

Module 9 : Experiments in Chemistry

Lecture 38 : Titrations : Acid-Base, Redox and Complexometric

Objectives

In this lecture you will learn the techniques to do following

- Determination of the amount of sodium carbonate and sodium hydroxide in a mixture by titration.
- Carrying out acid-base titration using a pH meter.
- Carrying out acid-base titration by conductometric measurement.
- Determination of the composition of a mixture of acetic acid and hydrochloric acid by conductometric titration.
- Determination of ferrous ion using potassium dichromate by internal indicator.
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- Determination of hardness (Ca^{2+}) of water using EDTA – complexometry method.

In this lecture, you will be introduced to a few experiments in chemistry. These experiments complement the theory you have learned in chemical equilibrium and kinetics.

38.1 Acid-Base Titrations:

Acid-base reactions are of great practical importance in analysis, not only because of their use in titrating a large number of inorganic and organic substances, but also because the hydrogen ion concentration of a solution often is of great importance in controlling reactions.

Titration :

The process of determining the volume of a given solution of a reagent equivalent to the amount of another reactant present in a standard solution is known as titration.

Equivalent Weight of Acids and Bases :

The equivalent weight of an acid is that weight which yields one mole of hydrogen ions in the reaction employed whereas the equivalent weight of a base is that weight which reacts with one mole of hydrogen ions in the reaction.

Normal solution :

A solution containing one equivalent weight of solute per litre of solution.

Equivalence Point :

When the number of equivalents of acid (respectively base) added is equal to the number of equivalents of base (respectively acid) taken initially, we have reached the equivalence point.

Acid-Base Indicators :

Weak organic acids or bases having different colours for their dissociated or undissociated forms e.g., phenol red which is yellow in colour in its undissociated form in acidic solution and red in its dissociated form in basic solution constitute these indicators.

Name of indicator	Colour in acid solution	Colour in basic solution	pH range
Methyl Orange	Red	Orange – yellow	3.1 – 4.6
Bromophenol Blue	Yellow	Blue – violet	3.0 – 4.6
Methyl Red	Red	Yellow	4.2 – 6.3
Bromothymol Blue	Yellow	Blue	6.0 – 7.6
Thymol Blue	Yellow	Blue	8.0 – 9.6

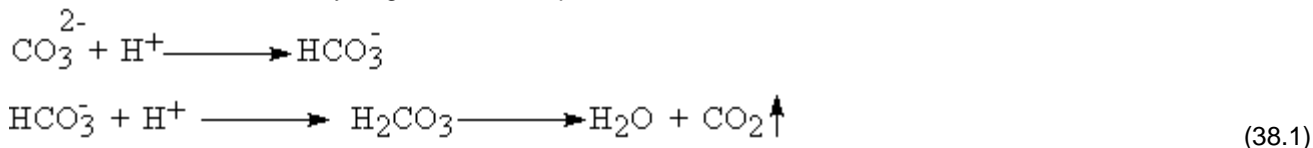
Phenolphthalein	Colourless	Red	8.0 – 9.8
Thymolphthalein	Colourless	Blue	9.4 – 10.6

◇ Table 38.1 Some acid-base indicators, their colour changes and pH range:

38.2 Experiment 1: Determination of the amount of sodium carbonate and sodium hydroxide in a mixture

Theory :

Carbonate ion reacts with hydrogen ions in steps:



The pK_{a1} and pK_{a2} values of H_2CO_3 are quite distinct and so when a carbonate solution is titrated against hydrochloric acid, there occur two distinct regions of sharp pH change. The first corresponding to the formation of HCO_3^- (pH 8 to 10) and the second due to complete neutralization at pH 4-6. The first is roughly in the pH range in which colour of phenolphthalein changes from red to colourless and the second is that at which methyl orange changes from yellow to orange red. This end point, however, is not very sharp in the titration of the strong base NaOH. The sharp change of pH occurs over a range of pH that includes the regions of colour change of both the indicators, so both of them give the end point correctly.

