CHE(N)-121

B.Sc. IInd Semester

ANALYTICAL CHEMISTRY

DEPARTMENT OF CHEMISTRY

SCHOOL OF SCIENCES

UTTARAKHAND OPEN UNIVERSITY

HALDWANI (NAINITAL), UTTARAKHAND-263139

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B.Sc. IInd SEMESTER

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BLOCK 1: QUALITATIVE AND QUANTITATIVE ASPECTS OF ANALYSIS

UNIT 1: ANALYTICAL APPROACHES

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1.1 INTRODUCTION

The analytical method involves using reason in a formal way to resolve problems. The first legal reasoning principles are attributed to Aristotle (384–322 BC). The premises, intermediate conclusions, and conclusions that comprise an argument are represented when one is reasoning correctly.

An analytical technique takes a problem, breaks it down into its constituent elements so that the problem may be understood, and then adds pieces that represent a solution. These make up the formal argument that this is the problem and the solution.An analytical approach is required when dealing with complicated circumstances because they become too complex to resolve naturally. Every element must be formally recorded in writing, for example, using exact words or formulas in a simulation model to guarantee correctness. This enables the person or persons who are solving the problem repeatedly to evaluate the analysis that is still being done. Complex problems comprise thousands of relationships between many pieces (dozens to hundreds). Still, the mind's short-term memory banks can only hold seven, give or take two. All save the most straightforward problems—those the mind has already encountered and remembered the solution—are thus subjected to a mental overload.

1.2 OBJECTIVES

After finishing this unit you will be able to know

- Accuracy, precision, and the different kinds of errors that might happen.
- In mathematics, you will be able to utilise significant figures for addition, subtraction, multiplication, and division.
- Finally, at the end of this unit, you will have access to the mean and standard deviation.

1.3 ERROR

A mistake is an action that you took that is considered incorrect, erroneous, or inappropriate. Any unexpected issue that stops a computer from functioning as planned is called an error. The word "error," which refers to a deviation from truth, accuracy, correctness, right, etc., is the most general in this comparison. The error does not necessarily indicate harsh criticism; instead, it means a thoughtless, inattentive, or misinterpreted error.

1.3.1 Type of the errors

1.3.1.1 Systematic Errors:

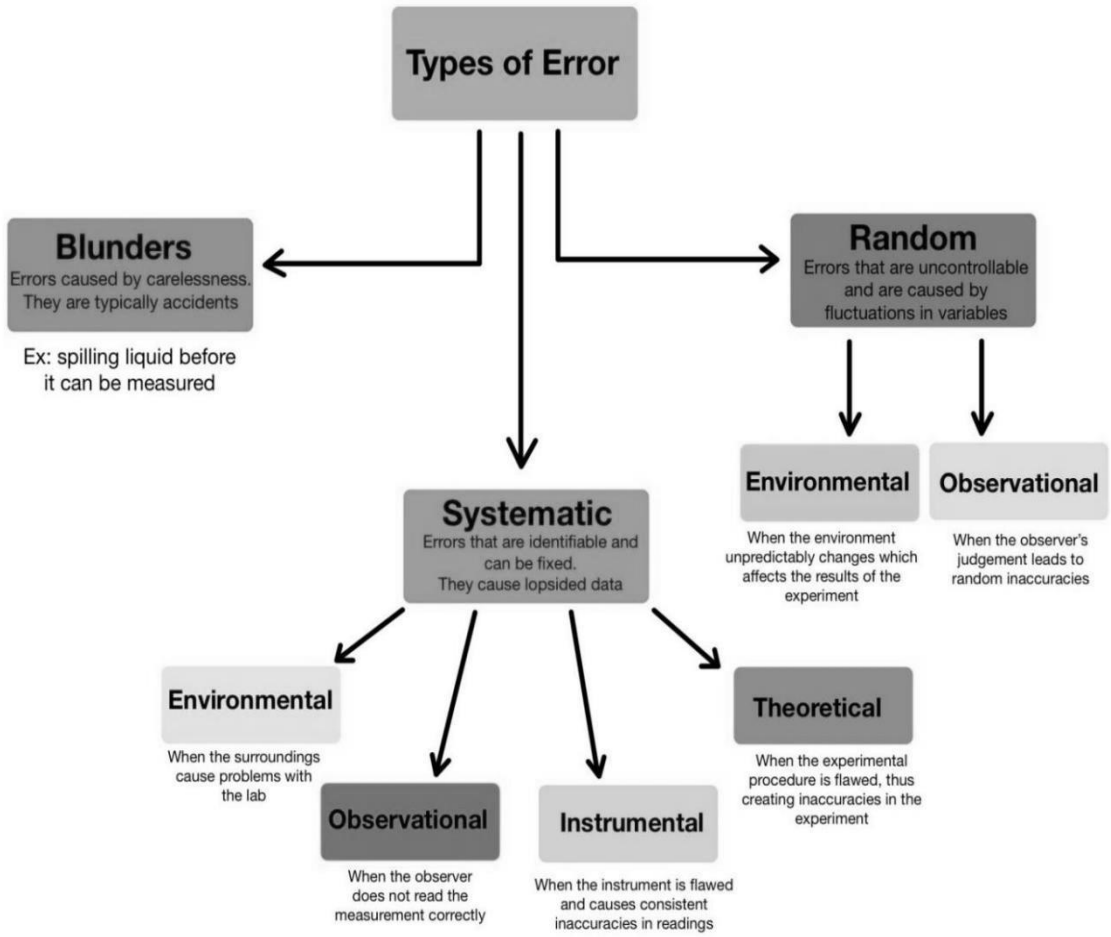
Systematic errors are those that have a recognized source and may be eliminated for subsequent experiments. There are four types of systematic errors:

