S. Latha Rajasekaran

74

CONTENTS

CHAPTER – 1

2 copies 1 — 153

DATA ANALYSIS

We will be dealing with a huge number of data in analytical chemistry. Hence, it becomes necessary to analyse and interpret these data. Let us discuss them in this chapter.

Errors in Chemical Analysis

(**Definition of error :** *The difference between the measured value of a property and its accurate value is called the error.*

Explanation : In the laboratory we may weigh a substance or measure the volume of a solution. Accurate results will be obtained only when a person with great skill is measuring with best instruments. But this is an impossible one. Usually the measured value of the property will never be the accurate value of the property. The difference between these two is called the **error**. Errors in measurement will affect the **accuracy** and **precision** of the property. Hence, the analytical data obtained in such circumstances become unreliable.)

Classification of errors

(The errors that we come across in a chemical analysis are classified into the following two types ———

(i) Determinate errors

(ii) Indeterminate errors or random errors

It should be kept in mind that it is impossible to ascertain the type of error. However, this classification of errors helps us to discuss analytical errors.)

Determinate Errors

(The other name is **systematic errors.**

Characteristics ———

1) These errors have a definite value.
2) One can assign the cause for the error.
3) The analyst can measure and account for these errors.
4) These can be avoided.
5) They are **unidirectional** i.e., the errors will be either more or less than the accurate value. Using this property, they can be identified.

Sources of these errors ———

Determinate errors appear due to the following factors______.

(i) Defective instruments
(ii) Careless operation
(iii) Procedural defects

Classification ———

(i) Instrumental errors
(ii) Errors of methods or methodic errors
(iii) Personal or operative errors

We shall discuss them.

Instrumental errors : These errors may occur ———

(i) using a balance which is not properly assembled.
(ii) using uncalibrated weights, burettes and pipettes.
(iii) presence of impurities in glassware.
(iv) heating a platinum crucible for a longer time at high temperature.

These errors can be avoided ———

(i) by periodic calibration of apparatus and weights.
(ii) by using best instruments.

These errors may be identified by changing the instruments. At that time, the errors will also change.

When the reagents employed in the analysis are contaminated, they also introduce errors. This error is called **reagent error**.

Methodic errors

These are introduced by defective experimental procedures. These are common in volumetric and gravimetric analyses. These errors may occur due to the ———

(i) Solubility of precipitates in precipitating solution.
(ii) Co-precipitation and post precipitation in gravimetric analysis.
(iii) Decomposition or vapourisation of the precipitate on heating.
(iv) Incomplete precipitation.
(v) Side reactions during the analysis.
(vi) Usage of improper indicators in volumetric analysis.

These errors are difficult to identify and these are the most serious of the three types of determinate errors. In order to avoid these, one must be thorough with theoretical part of the experiment.

Personal errors

These errors are introduced by personal defects or carelessness. The sources of this error are human defects in eyes, mind etc. For example, in colorimetric experiments, errors will be introduced by a person who is colour blind. A person with defective eyes will invariably note down the readings erroneously.

Carelessness, fatigue and improper instructions from the teacher will also introduce these errors.

These errors may creap in, when ———

(i) the precipitate is washed wrongly.
(ii) the precipitate is heated to an improper temperature.
(iii) the precipitate is not allowed to cool sufficiently before weighing the precipitate.
(iv) the reagent is contaminated with impurities.
(v) the deliquescent chemicals are employed.

Along with these, the analyst may also introduce this error by ———

(i) wrong calculations.
(ii) wrong placement of decimals.
(iii) noting wrong signs.
(iv) cooking up of results.

These errors can be avoided if one works scrupulously in the laboratory. These errors are identified by the fact that, they change when the measurement is repeated.

Determinate errors may also be classified into another two types as follows :

(i) Constant errors (ii) Proportional errors

Constant errors

The magnitude of this error is independent of the size of the sample taken for analysis.

For example, let us consider that 0.3 mg of precipitate is lost when washed with 100 ml of the wash liquid.

(i) If we wash 500 mg of the precipitate with 100 ml of wash liquid, 0.3 mg of the precipitate will be lost.

$$\text{Hence, the loss} = \frac{0.3 \times 100}{500} = 0.06\%$$

(ii) If we wash 50 mg of the precipitate with 100 ml of wash liquid, here also 0.3 mg will be lost.

$$\text{Hence, the loss} = \frac{0.3 \times 100}{50} = 0.6\%$$

From these we find that a constant error will become more serious as the size of the quantity measured decreases. In order to minimise the effect of constant error, it is necessary to use a large sample. That is why in gravimetric analysis, the solution to be estimated is so prepared that the weight of the precipitate is around 0.2 g.

Proportional errors

The magnitude of this type of errors increases or decreases in proportion to the size of the sample taken for analysis. If the impurities present in the sample is not removed, it will cause proportional error.

Correction for determinate errors

1) Determinate instrumental errors are corrected by calibrating the instruments used. The equipments are to be calibrated periodically. This is because instrumental errors arise due to wear, corrosion or mistreatment.

2) Determinate personal errors can be minimised by care and self discipline. By checking systematically the calculations, note book entries and instrument readings, the error can be minimised.

3) Determinate methodic errors are particularly difficult to detect. However, they may be corrected by using one or more of the following procedures ———

1) Independent method of analysis : If the sample to be analysed is contaminated with impurities i.e., not available in pure state, then this method can be used to minimise error. First, the sample is analysed in a particular method. Then it is analysed by a different method of established reliability.

For example, hydrochloric acid is estimated volumetrically by titrating against standard sodium hydroxide.

The sample, hydrochloric acid is added to silver nitrate solution to obtain silver chloride precipitate. The precipitate is weighed and the amount of hydrochloric acid is estimated. When the amount of hydrochloric acid estimated is the same in these two methods, this serves as a correction for methodic errors.

2) Blank determinations : Constant errors affecting pnysical measurements can be frequently evaluated with a blank determination. In this, all steps of the analysis are performed **without the sample.** This result is then applied as a correction to the actual measurements.

This method is useful to correct errors that are due to the introduction of interfering contaminants from reagents and glassware employed in the analysis. This method is useful to correct titration data in volumetric analysis.

3) By employing large sample size : As stated earlier that a constant error decreases as the size of the sample is increased. In order to correct such type of errors, large sample size is used for analysis.

Indeterminate errors

These errors arise from uncertainties in a measurement that are unknown and are not controlled by the person doing an experiment.

Sources

(i) instrument uncertainties

(ii) method uncertainties

(iii) personal uncertainties

It is difficult to identify indeterminate errors. Scattering of data about the mean can be regarded as the effect of an indeterminate error.

Error Analysis

When the indeterminate error or deviation from mean (dm) is plotted against its **frequency** (f) we obtain a curve as shown in the figure-1.1. This **bell shaped** curve is called **Gaussian** or normal error curve. The properties of this normal curve are

(i) The frequency is maximum where the indeterminate error is zero.

(ii) There is a symmetry about this maximum, suggesting that positive and negative errors occur with equal frequency.

(iii) As the magnitude of the error increases, the frequency decreases exponentially.

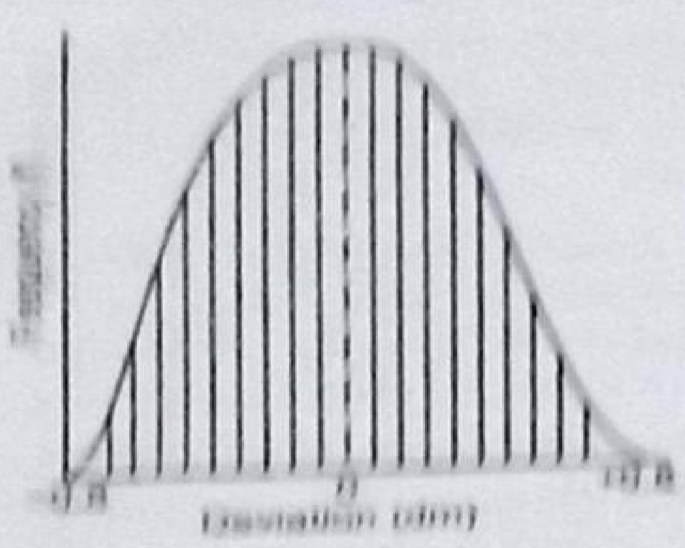


Fig. 1.1

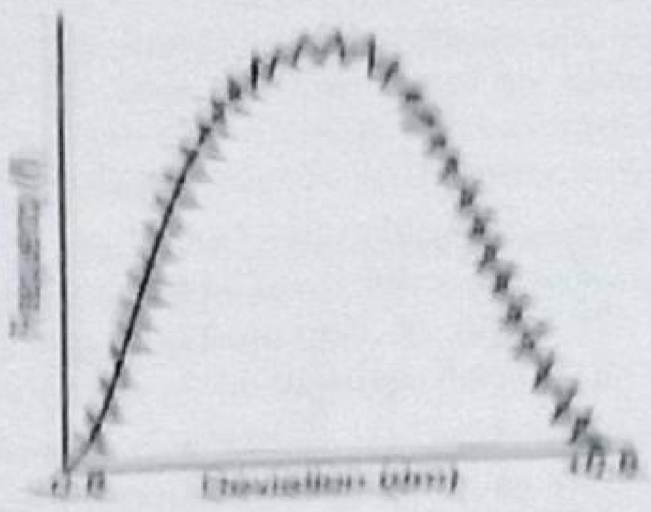


Fig. 1.2

In chemical analysis, Indeterminate errors follow the Gaussian type distribution. For example, if the deviation from mean of the hundreds of repetitive weighing measurements on a single object are plotted against frequency of occurrence of each deviation, we obtain a curve as shown in the figure-1.2. This curve proves the fact that a number of small independent and uncontrolled uncertainties are there in our normal measurements. These uncertainties manifest the result.

The Gaussian distribution of most analytical data, permits us to use statistical techniques to estimate the extent of indeterminate error. Thus, we use several statistical techniques like — **mean, median, average deviation, standard deviation** etc. We shall discuss them later in this chapter.

Suggestions to minimise errors

From the above discussions, it is clear that if we want to minimise error, we have to minimise both determinate and indeterminate errors.

The following are some specific suggestions to minimise determinate errors

(i) use standard instruments.

(ii) measuring aids must be calibrated periodically.

(iii) all reagents must be properly maintained.

(iv) dependable procedures must be adopted.

(v) one must be careful and honest in recording the observations.

(vi) manipulation of results must be avoided.

We know that indeterminate errors are uncontrollable. In order to minimise these errors, we repeat the experiment several times and adopt statistical techniques to obtain maximum precision.

Some other suggestions to minimise the error are

(i) Blank determinations are to be conducted.

(ii) Utmost care must be taken to avoid personal errors.

(iii) Arithmetic mistakes etc. should not be committed.

(iv) Note down the readings correctly.

(v) With proper and complete instructions, the experiment should be carried out.

(vi) When one becomes tired, the experiment must be stopped in a convenient place and then continued after taking sufficient rest.