When we have both sodium carbonate and sodium hydroxide present together in a solution, a titration using phenolphthalein gives the titre (volume at the equivalence point) corresponding to sodium hydroxide plus half the carbonate and the titre obtained with methyl orange corresponds to the total alkali. The individual sodium carbonate and hydroxide concentrations may be calculated from the data.

The HCl solution used may be standardized by titration with a standard solution of sodium tetraborate decahydrate (borax) or anhydrous sodium carbonate. The reaction involved in the case of borax is



Borax is preferable as a primary standard because of its higher equivalent weight.

Procedure :

Prepare 100 mL of a standard solution of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (approximately N/20) by weighing accurately about one gram of borax, dissolving it in distilled water and making up to 100 mL. Titrate 10 mL portion of this solution against the supplied hydrochloric acid till concordant titres are obtained, using 2 drops of methyl orange as indicator. Calculate the strength of the HCl solution.

Pipette out 10 mL solution of a mixture of sodium carbonate and sodium hydroxide into a conical flask, add two drops of methyl orange indicator and titrate against HCl, till the colour changes from pale yellow to orange. Note the titre value (V_1). Titrate 10 mL portions of the solution using phenolphthalein as indicator (1-2 drops). The color changes here at the end point is from red to colourless and is quite sharp. Let the titre be V_2 of HCl. Therefore, $2(V_1 - V_2)$ corresponds to carbonate, and $V_1 - 2(V_1 - V_2) = 2V_2 - V_1$ corresponds to sodium hydroxide. Calculate the amount of NaOH and Na_2CO_3 present in a litre of the given solution in g/L.

38.3 Experiment 2: Acid-base titration using a pH meter

Theory :

When a base is added (volume, V) to acid, pH increases and reaches to 7.0 at the inflection point. Change in pH is very fast near the inflexion point. Therefore, value of $\Delta\text{pH} / \Delta V$ is the highest at inflexion point. Hence, the end point of an acid base titration could be easily measured by a pH Meter. A representative curve for a pH-metric titration of a strong monobasic acid with strong base is shown below:

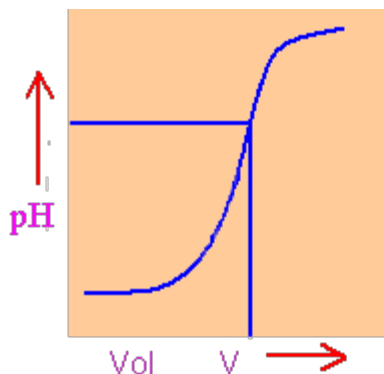


Figure 38.1 (a)

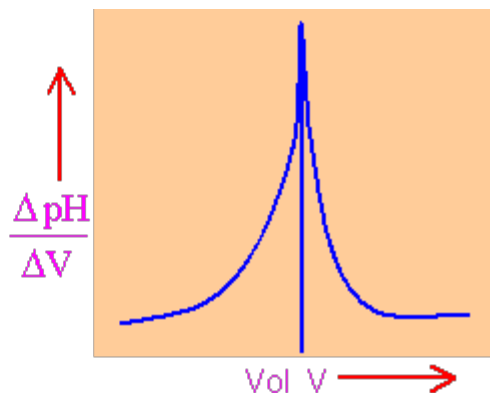


Figure 38.1(b) V = inflexion point

Figure 38.1(a) A graph of pH vs volume of base added (V). (b) The graph of $\Delta\text{pH} / \Delta V$ vs volume of base added, V.

Procedure :

Operation of pH meter

Switch on the instrument five minutes before use, then with the help of selector switch select the pH, mV or stand by mode of the instrument. Stand by means the instrument is not in operation to record pH or mV. Now keep the glass electrode in the standard buffer solution of known pH (say pH = 4) and adjust the pH with the adjustment knob. Take out the glass electrode from this buffer solution and wash it with distilled water, dry it gently with tissue paper and again use another buffer solution of known pH (say 9.0) and check the pH of the buffer. If the pH shown by the instrument is equal to the pH of the second buffer solution then the pH meter is supposed to be standardized and ready to record the pH of an unknown solution. Wash glass electrode with distilled water and dry it with tissue paper each time before putting it in other solution. The glass electrode is delicate and costly and hence the instrument must be handled carefully.