1. Instrumental: When a device breaks down and introduces a mistake into the experiment (for example, a scale that falsely reads an object's weight in grams, causing the measured values to be unnecessarily high).

2. Environmental: When the scientist's cell phone's RF waves cause the Geiger counters in a lab to display radiation incorrectly, contaminating the experiment.

3. Observational: A measurement needs to be corrected when a scientist misinterprets it, for example, when they don't stand squarely when determining the amount of a flask.

4. Theoretical: When the model system used to obtain the results causes errors in the results (e.g., being told that humidity does not influence experiment outcomes when it does).



1.3.1.2 Random Errors:

Sometimes, errors that occur randomly have no recognized cause or origin. Random errors fall into two kinds.

1. Observational: 1. When an observer consistently records values either too high or too low or misreads the scale.

2. Environmental: When unanticipated events occur in the experiment setting. (e.g., students opening and shutting the door frequently while the pressure is being recorded, which causes oscillations in the reading)?

1.3.1.3 Blunders: Errors are merely blatant mistakes leading to an experiment's fault.

1.4 ACCURACY

The ability of a device to measure an exact value is known as accuracy. In other words, it describes the degree to which the estimated value matches an actual or standard value. Taking minuscule readings is necessary to obtain precise measurements. The small reading reduces the calculation's error. The following three categories of system accuracy are distinguished:

1.4.1 Point Accuracy

Point accuracy is the instrument's precision at a single point on its scale. It's essential to remember that this precision doesn't reveal anything about the overall accuracy of the device.

1.4.2 Accuracy as Percentage of Scale Range

The consistent scale range establishes the measurement's precision. The example that follows will clarify this for you:

Consider a thermometer whose scale ranges up to 500ºC. The thermometer is accurate to within ±0.5% of the scale range, or 0.005 x 500 = ± 2.5 ºC. Consequently, the reading's maximum error will be ± 2.5 ºC.

1.4.3 Accuracy as Percentage of True Value

This kind of precision can be determined by comparing the measured value to the actual value of the instruments. Because of the accuracy of the equipment, up to ±0.5 per cent of the actual value is missed.

1.5 PRECISION

A substance's accuracy can be defined as the degree of agreement between two or more measurements. Your Measurement is pretty accurate, but it might need to be more accurate if you weigh a given substance five times, and the result is 3.2 kg each time. Precision and accuracy have no connection. You can be exact without being accurate, and vice versa, as demonstrated by the following examples. There are some situations where precision is separated into:

1.5.1 Repeatability

The difference appears when the same conditions are maintained and several measurements are made in a short time.

1.5.2 Reproducibility

Variations develop when different instruments and operators use the same measuring technique over extended periods.

The degree of correspondence between a measurement's actual value and its accuracy. The degree to which measures are repeated under the same circumstances and yield the same findings is known as precision.

Since you are here, you might want to check out the following articles:

- Errors in Measurement
- Measurement of length

1.5.3 Accuracy and Precision Examples

Picture a football player taking a shot at the goal to gain an idea of accuracy and precision. If the player's attempt goes in goal, it is deemed accurate. It is correct but not exact when a football player hits the same goalpost repeatedly. That means a football player can be honest without being exact if he smashes the ball all over the field and still scores. An accurate player will always hit the ball to the same spot, regardless of his score. Precision and accuracy in football would be used to aim at one place and achieve the goal.

1.5.4 Difference between Accuracy and Precision

Having discussed what each term means in the previous few sections, let us look at their differences.

Accuracy	Precision
The degree of agreement between the actual measurement and the absolute measurement is referred to as accuracy.	The degree of variance present in the results of multiple measurements of the same factor is implied by precision.
Shows the degree to which the findings agree with the reference value.	Shows the degree of agreement between outcomes.
There must be a single factor or measurement.	In order to comment on precision, several metrics or factors must be considered.
In order to comment on precision, several metrics or factors must be considered.should also be precise.	Accuracy can coexist with precision in results. On the other hand, the outcomes might be exact and accurate.