PRECISION

Definition : *Precision is the degree of agreement between two or more measured values of a property under identical conditions.*

Explanation with an example : Let the weight of a silica crucible be 25.6786 gram when weighed in a particular set of conditions. If the same crucible is weighed under identical conditions and if the weight obtained is the same, namely, 25.6786 gram, then we say that there is precision in the weighing. Thus, if a value is reproducible, then it is called a precise value.

Precision and range of a set of value : The difference between the highest and lowest values of a set of values is called the **range**. This range is a measure of precision. If the range is wide, then it means that the measurement is less precise.

ACCURACY

Definition : *Accuracy is the degree of agreement between the measured value and the expected or true value of a property.*

Explanation with example : As per the data available, the solubility product of $CaSO_4$ is 2.4×10^{-5} $mol^2\,dm^{-6}$. If an analyst gets this same value while determining the same in an experiment, then it is considered as the accuracy of the result is excellent. If it differs, then we calculate the deviation. This deviation gives a measure of the accuracy of experiment.

Methods of expressing accuracy

Accuracy is expressed in terms of absolute error or relative error. The lower these values are, the more will be the accuracy.

Absolute error (E) : *It is defined as the difference between the accepted value (x_t) and the observed value (x_i).*

Mathematical expression : $E = x_i - x_t$

Relative error (RE) : *It is the error percentage of the accepted value.*

Mathematical expression : $R.E = \frac{E}{x_t} \times 100$

$$R.E = \frac{x_i - x_t}{x_t} \times 100$$

Explanation with example

The dissociation constant of acetic acid at 25°C is 1.75×10^{-5}. It is the accepted value (x_t). A student determines it as 1.80×10^{-5}. It is the observed value (x_i).

$$\text{Then, Absolute error, } E = x_i - x_t$$

$$= 1.80 \times 10^{-5} - 1.75 \times 10^{-5}$$

$$E = 0.05 \times 10^{-5}$$

$$\text{Relative error, } R.E = \frac{x_i - x_t}{x_t} \times 100$$

$$= \frac{0.05 \times 10^{-5}}{1.75 \times 10^{-5}} \times 100$$

Relative error Advantage

Absolute error depends on the reliability of the accepted value itself. As a lot of uncertainty may be there about the accepted value, relative error is used to express accuracy.

TABLE 1.1

Differences between precision and accuracy

No.	Precision	Accuracy
1.	It is the degree of agreement between two or more values measured under identical conditions.	It is the degree of agreement between the measured value and the expected value.
2.	Precision may be achieved.	Accuracy is never known. It can be approached but never attained.
3.	Expresses the reproducibility of the results.	Expresses correctness of a measurement.

One must clearly understand the connotations of the terms precision and accuracy. An understanding of the two terms will make it clear that high precision does not imply accuracy. This can be proved with an example. In a volumetric analysis, an analyst can get concordant titre values. Yet, the result may turn out to be wrong. Here, as concordant values have been obtained, the result is precise. But as the answer does not agree with the expected value, it is not accurate. Thus, *a precise value may not be an accurate value.*

The reason for this may be one or more determinate errors or even some unknown indeterminate errors.

Confidence Limits

Definition : *These are the limits which may be set about the experimentally measured mean within which we may expect to find the true mean with a given degree of probability.*

Explanation : Only the mean of an infinite number of measurements can be true or accurate mean. The true mean is represented by μ and is not achieved as an infinite number of measurement is impossible. Hence, we make a finite number of measurements and calculate the

ACCURACY

Definition : *Accuracy is the degree of agreement between the measured value and the expected or true value of a property.*

Explanation with example : As per the data available, the solubility product of $CaSO_4$ is 2.4×10^{-5} $mol^2\,dm^{-6}$. If an analyst gets this same value while determining the same in an experiment, then it is considered as the accuracy of the result is excellent. If it differs, then we calculate the deviation. This deviation gives a measure of the accuracy of experiment.

Methods of expressing accuracy

Accuracy is expressed in terms of absolute error or relative error.

The lower these values are, the more will be the accuracy.

Absolute error (E) : *It is defined as the difference between the accepted value (x_t) and the observed value (x_i).*

Mathematical expression : $E = x_i - x_t$

Relative error (RE) : *It is the error percentage of the accepted value.*

Mathematical expression : $R.E = \frac{E}{x_t} \times 100$

$$R.E = \frac{x_i - x_t}{x_t} \times 100$$

Explanation with example

The dissociation constant of acetic acid at 25°C is 1.75×10^{-5}. It is the accepted value (x_t). A student determines it as 1.80×10^{-5}. It is the observed value (x_i).

$$\text{Then, Absolute error, } E = x_i - x_t$$
$$= 1.80 \times 10^{-5} - 1.75 \times 10^{-5}$$
$$E = 0.05 \times 10^{-5}$$
$$\text{Relative error, } R.E = \frac{x_i - x_t}{x_t} \times 100$$
$$0.05 \times 10^{-5} \times 100$$

Relative Error Advantage

Absolute error depends on the reliability of the accepted value itself. As a lot of uncertainty may be there about the accepted value, relative error is used to express accuracy.

TABLE 1.1

Differences between precision and accuracy

No.	Precision	Accuracy
1.	It is the degree of agreement between two or more values measured under identical conditions.	It is the degree of agreement between the measured value and the expected value.
2.	Precision may be achieved.	Accuracy is never known. It can be approached but never attained.
3.	Expresses the reproducibility of the results.	Expresses correctness of a measurement.

One must clearly understand the connotations of the terms precision and accuracy. An understanding of the two terms will make it clear that high precision does not imply accuracy. This can be proved with an example. In a volumetric analysis, an analyst can get concordant titre values. Yet, the result may turn out to be wrong. Here, as concordant values have been obtained, the result is precise. But as the answer does not agree with the expected value, it is not accurate. Thus, *a precise value may not be an accurate value.*

The reason for this may be one or more determinate errors or even some unknown indeterminate errors.

Confidence Limits

Definition : *These are the limits which may be set about the experimentally measured mean within which we may expect to find the true mean with a given degree of probability.*

Explanation : Only the mean of an infinite number of measurements can be true or accurate mean. The true mean is represented by μ and is not achieved as an infinite number of measurement is impossible. Hence, we make a finite number of measurements and calculate the experimental mean, $\bar{x}$. Then, we examine the closeness of $\bar{x}$ with μ by setting limits. Within these limits we can find μ with a given degree of probability. The interval between these limits is called the **confidence interval**. The size of the interval depends on the degree of probability that we require. If the requirement is 99% probability, then the interval is small. 99% probability means that 99 times out of 100, the true mean will be within this interval. Similarly, we can choose 95%, 90%, 85% probability etc. depending upon our requirements. This percentage probability is called **confidence level**.

Mathematical expression of confidence limits

The standard deviation, σ is for a large number of measurements. When the measurements are performed in a small number, then standard deviation, σ is approximately equal to s. i.e., $\sigma \approx s$. The confidence limit for a single measurement for μ is given by

$$\mu = \bar{x} \pm Z\sigma$$

$$\text{where,} \quad Z = \frac{\bar{x} - \mu}{\sigma}$$

The confidence limit for the μ of N measurements is given by

$$\mu = \bar{x} + \frac{Z\sigma}{\sqrt{N}}$$

When σ is unknown : The confidence limit for μ of N measurements is given by

$$\mu = \bar{x} + \frac{ts}{\sqrt{N}}$$

where, t is a statistical factor and $t = \frac{\bar{x} - \mu}{s}$

Thus, we find by applying statistical methods, we can fix the confidence limits within which the true average of a set of experimental results can be found for various confidence levels of probabilities. For this we must know the values of Z and t which are readily available in Statistics books or literature.

Explanation with example

In an analysis of ferrous alloy, the percentage of iron are 92.10 ; 92.50; 92.70; 92.80 and 92.90. Calculate the true mean in the confidence level of 90 %. The table for calculation is also given.

TABLE 1.2.

t values of various probabilities

No.	No. observations	80 % confidence	90 % confidence
1.	2	1.89	2.92
2.	4	1.53	2.13
3.	5	**1.48**	**2.02**
4.	6	1.44	1.94
5.	8	1.40	1.86
6.	10	1.37	1.81

Solution

Experimental mean,

$$\bar{x} = \frac{92.10 + 92.50 + 92.70 + 92.80 + 92.90}{5} = 92.60$$

Standard deviation, s = 0.3162. (Its details will be given in next few pages)

$$\text{True mean, } \mu = \bar{x} + \frac{ts}{\sqrt{N}}$$

$$= 92.60 \pm \frac{2.02 \times 0.3162}{\sqrt{5}}$$

$$= 92.60 \pm \frac{0.639}{2.237}$$

$$\mu = \mathbf{92.60 \pm 0.2856}$$

PROBLEM FOR EXERCISE

A student has reported the percentage of carbon in an organic compound as 20.36 ; 19.38 ; 20.26 ; 20.18 ; 19.72 and 19.86. The confidence level is 95 % and the value of statistical factor is 2.571. Calculate (i) mean (ii) standard deviation and (iii) true mean.

Ans : (i) 20.06 (ii) 0.25 (iii) 20.06 ± 0.26

Rejection of Data or Q Test

Q test was introduced by Dean and Dixon in 1951. In a set of data, we come across one or two values that are suspicious whether to reject such a data or not would become difficult. In such cases, we employ a test called, Q test. In this test, we compare two Q-values ———

experimental mean, $\bar{x}$. Then, we examine the closeness of $\bar{x}$ with μ by setting limits. Within these limits we can find μ with a given degree of probability. The interval between these limits is called the **confidence interval**. The size of the interval depends on the degree of probability that we require. If the requirement is 99% probability, then the interval is small. 99% probability means that 99 times out of 100, the true mean will be within this interval. Similarly, we can choose 95%, 90%, 85% probability etc. depending upon our requirements. This percentage probability is called **confidence level**.

Mathematical expression of confidence limits

The standard deviation, σ is for a large number of measurements. When the measurements are performed in a small number, then standard deviation, σ is approximately equal to s. i.e., $\sigma \approx s$. The confidence limit for a single measurement for μ is given by

$$\mu = \bar{x} \pm Z\sigma$$

$$\text{where,} \quad Z = \frac{\bar{x} - \mu}{\sigma}$$

The confidence limit for the μ of N measurements is given by

$$\mu = \bar{x} + \frac{Z\sigma}{\sqrt{N}}$$

When σ is unknown : The confidence limit for μ of N measurements is given by

$$\mu = \bar{x} + \frac{t\,s}{\sqrt{N}}$$

where, t is a statistical factor and $t = \frac{\bar{x} - \mu}{s}$

Thus, we find by applying statistical methods, we can fix the confidence limits within which the true average of a set of experimental results can be found for various confidence levels of probabilities. For this we must know the values of Z and t which are readily available in Statistics books or literature.

Explanation with example

In an analysis of ferrous alloy, the percentage of iron are 92.10 ; 92.50; 92.70; 92.80 and 92.90. Calculate the true mean in the confidence level of 90 %. The table for calculation is also given.