Titration :

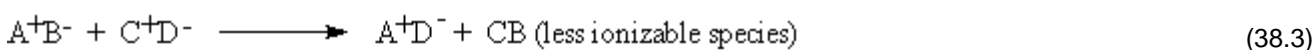
Before starting a titration be sure that pH meter is standardized as discussed above.

Now pipette out 25 mL solution of the acid of unknown strength into a 100 mL beaker and keep glass electrode in it in such a position that the bulb of the electrode is well inside the solution but not touching the bottom of the beaker. Note down the initial pH of this solution. Now run in NaOH (base) solution (which has been standardized by N/10 standard solution of oxalic acid using phenolphthalein as indicator) from the burette in small volume (0.5 mL) and gently stir the solution with a glass rod without striking the glass electrode. Determine and record the pH of the solution after each addition and also keep on recording the corresponding volume of base added to the solution. At the end point, there is a sharp change in pH. Continue adding of base and record pH until the pH ceases to rise remarkably. Plot titration curve (pH vs V) and differential titration curve $\Delta\text{pH} / \Delta V$ or $\left[(pH)_3 - (pH)_1 \right] / (V_3 - V_1)$ vs V_2 and locate the end point to record the volume of the base required for neutralization of the acid of unknown strength taken into a beaker.

38.4 Experiment 3: Acid-base titration by conductometric measurement

Theory :

Solution of electrolytes conduct electricity via cations and anions. The conductivity of the solution depends upon velocity and concentration (no. of ions) of the current carrying species. Ionic conductance is reciprocal to the resistance offered by the solution of the electrolyte. By measuring the variation in the conductance, the end point of acid base titration can be determined. The variation in conductance of the solution occurs due to the change in the number of current carrying ions on adding the titrant. This can be explained by taking an example of an electrolyte $A^+ B^-$ being titrated by another electrolyte $C^+ D^-$. The conductance of the solution on adding $C^+ D^-$ will depend upon the number and nature of the products formed on reacting $C^+ D^-$ with $A^+ B^-$.



Since the ions B^- and C^+ combine to give a neutral molecule, and charge carrying species are decreased in the

solution, hence the conductance will show a decreasing trend. The more conducting ion B⁻ could also be replaced by the less conducting ion D⁻.

Thus decreasing trend will continue till the end point is reached. After the end point, the conductance will start increasing due to the excess number of C⁺ and D⁻ ions. Thus by recording the variation in conductance, the end point can be determined. This method of analysis is applicable to any titration in which there is a sharp change in the conductivity at the end point. The method has the advantage that it can be used with a coloured solution as well and it will work where no indicator is found suitable. In order to get the accurate end point, it is necessary to keep one of the constituents (preferably titrant) fairly concentrated to avoid volume change of the solution.

Procedure :

Operation of the conductivity bridge: Switch on the instrument five minutes before the start of the exercise. Bring the 'function switch' to calibration position (cell constant position) and adjust the display reading with the cell constant knob. Keep the range selector at the maximum. Rinse the cell with the solution whose conductance is to be measured. After taking measurements, clean the cell with distilled water.

Titration :

To start the experiments, take 25mL of the acid (HCl) in a beaker and keep the conductivity cell in it in such a position that the electrodes of the cell are inside the acid solution and the body of the cell would not touch the bottom of the beaker. Note down the initial conductance of the solution. Now run NaOH in small volumes (0.5 mL) from the burette and gently stir the solution with a glass rod without striking the cell.

Determine the conductance of this solution. Repeat the determination of conductance of the solution after each addition of base volume of 0.5 mL. Carry out at least three – four more measurements after getting the minima of the conductance. Plot a graph between conductance and the volume of base added. extrapolate the straight line portions of the titration curve to obtain the correct end point.

Titration curve:

Figure shows the progress of titration of HCl with NaOH. The curve AC show the specific conductance of a mixture of acid and salt plotted against volume of NaOH added, while the curve BD corresponds to a mixture of salt and excess NaOH after the end point (the point at which the two lines cross) has reached.

