of an acid and one of a base.
- These two solutions can then be used to analyze unknown samples of acids and bases.
- Since acid solutions are more easily preserved than basic solutions.
- An acid is normally chosen as a permanent reference standard in preference to a base.

✓ *Primary Standards*

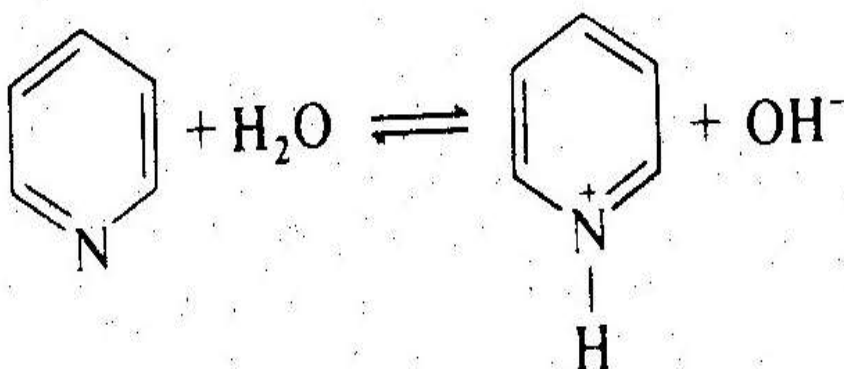
- In laboratory practice, it is customary to prepare solutions of an acid and a base of desired concentration and then to standardize the solutions against a primary standard.

✓ *Analyses Using Acid-Base Titrations*

- A wide variety of acidic and basic substances, both inorganic and organic, can be determined by an acid-base titration.

SOLVENT SYSTEMS

Several classifications of solvents have been proposed. Some, such as methanol and ethanol, have acid-base properties comparable to water and, along with water, are called neutral solvents. Others, called acid solvents, such as acetic acid, formic acid, and sulfuric acid, are much stronger acids and weaker bases than water. Basic solvents such as liquid ammonia and ethylenediamine have greater basicity and weaker acidity than water. Aprotic, or inert, solvents are neither appreciably acidic nor basic and hence show little or no tendency to undergo autoprotolysis reactions. Pyridine, for example, can accept a proton from an acid such as water:



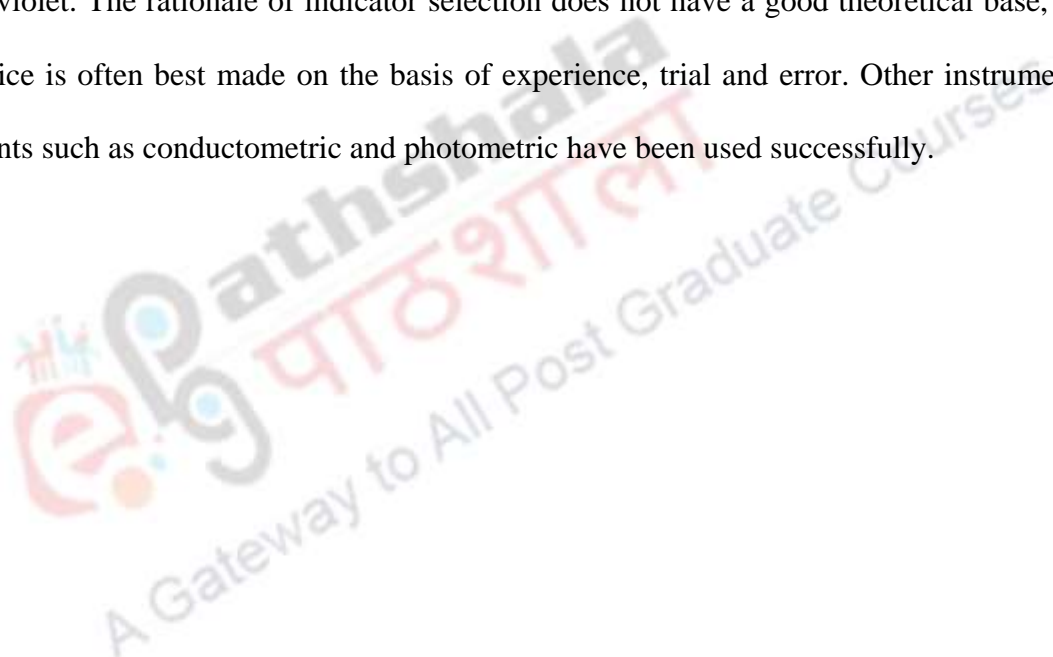
Pyridine has no tendency to furnish a proton. A fourth class of solvents would be with acidic but no basic properties.