TABLE 1.2.

t values of various probabilities

No.	No. observations	80 % confidence	90 % confidence
1.	2	1.89	2.92
2.	4	1.53	2.13
3.	5	**1.48**	**2.02**
4.	6	1.44	1.94
5.	8	1.40	1.86
6.	10	1.37	1.81

Solution

Experimental mean,

$$\bar{x} = \frac{92.10 + 92.50 + 92.70 + 92.80 + 92.90}{5} = 92.60$$

Standard deviation, s = 0.3162. (Its details will be given in next few pages)

$$\text{True mean, } \mu = \bar{x} + \frac{ts}{\sqrt{N}}$$

$$= 92.60 \pm \frac{2.02 \times 0.3162}{\sqrt{5}}$$

$$= 92.60 \pm \frac{0.639}{2.237}$$

$$\mu = \mathbf{92.60 \pm 0.2856}$$

PROBLEM FOR EXERCISE

A student has reported the percentage of carbon in an organic compound as 20.36 ; 19.38 ; 20.26 ; 20.18 ; 19.72 and 19.86. The confidence level is 95 % and the value of statistical factor is 2.571. Calculate (i) mean (ii) standard deviation and (iii) true mean.

Ans : (i) 20.06 (ii) 0.25 (iii) 20.06 ± 0.26

Rejection of Data or Q Test

Q test was introduced by Dean and Dixon in 1951. In a set of data, we come across one or two values that are suspicious whether to reject such a data or not would become difficult. In such cases, we employ a test called, Q test. In this test, we compare two Q-values ———

(i) Q_{exp} (ii) Q_{cri}

If $Q_{exp} > Q_{cri}$, we reject the data

If $Q_{cri} > Q_{exp}$, we retain the data

The various steps in Q test are explained as follows —

(i) To obtain Q_{exp}, the difference between the suscipious value and its nearest neighbour is divided by the spread of the entire set.

(ii) To obtain Q_{cri}, the following table giving various Q_{cri} values, is used.

D. T sub. TOP. ATTE

TABLE 1.3.

Calculation of Q_{cri}

No.	No. observations	90 % confidence	96 % confidence	99 % confidence
1	3	0.94	0.98	0.99
2	5	0.64	**0.73**	0.82
3	7	0.51	0.59	0.68
4	9	0.44	0.51	0.60

Let us illustrate how to decide whether to reject or retain a datum with an example.

WORKED EXAMPLE

The percentage of calcium oxide in a quick lime sample are 55.95; 56.00 ; 56.05 ; 56.10 and 56.25. Now we suspect that the last value and so we have to decide on this value whether to reject or retain.

For this set of data,

$$Q_{exp} = \frac{\text{Suscipious value} - \text{Its nearest neighbour}}{\text{The spread of the entire set}}$$

$$= \frac{56.25 - 56.10}{56.25 - 55.95} = \frac{0.15}{0.30} = 0.50$$

Let our results are in 96 % confidence level. We look under 96 % confidence column of the table. Since we have 5 observations, we look

for Q_{cri} against number of observations 5 under 96 % confidence. The value is 0.73.

Since, Q_{cri} (0.73) > Q_{exp} (0.50), we retain the data.

Though the Q-test is superior to other methods, one must be careful while deciding to either reject or retain a particular datum using this test. When the number of observations are small, the reliability of Q test decreases. Hence, in order to reject a value in a small set, a cautious approach is desirable.

SIGNIFICANT FIGURES

Definition : *Significant figures are figures in a number which contains only digits known with certainty plus the first uncertain one.*

Explanation : A measured value has some uncertainty about it. There is a convention to give the measured value as a number such that it contains only the figure about which there is uncertainty. This practice is called significant figure convention.

Example : If the weight of a crucible in a weighing is known with certainty only upto three decimals, the value should be reported only upto four decimals as 18.6642 gram.

Points to be remembered while using the concept of significant figures

1) The number of significant figures of a given number is found out by counting the number of figures from left to right in the number beginning with the first non zero digit and continuing till reaching the digit that contains the uncertainty.

   Example : Each of the following has three significant figures.

   538 ; 0.345 ; 2.34 ; 0.00567 and 1.23×10^4

2) Zero is a significant figure when used as a number. It is not a significant figure, when it is used to locate decimal points in very small and very large numbers.

   Example : 0.001230 has four significant figures. The three zeroes before 1 are used to imply only the magnitude. So, they are not significant. The zero beyond 3 is significant. This number can be rewritten as 1.230×10^{-3} and from this it is very easy to identify the significant number as four.

The following table will be of much useful to know about the significant figures in detail.

TABLE 1.4.

Significant figures

S.No.	Number	Significant figures
1.	0.00032	2
2.	0.0304	3
3.	6.65×10^{-4}	3
4.	1.987×10^{-5}	4
5.	8.314	4
6.	6.023×10^{23}	4
7.	96495	5
8.	42,00,000	7

Addition of numbers

The answer for 1.4 + 0.06 + 1.2 is 2.7.

The actual addition is,

$$\begin{array}{r} 1.4 \;+ \\ 0.06 \;+ \\ 1.2 \\ \hline 2.66 \\ \hline \end{array}$$

and the answer should be 2.66. But it is given as 2.7. The reason is that the second decimal in the sum value is not significant, because of an uncertainty in the first value of 1.4 and 1.2. decimal place in the given Hence, the sum should be reported as 2.7.

Subtraction of numbers

The answer for the subtraction, 133 − 2.2 is 131. However, the actual subtraction is,

$$\begin{array}{r} 133 \;- \\ 2.2 \\ \hline 130.8 \\ \hline \end{array}$$

and the answer should be 130.8 But it is given as 131. The reason is that the first decimal in the answer is not significant because of an uncertainty in the first decimal of 2.2. Hence, the answer should be reported as 131.

Multiplication and division of numbers

When multiplication and division are carried out, it is assumed that the number of significant figures of the result is equal to the number of significant figures of the component quantity that contains the least number of significant figures.

Consider,

(i) $\frac{22 \times 0.123}{20} = 0.1353$. But it is reported as 0.14 because in 22 and 20, there are only two significant figures.

(ii) $\frac{11 \times 0.122}{10.0} = 0.1342 = 0.13$. This is because of the significant figures of 11 is only two.

PROBLEMS FOR EXERCISE

Solve the following

(i) 0.3442 + 1207.6 + 1.33 − 5.002 **Ans :** 1204.3

(ii) $\frac{47.61 \times 0.0024}{2.83}$ **Ans :** 0.040

Importance of significant figures

While presenting scientific data, we have a set of data and usually we give mean or median as the best value. Now the uncertainty about the best value must also be indicated while presenting the data. The usage of significant figures is very helpful for this purpose.

On several cases, one has to round off numbers to give meaningful results. For this, the usual practice is to a number which contains only one uncertain figure in it, is adopted. Thus, significant figures become important.

Methods of expressing precision

Precision is expressed in two ways

(i) absolute method

(ii) relative method

We shall discuss them.

Absolute method : The precision is expressed in terms of average mean deviation in this method.

The smaller the value of average mean deviation, the greater will be the precision.

Relative method : The precision is expressed in terms as percentage deviation from the mean of a set of values.

Percentage deviation from the mean

TABLE 1.4.
Significant figures

S.No.	Number	Significant figures
1.	0.00032	2
2.	0.0304	3
3.	6.65×10^{-4}	3
4.	1.987×10^{-5}	4
5.	8.314	4
6.	6.023×10^{23}	4
7.	96495	5
8.	42,00,000	7

Addition of numbers

The answer for 1.4 + 0.06 + 1.2 is 2.7.

The actual addition is,

$$\begin{array}{r} 1.4\ + \\ 0.06\ + \\ 1.2 \\ \hline 2.66 \end{array}$$

and the answer should be 2.66. But it is given as 2.7. The reason is that the second decimal in the sum value is not significant, because of an uncertainty in the first decimal place in the given value of 1.4 and 1.2. Hence, the sum should be reported as 2.7.

Subtraction of numbers

The answer for the subtraction, 133 − 2.2 is 131. However, the actual subtraction is,

$$\begin{array}{r} 133\ - \\ 2.2 \\ \hline 130.8 \end{array}$$

and the answer should be 130.8 But it is given as 131. The reason is that the first decimal in the answer is not significant because of an uncertainty in the first decimal of 2.2. Hence, the answer should be reported as 131.

Multiplication and division of numbers

When multiplication and division are carried out, it is assumed that the number of significant figures of the result is equal to the number of significant figures of the component quantity that contains the least number of significant figures.

Consider,

(i) $\frac{22 \times 0.123}{20} = 0.1353$. But it is reported as 0.14 because in 22 and 20, there are only two significant figures.

(ii) $\frac{11 \times 0.122}{10.0} = 0.1342 = 0.13$. This is because of the significant figures of 11 is only two.

PROBLEMS FOR EXERCISE

Solve the following

(i) $0.3442 + 1207.6 + 1.33 - 5.002$ Ans : [illegible]

(ii) $\frac{47.61 \times 0.0024}{2.83}$ Ans : 0.040

Importance of significant figures

While presenting scientific data, we have a set of data and usually we give mean or median as the best value. Now the uncertainty about the best value must also be indicated while presenting the data. The usage of significant figures is very helpful for this purpose.

On several cases, one has to round off numbers to give meaningful results. For this, the usual practice is to a number which contains only one uncertain figure in it, is adopted. Thus, significant figures become important.

Methods of expressing precision

Precision is expressed in two ways —

(i) absolute method

(ii) relative method

We shall discuss them.

Absolute method : The precision is expressed in terms of average mean deviation in this method.

The smaller the value of average mean deviation, the greater will be the precision.

Relative method : The precision is expressed in terms as percentage deviation from the mean of a set of values.

Percentage deviation from the mean

$$= \frac{\text{Mean of a set of values} - \text{Particular value}}{\text{The mean}} \times 100$$

$$= \frac{\bar{x} - x_i}{\bar{x}} \times 100$$

In order to understand these two methods, let us know some terms used in Statistics.

Mean or Average

Definition : *It is the quotient obtained when the sum of a set of replicate measurements, by the number of individual results in the set.*

Explanation with an example

Calculate the mean for the following set of values : 20.20 ; 20.08 and 20.02.

$$\text{Mean} = \frac{20.20 + 20.08 + 20.02}{3}$$

$$= \frac{60.30}{3} = \mathbf{20.10}$$

PROBLEMS FOR EXERCISE

Find the mean value for the following :

i)	20.24 ; 20.64 ; 20.13 and 20.19	**Ans :** 20.30
ii)	30.26 ; 30.24 ; 30.30 ; 30.18 and 30.22	**Ans :** 30.24

Median

Definition : *It is the value about which all other values are equally distributed.*

Half the values will be greater and the other half will be smaller than the median.

Steps adopted to obtain median

i) Arrange the set of values in increasing or decreasing order.

of values, then the middle value gives

iii) If there are **even** number of values, then the average of the middle pair gives the median.

Explanation with examples

(i) Calculate the median for 10.20 ; 10.02 and 10.08

Arranging the values in the increasing order we get,

10.02 ; 10.08 and 10.20

This set contains odd (3) number of values. Hence, the median of this set is the middle value, **10.08**.

(ii) Calculate the median for 30.26 ; 30.20 ; 30.24 ; 30.18 ; 30.22 and 30.28.