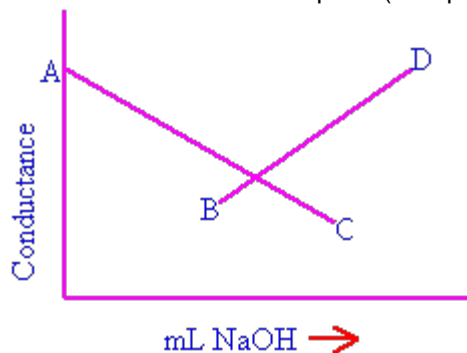


Figure 38.2 Conductometric titration: Progress of titration of HCl with NaOH

Precautions:

There should be no significant effect in conductivity due to dilution, so the titrant concentration used must be at least 10–100 times that of the solution being titrated.

38.5 Experiment 4: To determine the composition of a mixture of acetic acid and hydrochloric acid by conductometric titration.

Theory :

When a mixture containing acetic acid and HCl is titrated against an alkali, strong acid (HCl) will be neutralized first. The neutralization of a weak acid (CH₃COOH) commences only after the complete neutralization of strong acid. Thus, the conductance titration curve will be marked by two breaks, the first one corresponds to the equivalence point of HCl and second to that of CH₃COOH. In this way, knowing the volume of NaOH used to neutralize HCl and CH₃COOH and also knowing the exact strength of NaOH solution, concentration of the acids in the mixture and hence the composition can be calculated.

Procedure:

Take the mixture (say 40 mL 0.1 N CH₃COOH + 10 mL 0.1 N HCl) in a small beaker and titrate it against 1N

NaOH by addition 0.5 mL (or less volume each time from a micro-burette. Draw a conductance titration curve which will show two breaks.

Volume of NaOH at first break gives the value to neutralize HCl while difference between the two breaks will give equivalent volume of NaOH solution to neutralize CH₃COOH.

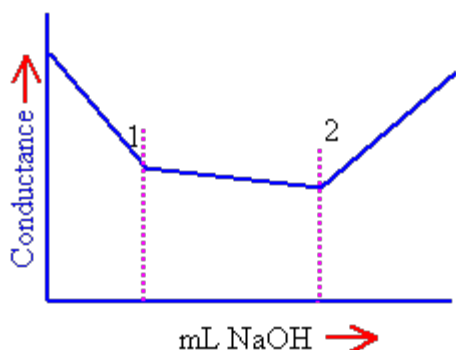
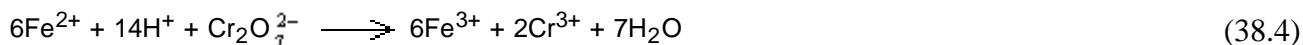


Figure 38.3: Conductometric titration curve for a mixture HCl and CH₃COOH

(a) equivalence point of HCl with NaOH (b) equivalence point of HCl with acetic acid

38.6 Redox Reactions

Oxidation-reduction reactions involve exchange of electrons between the reacting substances e.g., reaction between Fe²⁺ and Cr₂O₇²⁻.



The above reaction is called as redox reaction because it could be represented by two half reactions involving oxidation and reduction, respectively.

a) Oxidation of Fe²⁺ to Fe³⁺



b) Reduction of Cr⁶⁺ to Cr³⁺ ;



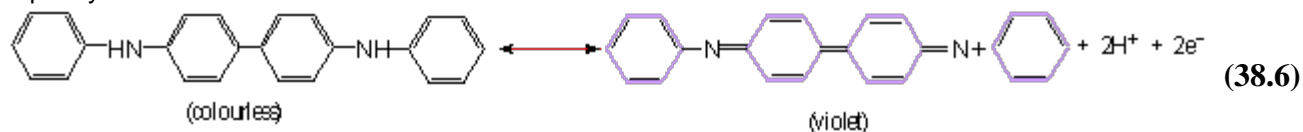
Equivalent weight of an oxidizing or reducing agent :

The equivalent weight of an oxidizing agent is the weight that accepts one mole of electrons and similarly the equivalent weight of a reducing agent is the weight that loses one mole of electrons.