Using significant figures, the number displayed as digits is determined. These digits represent these numbers meaningfully. Another common word used in place of figures is substantial digits. The number of significant digits can be found by counting all the values, starting with the first non-zero digit on the left. One example of a substantial figure is 12.45.

Any number that accurately conveys meaning based on its digits is considered to have significant figures. With four significant digits, for instance, it is 6.658. These large numbers give the accuracy of the statistics. Significant digits are another name for them.

1.6 RULES FOR SIGNIFICANT FIGURES

- It is meaningful to all non-zero numbers. 198745 is composed of six essential digits.
- Each zero that exists between two non-zero numbers is significant. In 108.0097, for example, there are seven significant numbers.
- Every zero preceding a decimal point and to the right of a non-zero value is insignificant. In 0.00798, for example, there were three significant digits.
- They are significant Only when there isn't a non-zero digit after the rightmost zeros of a decimal point. For example, 20.00 has four critical numbers.
- After the decimal point, every zero to the right of the last non-zero digit matters. In 0.0079800, for example, there are five significant numbers.
- Every measurement holds significance if it contributes to any of the zeros located to the right of the ultimate non-zero figure. For example, 1090 m contains four essential integers.

Rounding a number to the required number of significant digits involves moving one or more digits to the left from the right. The final digit shall remain unchanged if the leftmost digit is fewer than five. If the initial digit exceeds five, the last digit is rounded up. When the number of remaining digits is exactly 5, the retained integer is rounded up or down to an even value. With numerous remaining digits, rounding off should be done as a whole instead of one digit at a time.

1.6.1 Examples of Significant Figures

Example 1: Identify the number of significant digits/figures in the following numbers.

45, 0.046, 7.4220, 5002, 3800

Solution:

Number	Number of significant digits/figures
45	**Two**
0.045	**Two**
7.4220	**Five**
5002	**Four**
3800	**Two**

Example 2: Write 12.378162 correct to 4 significant digits**.**

Solution:

The number 12.378162, rounded to 4 significant digits, is 12.38

Hence, 12.38 is the answer.

That is the number of significant figures in a result known with a certain degree of reliability. According to 13.2, there are three significant figures. Positive and non-zero digits are always significant. 3.14159 has six significant numbers, each of which indicates helpful something. Thus, 67 has two significant numbers, while 67.3 has three. This article covers the rules for calculations with significant figures in arithmetic.

1.7 RULES FOR ARITHMETIC OPERATION OF SIGNIFICANT FIGURES

According to the weakest link concept, a chain is only as strong as its weakest link, which must be adhered to in most cases. The maximum precision of the calculation is determined by the measurement that is the least accurate. In significant figures, the following arithmetic procedures are used:

- Addition
- Subtraction
- Multiplication
- Division

1.7.1 Addition and Subtraction

The final standard digit in each component located farthest to the right is utilized to round the outcome. Another way to put this rule is as follows: by counting from left to right, the result of Addition or Subtraction is rounded off to equal the measurement with the fewest decimal places. Assuming three significant digits, the formula is 200 + 69.693 (5 significant numbers) = 269.693.

Rounding this will get a result of 269 (3 significant figures). But notice that relevant statistics in the same digit column may not share any digits between two numbers.

$$13.214 + 234.6 + 7.0350 + 6.38 = 261.2290$$

Observing closely, we see that the second figure, 234.6, is only accurate to the tenth place, while all the other figures are accurate to numerous decimal points. The answer will satisfy the weakest link criterion if rounded to the tenth position. We acquire,

$$13.214 + 234.6 + 7.0350 + 6.38 = 261.2$$

1.7.2 Multiplication and Division

Let's look at some methods for dividing and multiplying numbers that make sense. The Multiplication is standard, and all the decimal points are noted. The weakest link rule also holds when bearing significant figures. It is necessary to round off the results of division and Multiplication to equal the component with the fewest influential figures.

$$16.235 \times 0.217 \times 5 = 17.614975$$

Because the component with the fewest significant digits has only one significant digit, we must round 17.614975 to 20, the closest response with one significant digit. As an extra example,

$$0.00435 \times 4.6 = 0.02001$$

4.6 here has only two significant digits; we will round 0.02001 to two significant digits. From this, we get,

$$0.00435 \times 4.6 = 0.020$$

Since there is just one significant digit in this example the "2" in 0.02 is erroneous. The trailing zero in 0.020 indicates that "this is accurate to the thousandth place, or two significant digits," is necessary to complete the solution.

1.8 MEAN

The mean is one of the statistics' measures of central tendency, along with the mode and median. The mean is just the average of the given collection of numbers. It shows that there is an equal distribution of values within a given data collection. The mean, median, and mode are the three often employed metrics for assessing central tendency.To find the mean, add up all of the values listed on a data sheet, then divide that total by the total number of values.The middle value in a given set of data is called the median when all the values are arranged in ascending order. Conversely, the mode is the number in the list that appears the most times.