Arranging the values in the increasing order we obtain,

30.18 ; 30.20 ; 30.22 ; 30.24 ; 30.26 and 30.28

This set contains even (6) number of values. Hence, the median of this set is the average of the middle pair of values.

$$\frac{30.22 + 30.24}{2} = \frac{60.46}{2} = \mathbf{30.23}$$

PROBLEMS FOR EXERCISE

Calculate the median for the following :

(i)	20.20 ; 20.08 and 20.02	**Ans :** 20.08
(ii)	20.21 ; 20.04 ; 20.13 and 20.19	**Ans :** 20.16

Mean Deviation or Average Deviation

Definition : *The average deviation of a value in a set of values is the average of the deviations of all the individual values from their average.*

Steps adopted to obtain average deviation

(i) The average of the given set of values is calculated.

(ii) The deviation of each value from the average is calculated.

(iii) The average of all these deviation (ignoring signs) gives the average deviation.

$$= \frac{\text{Mean of a set of values} - \text{Particular value}}{\text{The mean}} \times 100$$

$$= \frac{\bar{x} - x_i}{\bar{x}} \times 100$$

In order to understand these two methods, let us know some terms used in Statistics.

Mean or Average

Definition : *It is the quotient obtained when the sum of a set of replicate measurements, by the number of individual results in the set.*

Explanation with an example

Calculate the mean for the following set of values : 20.20 ; 20.08 and 20.02.

$$\text{Mean} = \frac{20.20 + 20.08 + 20.02}{3}$$

$$= \frac{60.30}{3} = \mathbf{20.10}$$

PROBLEMS FOR EXERCISE

Find the mean value for the following :

i) 20.24 ; 20.64 ; 20.13 and 20.19 **Ans :** 20.30

ii) 30.26 ; 30.24 ; 30.30 ; 30.18 and 30.22 **Ans :** 30.24

Median

Definition : *It is the value about which all other values are equally distributed.*

Half the values will be greater and the other half will be smaller than the median.

Steps adopted to obtain median

i) Arrange the set of values in increasing or decreasing order.

ii) If there are **odd** number of values, then the middle value gives the median.

iii) If there are **even** number of values, then the average of the middle pair gives the median.

Explanation with examples

(i) Calculate the median for 10.20 ; 10.02 and 10.08

Arranging the values in the increasing order we get,

10.02 ; 10.08 and 10.20

This set contains odd (3) number of values. Hence, the median of this set is the middle value, **10.08**.

(ii) Calculate the median for 30.26 ; 30.20 ; 30.24 ; 30.18 ; 30.22 and 30.28.

Arranging the values in the increasing order we obtain,

30.18 ; 30.20 ; 30.22 ; 30.24 ; 30.26 and 30.28

This set contains even (6) number of values. Hence, the median of this set is the average of the middle pair of values.

$$\frac{30.22 + 30.24}{2} = \frac{60.46}{2} = \mathbf{30.23}$$

PROBLEMS FOR EXERCISE

Calculate the median for the following :

(i) 20.20 ; 20.08 and 20.02 **Ans :** 20.08

(ii) 20.21 ; 20.04 ; 20.13 and 20.19 **Ans :** 20.16

Mean Deviation or Average Deviation

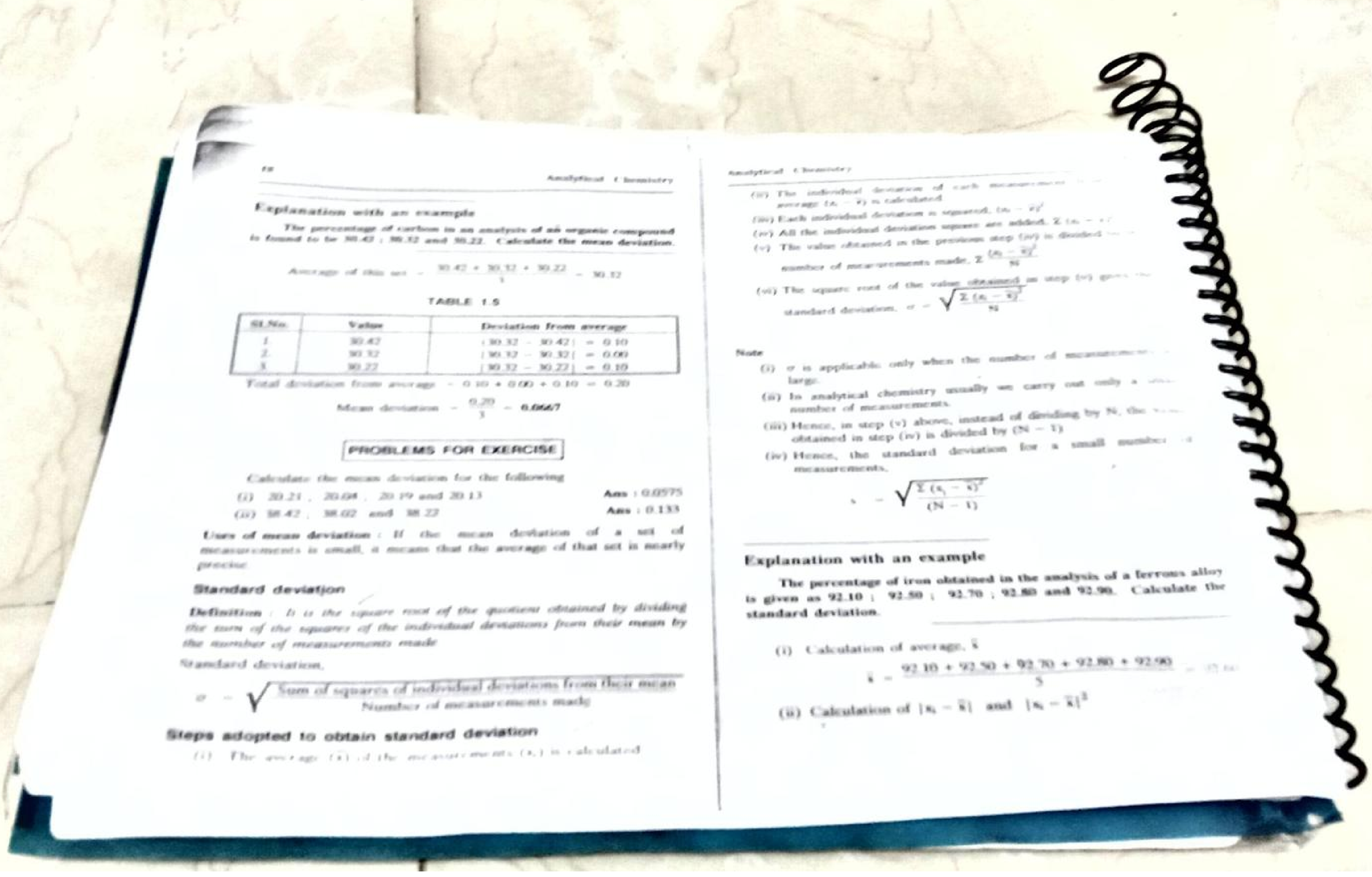
Definition : *The average deviation of a value in a set of values is the average of the deviations of all the individual values from their average.*

Steps adopted to obtain average deviation

(i) The average of the given set of values is calculated.

(ii) The deviation of each value from the average is calculated.

(iii) The average of all these deviation (ignoring signs) gives the average deviation.



Explanation with an example

The percentage of carbon in an analysis of an organic compound is found to be 30.42 ; 30.32 and 30.22. Calculate the mean deviation.

$$\text{Average of this set} = \frac{30.42 + 30.32 + 30.22}{3} = 30.32$$

TABLE 1.5

Sl.No.	Value	Deviation from average
1.	30.42	$\lvert 30.32 - 30.42 \rvert = 0.10$
2.	30.32	$\lvert 30.32 - 30.32 \rvert = 0.00$
3.	30.22	$\lvert 30.32 - 30.22 \rvert = 0.10$

Total deviation from average = 0.10 + 0.00 + 0.10 = 0.20

$$\text{Mean deviation} = \frac{0.20}{3} = \mathbf{0.0667}$$

PROBLEMS FOR EXERCISE

Calculate the mean deviation for the following

(i) 20.21 , 20.04 , 20.19 and 20.13 **Ans** : 0.0575

(ii) 38.42 , 38.02 and 38.22 **Ans** : 0.133

Uses of mean deviation : If the mean deviation of a set of measurements is small, it means that the average of that set is nearly precise.

Standard deviation

Definition : *It is the square root of the quotient obtained by dividing the sum of the squares of the individual deviations from their mean by the number of measurements made.*

Standard deviation,

$$\sigma = \sqrt{\frac{\text{Sum of squares of individual deviations from their mean}}{\text{Number of measurements made}}}$$

Steps adopted to obtain standard deviation

(i) The average $(\bar{x})$ of the measurements (x_i) is calculated

(ii) The individual deviation of each measurement average $(x_i - \bar{x})$ is calculated

(iii) Each individual deviation is squared, $(x_i - \bar{x})^2$

(iv) All the individual deviation squares are added, $\Sigma (x_i -$

(v) The value obtained in the previous step (iv) is divided number of measurements made, $\Sigma \frac{(x_i - \bar{x})^2}{N}$

(vi) The square root of the value obtained in step (v) gives standard deviation, $\sigma = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{N}}$

Note

(i) σ is applicable only when the number of measurements large.

(ii) In analytical chemistry usually we carry out only a number of measurements.

(iii) Hence, in step (v) above, instead of dividing by N, the obtained in step (iv) is divided by (N − 1)

(iv) Hence, the standard deviation for a small number measurements,

$$s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{(N - 1)}}$$

Explanation with an example

The percentage of iron obtained in the analysis of a ferrous alloy is given as 92.10 ; 92.50 ; 92.70 ; 92.80 and 92.90. Calculate the standard deviation.

(i) Calculation of average, $\bar{x}$

$$\bar{x} = \frac{92.10 + 92.50 + 92.70 + 92.80 + 92.90}{5}$$

(ii) Calculation of $\lvert x_i - \bar{x} \rvert$ and $\lvert x_i - \bar{x} \rvert^2$

Explanation with an example

The percentage of carbon in an analysis of an organic compound is found to be 30.42 ; 30.32 and 30.22. Calculate the mean deviation.

$$\text{Average of this set} = \frac{30.42 + 30.32 + 30.22}{3} = 30.32$$

TABLE 1.5

Sl.No.	Value	Deviation from average
1.	30.42	$\lvert 30.32 - 30.42 \rvert = 0.10$
2.	30.32	$\lvert 30.32 - 30.32 \rvert = 0.00$
3.	30.22	$\lvert 30.32 - 30.22 \rvert = 0.10$

Total deviation from average = 0.10 + 0.00 + 0.10 = 0.20

$$\text{Mean deviation} = \frac{0.20}{3} = \mathbf{0.0667}$$

PROBLEMS FOR EXERCISE

Calculate the mean deviation for the following

(i) 20.21 ; 20.04 ; 20.19 and 20.13 **Ans** : 0.0575

(ii) 38.42 ; 38.02 and 38.22 **Ans** : 0.133

Uses of mean deviation : If the mean deviation of a set of measurements is small, it means that the average of that set is nearly precise.