This implies that in the reaction of ferrous ammonium sulphate with K₂Cr₂O₇ in acidic medium, equivalent weight of ferrous ammonium sulphate is the same as its molecular weight.

Oxidation Reduction Indicator :

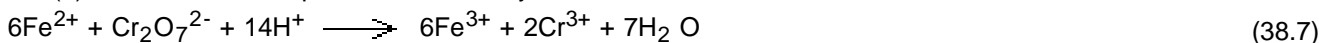
The change in potential at equivalence point of a titration may be detected by the addition of a suitable indicator. An indicator that exhibits a change in colour corresponding to a change in oxidation state is known as redox indicator. For example, colourless diphenyl-benzidine is oxidized to a coloured substance, diphenylbenzidine violet as shown:



38.7 Experiment 6: Determination of ferrous ions using potassium dichromate by internal indicator method

Theory :

Iron(II) is oxidized in the presence of acid by dichromate.



This disappearance of the colour of dichromate cannot be used to locate the end point because the Cr³⁺ ions have green colour that makes the Cr₂O₇²⁻ colour indistinguishable. The end point is conveniently detected by

using a redox indicator N-phenyl anthranilic acid. The dichromate solution could be used as a primary standard in this determination but it is better to standardize using a standard solution of ferrous ammonium sulphate; this obviates the need for using extra oven dried sample of $K_2Cr_2O_7$.

Procedure :

Prepare 100 mL of an approximately N/30 solution of ferrous ammonium sulphate, $FeSO_4 (NH_4)_2SO_4 \cdot 6H_2O$, adding ~10 mL of dilute 2N H_2SO_4 solution during the dissolution (why?). 10 mL of this solution is pipetted out into a conical flask, 10 mL of dilute H_2SO_4 solution and three to five drops of N-phenyl anthranilic acid solution are added, and titrated against the supplied potassium dichromate solution. The solution acquires a pale green colour due to the Cr^{3+} ions; at the end point, the colour changes sharply to red-purple.

The given solution of ferrous ammonium sulphate of unknown concentration is also titrated similarly against the same solution of $K_2Cr_2O_7$. From the titre values, calculate and report:

- The normality of the given ferrous ammonium sulphate solution.
- The strength of iron in gm/ litre.
- its strength in gms of ferrous ammonium sulphate/ litre.

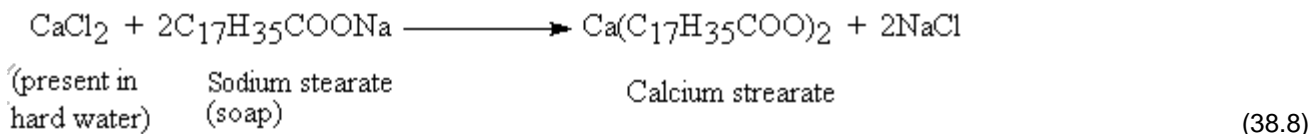
In your report, explain the following points:

- What are the equivalent weights of $K_2Cr_2O_7$ and $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$?
- How does a redox indicator function?
- What is the function of a dilute sulphuric acid in this titration? Can you use dilute hydrochloric acid?
- What is the structure of N-phenyl anthranilic acid?
- An oxidation-reduction which has E_o nearly equal to the potential of the equivalence-point is suitable for that reaction. Explain.

38.8 Experiment 7: Complexometric Titration: Determination of hardness (Ca^{2+}) of water using EDTA - complexometry

Theory :

Hard water is one which does not easily lather with soap. This is due to the formation of precipitates of Ca and Mg stearates.