TITRANTS

The **titrant** is the solution used in a titration to determine the concentration of an unknown solution. The **titrant** is a solution of known concentration that is by a burette delivered into a known quantity of the solution of unknown concentration. Perchloric acid is by far the most widely used acid for the titration of weak bases.

END-POINT DETECTION

A number of visual indicators are available such as cresol red methyl red, azo violet and crystal violet. The rationale of indicator selection does not have a good theoretical base, and the choice is often best made on the basis of experience, trial and error. Other instrumental end points such as conductometric and photometric have been used successfully.



I. Multiple choice questions

- 1. Titrimetric method of analysis is based on a**
 - a. Physical parameters
 - b. Chemical reaction
 - c. Both a & b
 - d. None of these

- 2. Substance concentration is a measure of the concentration of a solute in a solution, or of any chemical species, in terms of amount of substance in a given volume is known as**
 - a. Molarity
 - b. Molality
 - c. Normality
 - d. Formality

- 3. Acid-base reactions a titration curve consists of a plot of**
 - a. pH or pOH vs. moles/liters of titrant.
 - b. pH or pOH vs. milliliters of titrant.
 - c. Both a & b
 - d. None of these

Answers

1. B
2. A
3. B

II. Fill in the blanks:

1. The is the solution involved or used in a titration to determine the concentration of an unknown solution.
2. Conversion of the analyte into product at the _____
3. Indicator range of methyl orange _____
4. Indicator range phenolphthalein _____

Answers:

1. Titrant
2. Equivalence point.
3. 3.1 to 4.4
4. 8.0 to 9.6

III. Match the following:

- | | |
|------------------------|---|
| 1. Acid –base | a. $\text{Fe}^{2+} + \text{Ce}^{4+} \rightleftharpoons \text{Fe}^{3+} + \text{Ce}^{3+}$ |
| 2. Oxidation rediction | b. $\text{HA} + \text{OH}^- \rightleftharpoons \text{A}^- + \text{H}_2\text{O}$ |
| 3. Precipitation | c. $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$ |
| 4. Complex formation | d. $\text{Ag}^+ + \text{X}^- \rightleftharpoons \text{AgX}(\text{s})$ |

Answers:

1. B

2. A
3. D
4. C

IV. Which statement is true or false?

1. The term gram formula weight (or formula weight) is the summation of the atomic weights of all the atoms in the chemical formula of a substance and is normally the same as the molecular weight.(TRUE)
2. Stoichiometric, are based on the mole and mass relations between the elements and compounds.(TRUE)
3. A solution with a concentration of 1 mol/L is equivalent to 1 molar (1 m). (TRUE)
4. Indicator range of bromthymol blue is 3.1 to 4.4. (FALSE)

V. Do you know?

1. Formality and analytical concentration are useful in situations where dissociation or complex formation occurs.
2. The percent -by -weight system is commonly employed to express approximate concentrations of laboratory reagents.
3. For very dilute solutions parts per million or parts per billion units are convenient.

VI. Interesting facts:

1. In 1923, Bronsted presented a new view of acid-base behaviour.
2. The quantitative treatment of acid -base equilibria became possible after 1887, when Arrhenius presented his theory of electrolytic dissociation water solution.
3. The Debye-Huckel theory (1923) permitted a refined treatment that was even better.

VII. Points to remember:

1. Normality = number of equivalents per liter of solution.
2. The weight in grams of 1 mol of the substance is called the gram atomic weight.
3. For very dilute solutions parts per million or parts per billion units are convenient.
4. The number of parts of solute in 1 million parts of solution.

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