Standard deviation

Definition : *It is the square root of the quotient obtained by dividing the sum of the squares of the individual deviations from their mean by the number of measurements made.*

Standard deviation,

$$\sigma = \sqrt{\frac{\text{Sum of squares of individual deviations from their mean}}{\text{Number of measurements made}}}$$

Steps adopted to obtain standard deviation

(i) The average $(\bar{x})$ of the measurements (x_i) is calculated.

(ii) The individual deviation of each measurement from the average $(x_i - \bar{x})$ is calculated.

(iii) Each individual deviation is squared, $(x_i - \bar{x})^2$

(iv) All the individual deviation square are added, $\Sigma (x_i - \bar{x})^2$

(v) The value obtained in the previous step (iv) is divided by the number of measurements made, $\Sigma \frac{(x_i - \bar{x})^2}{N}$

(vi) The square root of the value obtained in step (v) gives the standard deviation, $\sigma = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{N}}$

Note

(i) σ is applicable only when the number of measurements is large.

(ii) In analytical chemistry usually we carry out only a small number of measurements.

(iii) Hence, in step (v) above, instead of dividing by N, the value obtained in step (iv) is divided by (N − 1)

(iv) Hence, the standard deviation for a small number of measurements,

$$s = \sqrt{\frac{\Sigma (x_i - \bar{x})^2}{(N - 1)}}$$

Explanation with an example

The percentage of iron obtained in the analysis of a ferrous alloy is given as 92.10 ; 92.50 ; 92.70 ; 92.80 and 92.90. Calculate the standard deviation.

(i) Calculation of average, $\bar{x}$

$$\bar{x} = \frac{92.10 + 92.50 + 92.70 + 92.80 + 92.90}{5} = 92.60$$

(ii) Calculation of $\lvert x_i - \bar{x} \rvert$ and $\lvert x_i - \bar{x} \rvert^2$

CHAPTER - 4

SEPARATION AND PURIFICATION TECHNIQUES

General principles involved in the separation of precipitates

Precipitation is the one of the several separation techniques used in analytical chemistry. The basic principle of separation by precipitation is that **the concentration of a substance should exceed its solubility in a particular solvent.** Solubility (s) of a substance is **the amount of the substance required to give a saturated solution of the substance in a particular solvent at a particular temperature.** Thus, precipitation of a substance depends on its solubility (s) which in turn depends upon the nature of the solvent, temperature etc.

Another important principle in effective precipitation is the **solubility product** (K_{sp}). Solubility product of a sparingly soluble salt is *the product of the concentration of ions raised to suitable powers in a saturated solution.*

Let as consider a sparingly soluble salt $A_x\,B_y$. In its saturated solution, the following equilibrium will exist.

$$A_x\,B_y \rightleftharpoons x\,A^{y+} + y\,B^{x-}$$

The solubility product (K_{sp}) of this salt is given by

$$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y$$

For example,

(i) $\quad Ba\,SO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$

$$K_{sp} = [Ba^{2+}]\,[SO_4^{2-}]$$

(ii) $\quad Ag_2\,Cr\,O_4 \rightleftharpoons 2Ag^{+} + Cr\,O_4^{2-}$

$$K_{sp} = [Ag^{+}]^2\,[Cr\,O_4^{2-}]$$

(iii) $\quad Ca\,F_2 \rightleftharpoons Ca^{2+} + 2F^{-}$

$$K_{sp} = [Ca^{2+}]\,[F^{-}]^2$$

Let the solubility of the sparingly soluble salt $A_x\,B_y$ be s mole/lit. The relationship between the solubility (s) and the solubility product (K_{sp}) can be written as follows.

$$\underset{}{A_x\,B_y} \rightleftharpoons \underset{xs}{x\,A^{y+}} + \underset{ys}{y\,B^{x-}}$$

$$\therefore\ K_{sp} = [A^{y+}]^x\,[B^{x-}]^y$$
$$= (xs)^x\,(ys)^y$$
$$= x^x\,y^y\,s^{x+y}$$

For example ———

(i) $\quad Ag\,Cl \rightleftharpoons Ag^{+} + Cl^{-}$

Here, $x = y = 1$.

$$\therefore\ Ksp = 1^1\,1^1\,(s)^{1+1} = s^2$$

(ii) $\quad Ca\,F_2 \rightleftharpoons Ca^{2+} + 2\,F^{-}$

Here, $x = 1;\quad y = 2$

$$\therefore\ K_{sp} = 1^1\,2^2\,(s)^{1+2} = 4s^3$$

In the same way we can write for other sparingly soluble salts.

By employing suitable methods, when we make the ionic product to exceed solubility product, then the substance is precipitated. Using this principles, substances are separated by precipitation.

Explanation with examples

I.Precipitation of sulphides of group II in qualitative analysis

In qualitative analysis, the sulphides of group II (Cu, Cd, As, Sb, Bi and Sn) are precipitated in presence of dil. HCl. It can be explained as follows.

Hydrogen sulphide is a weak acid and ionises to a lesser extent as follows :

$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

But, HCl is a strong acid and is ionised completely.

$$HCl \rightarrow H^+ + Cl^-$$

The ionisation of H_2S is further suppressed by the addition of dil. HCl due to **common ion effect.** Therefore, the concentration of S^{2-} becomes still smaller. But even this low concentration is larger than that required to exceed the solubility product of sulphides of Cu, Cd, Bi, As, Sb and Sn (The K_{sp} of CuS is 8.5×10^{-36}). Thus, these cations are precipitated as sulphides in the group II analysis.

II. Precipitation of sulphides of group IV in qualitative analysis

The solubility product of sulphides of Ni, Co, and Zn are comparatively higher (For example, K_{sp} of Ni S is 1.4×10^{-24}) than that of group II metal ions like Cu, Cd, Bi, As etc. The sulphide ion concentration in the presence of dil. HCl is insufficient for their precipitation. So, they are not precipitated in group II. The sulphides of group IV are precipitated only in the presence of NH_4OH.

In the presence of NH_4OH, the hydroxyl ions combine with H^+ ions of H_2S to give unionised water. Hence, more of H_2S ionises and thus the concentration of S^{2-} ions in solution increases. It becomes so high that the solubility product of Ni S etc. are exceeded and so they are precipitated out.

III. Precipitation of hydroxides of group III in qualitative analysis

Ammonium hydroxide is a weak base and ionises in solution to a very small extent as follows :

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

But, NH_4Cl salt is ionised completely.

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

In the presence of highly ionised NH_4Cl due to an increase in the number of NH_4^+ ions, the ionisation of NH_4OH is further suppressed due to common ion effect. Thus, the concentration of OH^- ions becomes very low. Under these conditions, the solubility product of the hydroxides of Al, Fe, Cr and Mn alone is reached (For example, the K_{sp} of $Fe(OH)_3$ is 1×10^{-38}) and these are precipitated out.

The hydroxides of Zn, Ni, Co, Mg are not precipitated from their salt solutions. It is because these hydroxides have comparatively higher K_{sp} values (K_{sp} of $Zn(OH)_2$ is 1.8×10^{-17}).

IV. Quantitative Analysis

In quantitative analysis an excess of the precipitating reagent is always employed to ensure complete precipitation.

For example, in the precipitation of barium chromate, a small quantity of $BaCrO_4$ may be left out in solution if equal quantities of reactants are used.

$$BaCl_2 + K_2CrO_4 \rightleftharpoons 2KCl + BaCrO_4$$

If a little excess of K_2CrO_4 is used, the ionic product $[Ba^{2+}][CrO_4^{2-}]$ far exceeds the solubility product of $BaCrO_4$ and it is precipitated completely.

Solvent Extraction

It is a separation technique employed to separate a solid or liquid present in a mixture by extracting it with a solvent.

Principle: The substance to be extracted should be soluble in a particular solvent while all the other constituents in the mixture should be insoluble. After the extraction, the solvent should be easily separable.

Superiority of solvent extraction over precipitation methods

(i) 100 % separation is possible in solvent extraction method, whereas in precipitation methods, there is a possibility of some substance remaining in the mixture.

(ii) The procedural portion is simple.

(iii) In solvent extraction methods, a small amount of solvent is enough as it is recovered and recycled.

Uses of solvent extraction

Solvent extraction is used to separate ——

(i) Dissolved substances from their solutions.

(ii) One constituent from a solid mixture.

(iii) Unwanted impurities from substances.

Nernst Distribution law

Separation of a substance from a solution in a solvent from other dissolved substances, using another solvent is achieved using solvent extraction which is based on Nernst distribution law.

Law : *At constant temperature, a solute distributes itself between two immiscible solvents only in a particular ratio.*

The ratio of the concentrations in the solvents is called the **partition coefficient or distribution coefficient, K_D.**

Let C_A and C_B be the concentrations of the solute in liquids A and B at constant temperature, then $C_A/C_B = K_D =$ constant.

Larger the value of K_D, more efficient is the extraction.

When a solute distributes itself between two solvents without dissociation or association, it is possible to calculate the weight of the solute which can be removed by a series of extraction.

If V ml of a solution contains W g of a solute and if the solute is repeatedly extracted with v ml of another solvent, the weight of the solute W_n remaining in the first solvent after n extraction is given by.

$$W_n = W\left[\frac{K_D V}{K_D V + v}\right]^n$$

Here, K_D is the distribution coefficient.

From the above equation we find that ——

(i) In order to make W_n as small as possible for a given value of K_D, n should be as large as possible.

(ii) nv is equal to the total volume of the extracting liquid available and is a constant. Hence, if n should be large, then v should be small.

(iii) For a given volume of extracting solvent, the extraction process is more efficient when the extracting solvent is added in small portions instead of using the whole of it in one lot. This is explained with the following worked example.

WORKED EXAMPLE

The partition coefficient of a solute (A) between water and ether is 10. Calculate how much solute A would be extracted from 1 lit of water containing 20 g of the solute if extracted with 200 ml of ether in (i) one lot (ii) using 100 ml ether in two stages.

I. Using 200 ml ether in one lot

The amount of solute that remains unextracted at the end of one extraction, W_1 is given by,

$$W_1 = W\left(\frac{K_D V}{K_D V + v}\right)^1$$

Here, $W = 20\,g;\ K_D = \frac{1}{10} = 0.1;\ V = 1000\ ml;\ v = 200\ ml.$

$$\therefore W_1 = 20\left(\frac{0.1 \times 1000}{0.1 \times 1000 + 200}\right)$$

$$= 20\left(\frac{100}{100 + 200}\right) = 20 \times \frac{100}{300} = 6.67\ g.$$

$\therefore$The amount of solute extracted $= 20 - 6.67 = 13.33$ g.