Calcium and magnesium salts in water may be determined by a complexometric titration with ethylenediamine tetraacetic acid (EDTA, H_4Y) which forms 1:1 complexes with most metal ions. Usually disodium salt of EDTA is used. The end points are obtained by using indicators appropriate to the specific metals. For determining calcium and magnesium, the indicator Eriochrome black-T is useful. A small amount of magnesium is essential for the indicator to function and is usually added to a buffer solution. The reactions involved are :



The indicator also forms complexes with Ca^{2+} and Mg^{2+} , the Mg - indicator complex being wine-red. The free indicator is blue in colour. The Ca-EDTA complex is more stable than the Mg-EDTA complex. The Mg-indicator complex is stabler than the Ca-indicator complex, but less stable than the Ca-EDTA complex. As EDTA is added to the buffered (pH = 10) solution of Ca and Mg salts in the presence of Eriochrome black-T, EDTA reacts with free Ca^{2+} ions first and then with free Mg^{2+} ions, if any, and finally with the Mg - indicator complex. The end point is a sharp colour change from wine red to blue. The results are reported in mgs of $CaCO_3$ per litre of the sample (ppm), irrespective of whether Mg was present or not.

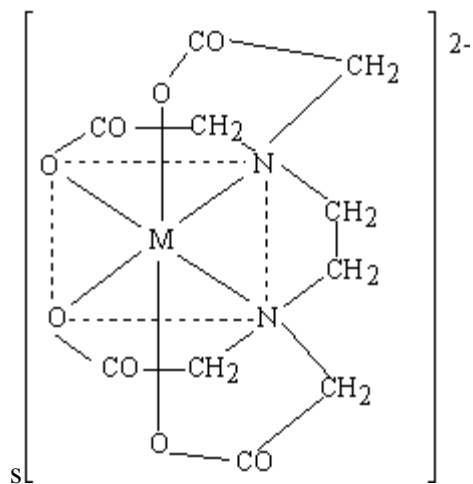


Figure 38.4 EDTA complex with a divalent metal

Procedure :

Prepare a 0.1% w/v (weight by volume) solution of calcium carbonate as a standard. Weigh out about 0.1 g of CaCO_3 into the 100 mL volumetric flask. Add dilute HCl dropwise till efferevescence ceases and the solution is clear. Make up to the mark with distilled water.

Pipette out 10 mL of the solution into a conical flask and neutralize excess acid present by adding about 2 mL of ammonia solution and 5 mL of ammonia/ ammonium chloride buffer solution and 2-3 drops of indicator (Erichrome black-T). Titrate it against the EDTA solution ($\sim M/50$), till the colour changes from wine-red to blue. To determine the hardness of water, pipette out 50 mL of water sample into a conical flask, add 5 mL buffer and 2-3 drops of indicator and titrate it using EDTA solution. Report the hardness of water in ppm, i.e., parts of CaCO_3 per million (mg/L)

In your report, explain how the choice of indicators for EDTA titrations is made in general, and list a few indicators used in EDTA titrations along with the metals they are used for and the pH at which the titrations are to be performed.

38.9 Problems

38.1)

- 1) Write the structures of phenolphthalein and methyl red indicators.
- 2) What is the basis of the colour changes in the indicators used in this study?
- 3) Why does phenolphthalein change colour around pH 9.0 and methyl red around pH 5.0?
- 4) Can we use a strongly acidic or basic dye as an indicator?
- 5) Is the second end point sharp? If not, how can you make it sharp?

38.2)

- 1) Explain to curves drawn for the titration of oxalic acid and H_3PO_4 with NaOH.
- 2) Explain the curve for the titration of Na_2CO_3 with HCl.
- 3) How could pK_1 and pK_2 of a dibasic acid be determined?

38.3)

What would be the nature of the curve for titration of

- i) A weak acid with a strong base?
- ii) weak acid with weak base?
- iii) Strong acid with weak base?
- iv) AgNO_3 with NaOH?

38.4)

List a few indicators used in EDTA titrations along with the metals they are used for and the pH at which the titrations are to be performed.

38.5)

What are the equivalent weights of $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{FeSO}_4 (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$?

How does a redox indicator function? An oxidation-reduction which has E_0 nearly equal to the potential of the equivalence-point is suitable for that reaction. Explain.

Recap

In this lecture you have learnt the following

38.10 : Summary

In this lecture you have been introduced to various titration methods such as acid base, redox, conductometric and complexometric titrations. The experimental details, theoretical background and the precautions to be taken have been outlined. The details of the reaction conditions dictate which method of analysis has to be employed in a given problem.