II. Using 100 ml ether in two extractions

$$W_2 = W\left(\frac{K_D V}{K_D V + v}\right)^2$$

Here, $W = 20\,g;\ K_D = \frac{1}{10} = 0.1;\ V = 1000\ ml;\ v = 100\ ml$

$$W_2 = 20\left(\frac{0.1 \times 1000}{0.1 \times 1000 + 100}\right)^2$$

$$= 20 \times \left(\frac{100}{200}\right)^2 = 20 \times (\frac{1}{2})^2 = 20 \times \frac{1}{4} = 5\,g$$

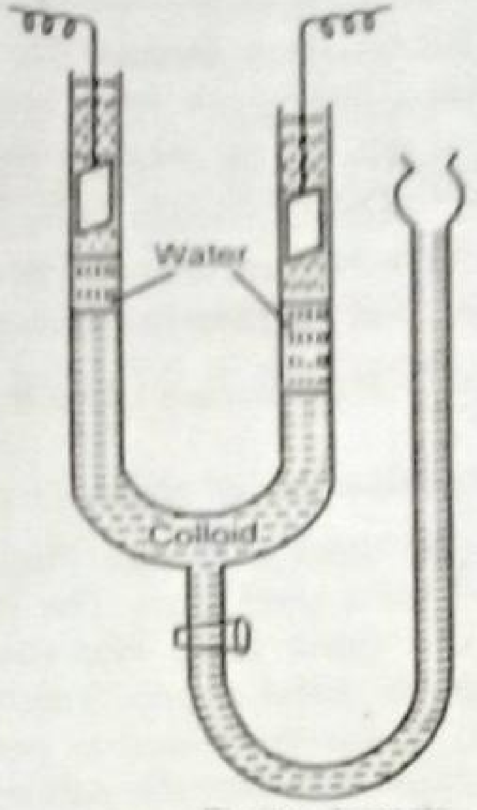
$\therefore$ The amount of solute extracted $= 20 - 5 = 15$ g

Hence, the second process (two steps extraction) is more efficient.

ELECTROPHORESIS

The colloidal particles carry specific charge. *When current is passed through colloidal solution, the colloidal particles migrate and when the dispersion medium does not migrate, the phenomenon is known as electrophoresis.* This can be demonstrated by Burton tube experiment. (Fig 4.1).

This consists of a U - tube provided with a stop cock through which it is connected to a funnel shaped reservoir. A small amount of water is first placed in the U - tube and a reasonable quantity of the colloid is taken in the reservoir. The stop cock is then slightly opened and the reservoir is gradually raised so as to introduce the colloid into the U - tube gently. The water is displaced upwards producing a sharp boundary in each arm. A voltage of 50 to 200 volts is then applied by means of platinum electrodes which are immersed in water layer only.



Electrophoresis

The movement of the particles can be readily ' followed by observing the position of the boundary by means of a naked eye or a lens or a cathetometer. When the particles are negatively charged, as in the case of $As_2 S_3$ colloid, the boundary on the negative electrode side is seen to move down and that on the positive electrode side to move up showing that the particles move towards the positive electrode.

APPLICATIONS

(i) By noting the direction of motion of the particles in the electric field, it is possible to determine the sign of the charge carried by the particles.

(ii) It is also possible by this technique to determine the rate at which colloidal particles migrate in an electric field.

(iii) The sign of charge on bacteria and viruses can be determined

(iv) Rubber can be electrodeposited on metal objects as in electroplating.

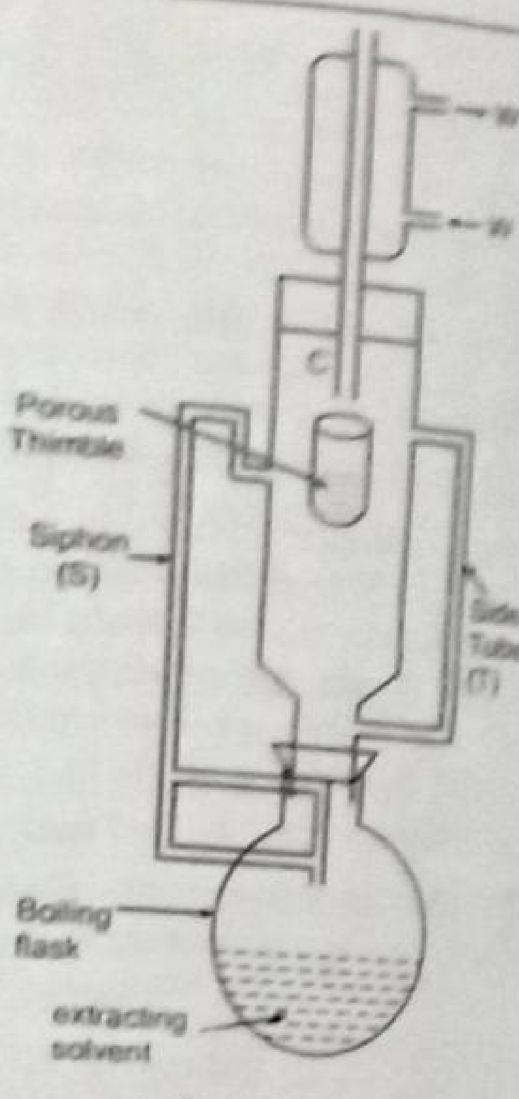
(v) Biomolecules like proteins, carbohydrates, nucleic acids can be separated using electrophoresis from their solutions.

PURIFICATION OF ORGANIC SOLIDS

Soxhlet Extraction: *It is the extraction of a solid with an organic solvent, in which the impurities are insoluble using the Soxhlet extractor* (Fig. 4.2)

Principle: The substance to be extracted should be soluble in a particular solvent while all other constituents in the mixture should be insoluble. After the extraction, the solvent should be easily separable.

Procedure : Soxhlet extractor consists of a glass cylinder C with a side tube T and a siphon, S. A water condenser is attached at the top of C. The sample from which the solid to be extracted is powdered. It is placed in a thimble made up of a thick filter paper. The thimble is placed at the bottom of the water condenser. The extracting solvent is taken in the boiling flask. The solvent is boiled. Its vapour rises through T and enters the water condenser. The vapours condense there. The condensed solvent falls on the sample in the thimble. The substance to be extracted dissolves while the impurities do not. The solution is filtered by the thimble and collects in the cylinder C. When C becomes full, the solution reaches the flask through S. The solvent becomes vapour again and rises up through T. The extracted solid remains in the flask.



Soxhlet Extractor
Fig. 4.2

Thus, the solvent extracts the solid continuously from the sample and brings it to the flask. Finally, the solution from the flask is distilled The solvent distills off, leaving behind the organic substance.

Advantages

(i) This method provides a thorough contact and heating with the solvent.

(ii) A small quantity of the solvent is enough to extract a maximum amount of solid as the solvent is recycled.

(iii) This is a continuous process. Hence, the efficiency of extraction is more in this method.

Applications

(i) This method is used to extract oils and fats from flowers and seeds.
(ii) This method is used to extract alkaloids from plants.

Crystallisation

This is a technique employed to purify organic solids.

Principle : The impure solid is dissolved in the minimum volume of suitable solvent. The soluble substances go into solution while the insoluble substances are left behind. The hot solution is then filtered and allowed to cool without disturbance till the crystallisation is complete. The crystals are separated from the mother liquor by filtration and then dried to obtain pure compound.

The efficiency of the method depends on ——

(i) Selection of the suitable solvent.
(ii) Preparation of the solution.
(iii) Filtration of the solution.
(iv) Crystallisation.
(v) Separation and drying of the crystals.

Procedure: The impure solid is dissolved in enough hot solvent so as to obtain a supersaturated solution. The hot solution is filtered to remove insoluble particles and dust. The filtrate is cooled. Pure crystals of the solid separate out. The impurities remain in solution.

The solvents employed in crystallisation method are benzene, petroleum ether, methyl alcohol, ethyl alcohol and acetone.

Fractional crystallisation

This process is suitable to separate two or more substances from a solution. When a hot solution containing two or more solids is cooled, the solid with low solubility crystallises out first. The other solids crystallise out in the order of their increasing solubilities. If coloured impurities are present, they are removed by the addition of animal charcoal to the hot solution.

Sublimation

It is a process in which a solid, when heated passes directly into the vapour state without melting and the vapours when cooled become solid directly without condensing into a liquid.

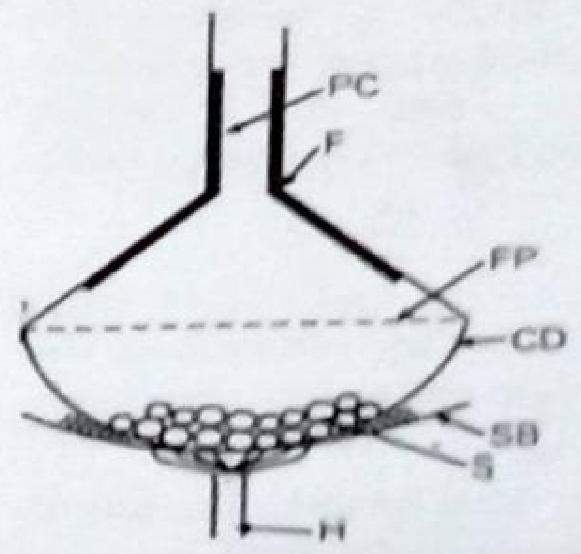
Sublimation is used to purify volatile solids like naphthalene, camphor, iodine etc. from non volatile impurities. Sublimation may be carried out in two ways as follows depending upon the nature of the impurities present and solid to be recovered ——

(i) Sublimation under ordinary pressure
(ii) Sublimation under reduced pressure

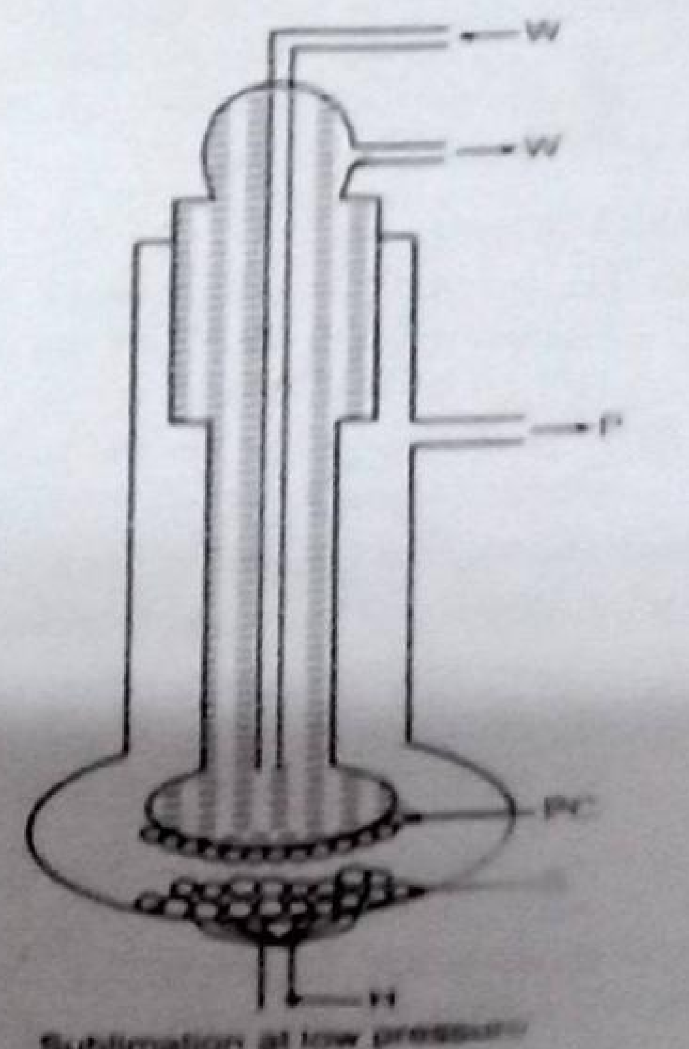
We shall discuss them in detail.

Sublimation under ordinary pressure

The solid to be purified by sublimation is taken in china dish placed on a sand bath. The funnel is placed in the inverted position over the china dish. The china dish is heated gently. The volatile, sublimable solid evaporates, passes through the pores of the filter paper and is deposited as pure solid on the walls of the funnel. The filter paper prevents the sublimed solid from falling back into the china dish and prevents the funnel from getting heat.



Sublimation
Fig. 4.3



Sublimation at low pressure
Fig. 4.4

Illustration

PC = Pure crystal
F = Funnel
FP = Filter paper
CD = China dish
SB = Sand bath
S = Sample
H = Heating
W = Water
P = To pump.

Sublimation under reduced pressure

Substances having low vapour pressure are decomposed on heating and cannot be purified by sublimation under ordinary pressure. Sublimation under reduced pressure is recommended for them. The apparatus used is shown in fig 4.4. In this apparatus, there is a small space between a large heating surface and a large cooling surface. On heating, the solid sublimes and condenses as a solid at the bottom of the surface cooled by water.

Purification of organic liquids

The following methods are used to purify organic liquids ——

(i) distillation
(ii) distillation under reduced pressure
(iii) fractional distillation
(iv) steam distillation

We shall discuss them in detail

Distillation

Principle: On heating a liquid under atmospheric pressure it boils at a temperature at which its total vapour pressure becomes equal to the atmospheric pressure. The temperature of the liquid remains constant till all the liquids distill over. This constant temperature is known as the boiling point.

Procedure. The distillation apparatus is shown in fig 4.5.

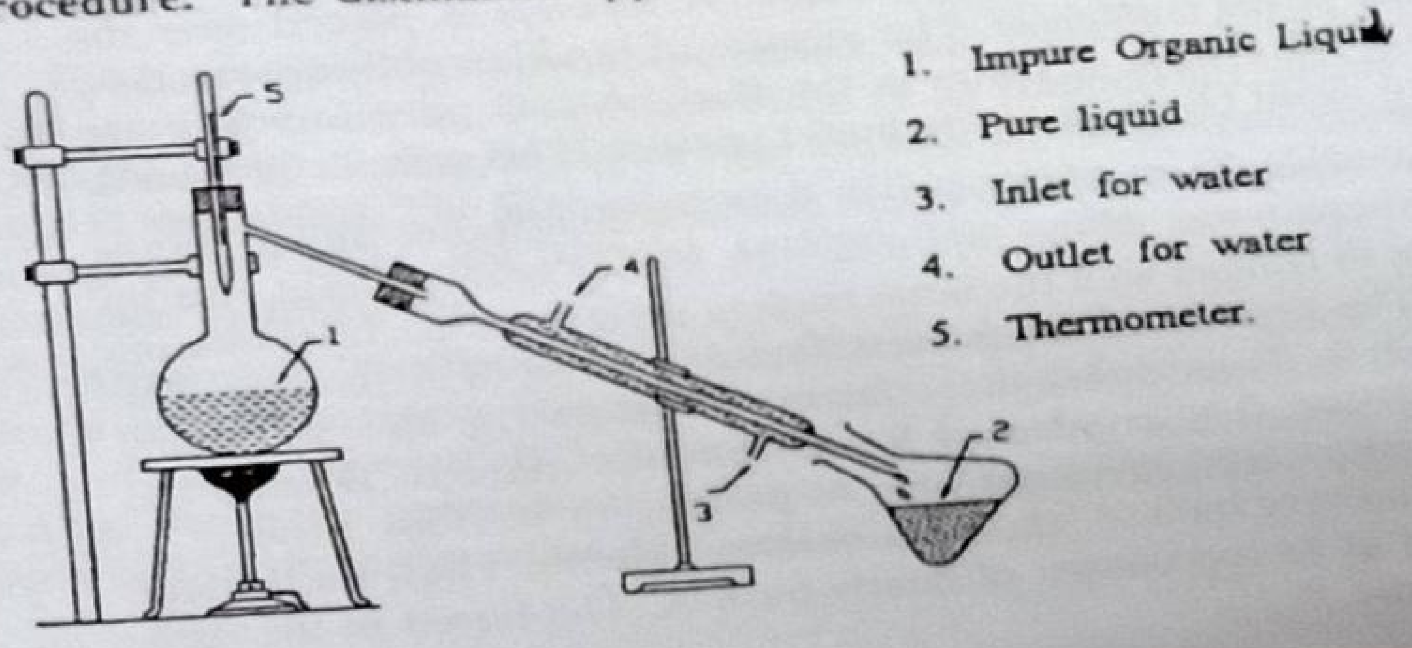


Fig. 4.5

The apparatus consists of a round bottomed flask with a side tube. The flask is fitted with an one holed cork. A thermometer is inserted through the hole so that its bulb is near the opening of the side tube. A water condenser is attached to the tube. The impure liquid is taken in the flask. A few porcelain bits are added to avoid bumping of the liquid. The liquid is heated. When the liquid starts boiling the thermometer reading attains a constant value equal to the boiling point of the liquid. A receiver is now placed near the end of the condenser and the distillate is collected. The collection of the liquid is stopped when the thermometer reading starts to rise. When the process is repeated for few more times, we obtain pure liquid.

The following aspects should be borne in mind while distilling a liquid ——

(i) A round bottom flask and not a flat bottom flask should always be used for smooth boiling.
(ii) Heating must be slow and uniform either with a small flame or by an electrical heater.
(iii) The main fraction which distills at the boiling point should be collected separately rejecting the first and the last portions which are likely to be impure.
(iv) In clamping a flask in which a liquid is distilled, the clamp should hold the flask at the coldest part of the neck. Otherwise the neck will crack during the distillation.
(v) The bulb of the thermometer should be below the position where the side tube is fused into the neck of the flask and should not be immersed in the liquid.
(vi) The glass units must be assembled tightly to avoid loss of vapour or liquid.
(vii) Distillation should be stopped when some liquid is left in the flask.
(viii) The distillation assembly should be dismantled when it is slightly warm to avoid the various parts getting stuck.
(ix) Flammable liquids should never be heated with a bunsen burner. They must be distilled with a steam bath or with a controlled electric heating mantle.

Distillation under reduced pressure

The apparatus for distillation under reduced pressure is shown in fig 4.6. It consists of a Claisen flask having two necks. Through one neck, a long jet is inserted so that it dips into the liquid to be purified. During the distillation, the vapours of the liquid bubble up through the capillary of this jet. This prevents bumping.

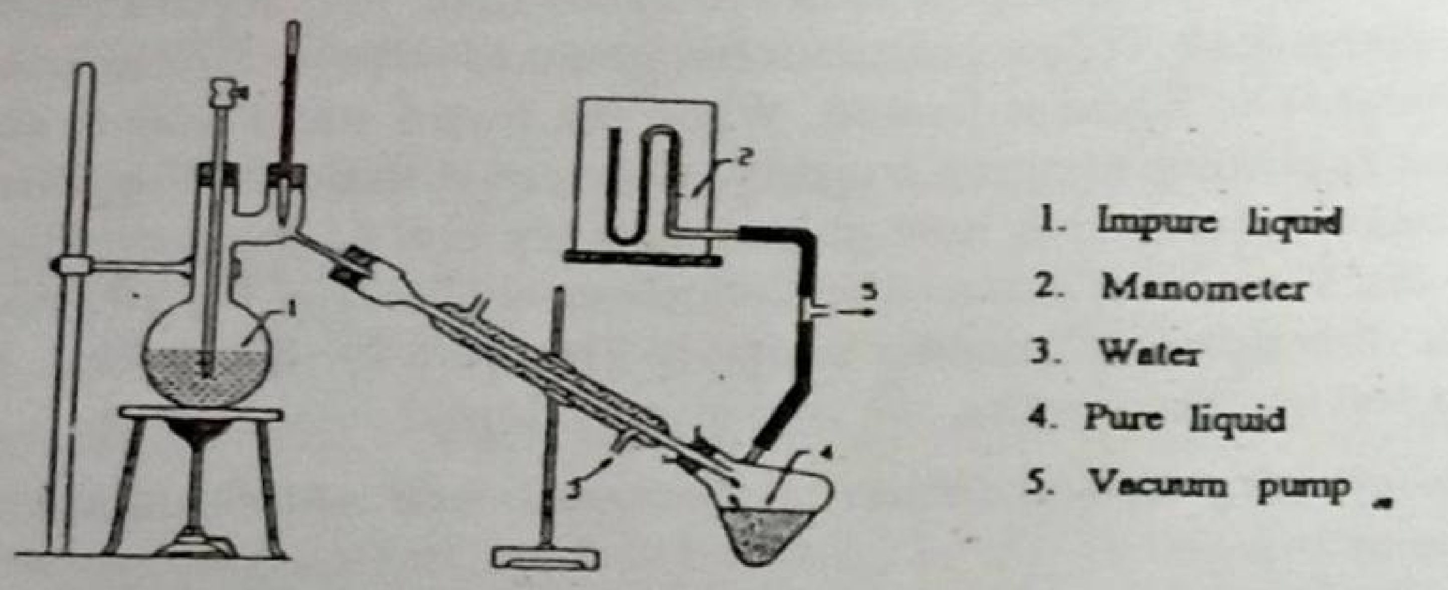


Fig. 4.6

One end of a water condenser is connected to the Claisen flask. The other end of the condenser is connected to a filteration flask which serves as the receiver. The receiver is connected to a pump and mercury manometer. The pressure in the apparatus is reduced using a mercury pump. Now the distillation is carried out in reduced pressure.

This method is used to purify liquids which decompose near their boiling points.

Example

Glycerol from spent lye in soap industries is recovered by this method. Glycerol decomposes at its boiling point (298°C) but can be distilled unchanged at 12 mm pressure when it boils at 180°C.

Fractional Distillation

Principle : A mixture containing two or more volatile liquids can be separated by this method. When their boiling points differ by more than 30°, they can be separated by fractional distillation. During the process, the more volatile liquid passes over first and is collected in a receiver. When the temperature begins to rise for the second time,the first receiver is disconnected, a new receiver is attached as soon as the temperature becomes constant once again. Thus, the distillate is collected in fractions and the process is termed as fractional distillation. For example, benzene (b.p 80°C) is separated from toluene (b.p.110°C) using fractional distillation.

When the liquids present in the mixture have their boiling points close to each other, the separation is best effected by fitting the distillation flask with a **fractionating column** as shown in fig 4.7

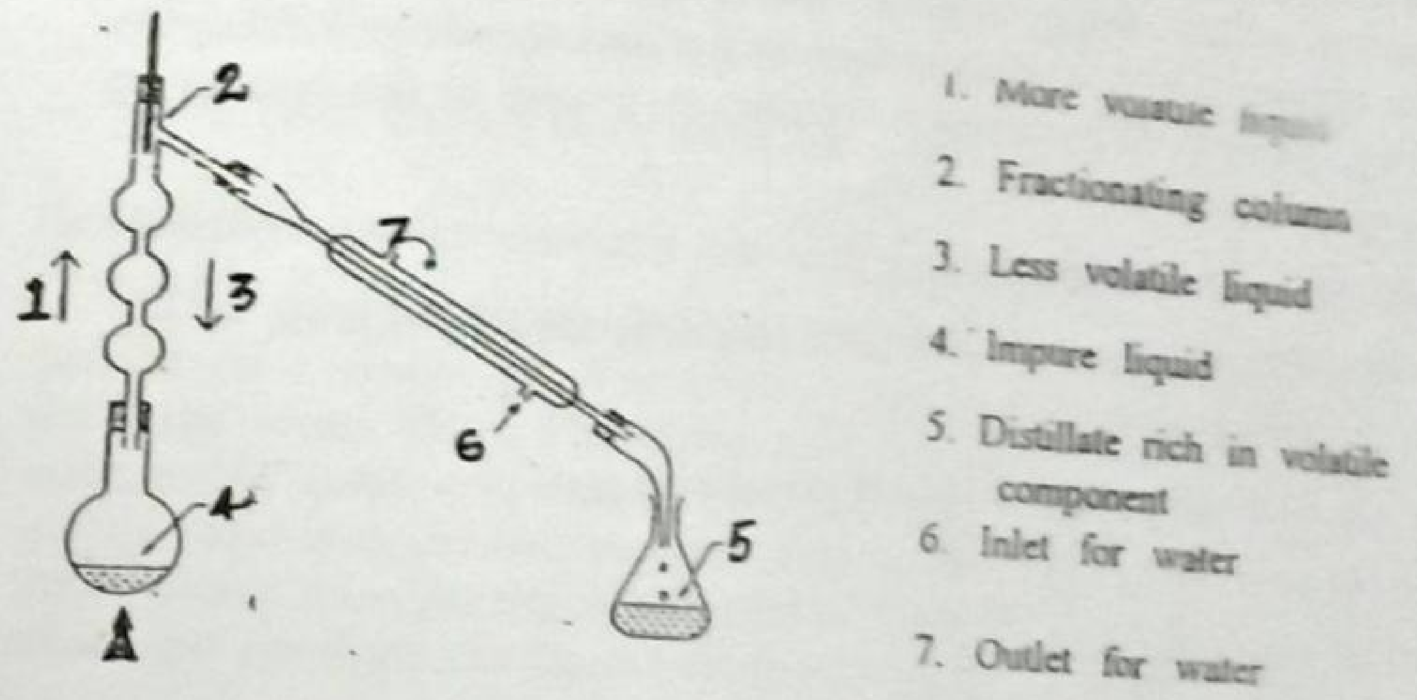


Fig. 4.7

Procedure : The apparatus consists of a round bottomed flask which is fitted with an one holed cork. A fractionating column consisting of a long glass tube blown into bulbs is inserted through the hole. A thermometer is inserted so that its bulb is near the opening of the side tube of the fractionating column. A water condenser is attached to the side tube of the fractionating column. A receiver is placed near the other end of the condenser. The mixture of liquids to be separated by fractional distillation is taken in the flask. A few porcelain bits are added to avoid bumping of the liquid mixture. The mixture is heated

The vapours of liquid A with lower boiling point along with a little of the vapours of the liquid B with higher boiling point rise up and come in contact with the large cooling surface of the fractionating column. The vapours of B condense first and those of A pass on. The condensed B flows down the column. It meets the hot ascending vapour mixture. The condensed liquid removes more of B from the vapour mixture and gives up any A present in it. This process is repeated in every bulb of the fractionating column. Thus, the vapour coming out at its top consist of nearly pure A. The liquid in the flask is nearly pure B.

Azeotropic Distillation

An azeotrope is a mixture of two or more miscible liquids having constant boiling point and constant composition. The composition of the liquid phase is identical with that of the vapour phase for an azeotrope. Hence, an azeotrope behaves as a single liquid. When an azeotrope is distilled, it distils over as such, without a change in its composition. The components of an azeotrope cannot be separated by ordinary distillation process. Few azeotropes are reported in the table 4.1.

TABLE 4.1

Azeotropic Mixtures

S.No.	Components		Percentage composition of B	Boiling Point °C		
	A	B		A	B	Mixture
1.	H_2O	C_2H_5OH	95.6	100	78.3	78.15
2.	CH_3COCH_3	CS_2	67.0	55.25	46.25	39.25
3.	$CHCl_3$	C_2H_5OH	6.8	61.2	78.3	59.3
4.	H_2O	HCl	20.3	100	-85	110
5.	H_2O	HNO_3	68	100	86	120.6
6.	H_2O	$HClO_4$	71.6	100	110	203

Close examination of the above table reveals that the boiling point of an azeotrope may be lower than those of its components (items 1 to 3 in the table) or may be higher than those of its components (items 4 to 6 in the table). The first category is called **azeotrope of minimum boiling point** while the second category is called **azeotrope of maximum boiling point.**

Azeotropic distillation is a distillation process in which the formation of azeotropes is used to separate a liquid component from an azeotropic mixture. It is a process of breaking azeotropes and getting the pure components from an azeotrapic mixture. This is explained in the preparation of absolute alcohol.

Preparation of Absolute Alcohol from Rectified Spirit

Absolute alcohol is obtained in some industries by azeotropic distillation. To the ethyl alcohol contaminated with water, a calculated amount of benzene is added and the mixture is distilled through a fractionating apparatus. Benzene removes water from alcohol by forming a ternary azeotropic mixture of water, alcohol and benzene of minimum boiling point, 65°C and containing 7.4% of water, 18.5% of alcohol and 74.1% of benzene. Once this azeotrope is distilled off, a second azeotrope, benzene and alcohol boiling at 68.3°C, containing 32.4% of benzene distils off. At the end of this, absolute ethyl alcohol distils over.

An azeotrope may be broken into its components by a chemical method, preferential adsorption, fractional extraction or fractional freezing.

Steam Distillation

Principle

The separation and purification of volatile organic compounds which are immiscible with water is accomplished with the help of steam distillation. The non volatile impurities are left behind in the distillation flask.

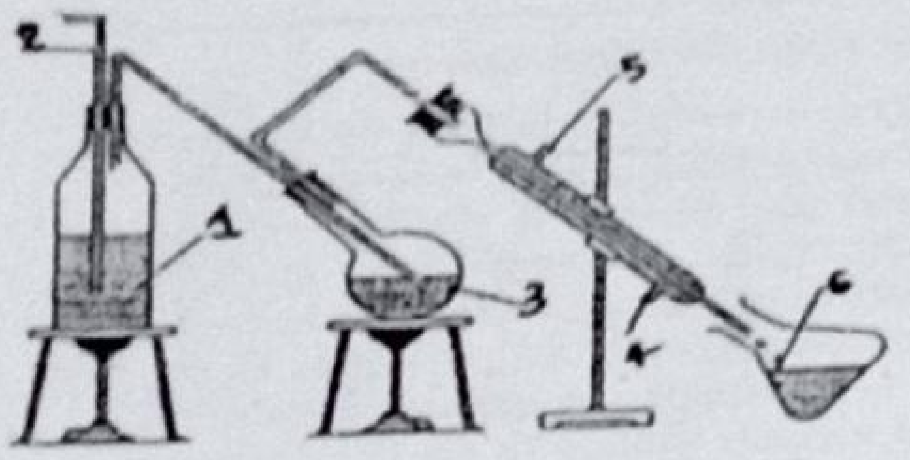
We know that a liquid boils when its vapour pressure is equal to the atmospheric pressure. In steam distillation, a mixture of water and an organic liquid is heated. The mixture boils when the combined vapour pressure of water (P_1) and that of the organic liquid (P_2) is equal to the atmospheric pressure (P). i.e. $P = P_1 + P_2$

Naturally, the boiling temperature of the mixture would be lower than the boiling temperature of the pure organic liquid. Thus, in steam distillation, the liquid is distilled at a lower temperature than its boiling point, where it might decompose. The apparatus for steam distillation is shown in fig 4.8.

Method

The apparatus consists of a round bottomed flask with a two holed cork. Through one hole, it is connected to a steam generator. Through the another hole a water condenser and a receiver are attached. The flask is placed in a slanting position in such a way that the mixture which is steam distilled does not splash into the condenser on bubbling steam through it.

neck, a long jet is inserted so that it



1. Water
2. Protective tube
3. Impure liquid
4. Inlet for water
5. Outlet for water
6. Pure liquid

Fig. 4.8

The mixture is taken in the flask and is gently heated to maintain the required temperature so that unnecessary steam condensing in the flask is avoided. Steam is passed through it. The steam carries with it the steam volatile constituent in the mixture and enters the condenser where it condenses. The condensed water and the steam distilled liquid collecting the receiver as two immiscible layers.

The distillate is then treated to recover the organic substance by suitable method. In case the organic substance is a solid, the solid may be separated by filtration. If it is a liquid, it can be removed by means of a separating funnel. The aqueous layer in both cases may be extracted with a suitable solvent.

Aniline, nitrobenzene, iodobenzene etc. are purified by steam distillation.

Applications

(i) Steam volatile turpentine is separated from crude pine resin by this technique.

(ii) Peppermint oil is obtained by steam distillation from the crushed peppermint plant.

(iii) The volatile components of several essential oils can be recovered by steam distillation.

(iv) Steam distillation is employed in the purification and manufacture of many aromatic compounds.

Chemical methods of purification

This is based on the addition of a suitable reagent to the impure substances. The reagent will react with the substance and the pure sample is recovered from the product by suitable methods. Organic compounds with contaminants are usually purified by this method.

Some examples are given below.

(i) When an organic acid is present in an organic solvent, the ac is recovered by adding NaOH, Na HCO_3 or Na_2 CO_3 solutio Usually the sodium salt of the acid is formed. The acid recovered from the salt by adding dilute HCl.

(ii) Sparingly soluble phenols like β - naphthol present in a organic solvent is purified by the addition of sodium hydroxide solution.

(iii) Organic bases like amines are purified by adding dilute acids. They usually form water soluble salts. If bases are added to their aqueous solution, pure amines are obtained.

(iv) It is also possible to add a reagent which will react with a substance (and not with the impurities) to form a solid derivative. The derivative is separated and suitably treated so as to obtain the pure substance.

For example, impure acetone is treated with Na HSO_3 and acetone alone forms a solid derivative. The derivative is separated by filtration. When the derivative is treated with NaOH or Na_2 CO_3 in warm condition, pure acetone is obtained.

Methanol, ethanol can be purified by this method.

Tests of purity

After the recovery of the substance from impurities, it becomes necessary to test for its purity. Some methods used to test the purity of the compounds are discussed.

(i) Chromatography : The sample is dissolved in suitable solvent and is subjected to paper chromatography or thin layer chromatography technique. If a single spot is obtained in the technique, then the sample is pure. If several spots are obtained, then the sample requires further purification.

(ii) Melting point : The purity of the solid substances can be tested using melting point method. If the solid sample is chemically pure, then it will have a sharp melting point otherwise the sample is impure.

(iii) Boiling point : The purity of the liquid substances can be tested using boiling point method. If the liquid sample is chemically pure, then it will have a sharp boiling point.

(iv) The purity of the liquid substances can be ascertained from their density and refractive index values.