1.8.1 Definition of Mean in Statistics

The mean, which is computed by dividing the sum of the provided numbers by the total number of numbers, is the average of the given numbers.

Mean = (Sum of all the observation/ total number of observations)

Example:1 What is the mean of 2, 4, 6, 8 and 10?

Solution: First, add all the numbers.

$$2 + 4 + 6 + 8 + 10 = 30$$

Now divide by 5 (total number of observations).

Mean = 30/5 = 6

Example:2 Find the mean of the first five natural odd numbers, using the mean formula.

Solution: The first five natural odd numbers = 1, 3, 5, 7, and 9

Using mean formula,

$$\text{Mean} = (1 + 3 + 5 + 7 + 9) \div 5 = 25/5 = 5$$

The first five natural odd integers {1, 3, 5, 7, 9} have a mean of 5.

Example:3 The five students are the following heights: 161 inches, 130 inches, 145 inches, 156 inches, and 162 inches. Find out the students' average height.

Solution: To determine the students' average height.

The five students' heights are as follows: 161 in, 130 in, 145 in, 156 in, and 162 in.

The five students' combined heights equal (161 + 130 + 145 + 156 + 162) = 754.

Applying the mean formula,

$$\text{Mean} = 754/5 = 150.8$$

Answer: The students average height is 150.8 inches.

Example:4 : There are one hundred members in a basketball club. The members' various age groups and the overall number of members in each age group are listed in the following table. Find out how old the club members are on average.

Age Group	Number of members
10-20	**17**
20-30	**22**
30-40	**20**
40-50	**21**
50-60	**20**

In this instance, the Class Mark for each age group needs to be determined first.

Solution : We will determine the class mark for each age group using the formula below.

(Upper Limit + Lower Limit)/2 is the class mark. For instance, the class mark for the first interval, 10–20, is equal to (10 + 20) / 2 = 30–2 = 15.

Age Group	Class Mark (xi)	Frequencies(fi)	xifi
10-20	**15**	**17**	**x_1f_1 = 15 X17 = 255**
20-30	**25**	**22**	**X_2f_2 = 25 X 22 = 550**
30-40	**35**	**20**	**X_3f_3 = 35 X 20 = 700**
40-50	**45**	**21**	**x_4f_4 = 45 X 21 = 945**
50-60	**55**	**20**	**X_5f_5 = 55 X 20 = 1100**

Now

$\Sigma xifi = x_1f_1 + x_2f_2 + x_3f_3 + x_4f_4 + x_5f_5$

$\Sigma xifi = 15 X 17 + 25 X 22 + 35 X 20 + 45 X 21 + 55 X 20$

$\Sigma xifi = 255 + 550 + 700 + 945 + 1100$

$\Sigma xifi = 3550$

We will use the formula given below.

$\bar{x} = \Sigma fixi/\Sigma fi$

$\Sigma xifi = 3550/100$

$\Sigma xifi = 35.50$

The mean age of the members = 35.5

The mean of a random variable X with a discrete probability distribution is the total of all possible values, each weighted by its likelihood. Put another way, the method for calculating the mean involves multiplying each potential value (x) of X by its probability (P(x)), aggregating the results, and then calculating the mean.

1.8.2 Mean Symbol (X Bar)

The symbol of mean is usually given by the symbol '$\bar{x}$'. The bar above the letter x, represents the mean of x number of values.

$\bar{X}$ = (Sum of values ÷ Number of values)

$\bar{X} = (x1 + x2 + x3 + \ldots + xn)/n$

1.8.3 Mean Formula

The primary mean formula is produced using the given data set. All of the data set's terms are considered when calculating the mean. The general mean formula can be found by dividing the total number of terms by the Sum of all the terms. Therefore, we may say,

Mean = Sum of the Given Data/Total number of Data.

The arithmetic mean of a set of data can only be found by adding up (summarising) all of the data values (x). The outcome must be divided by the total number of values (n) next. Because ∑ it indicates that values should be averaged (see Sigma Notation), the mean ($\bar{x}$) can be found using the following formula:

$$\bar{x} = \sum x/n$$

1.8.4 How to Find Mean?

Since, as we all know, data can be either grouped or ungrouped, we must first ascertain whether the presented data is ungrouped before computing the mean. The mean can be found using several grouped and ungrouped data formulas. This section will teach you how to find the mean for each scenario.

1.8.5 Mean for Ungrouped Data

The example below will help you understand **how to find the mean** of ungrouped data.

Example: 1 In a class, there are 20 students, and they have secured a percentage of 88, 82, 88, 85, 84, 80, 81, 82, 83, 85, 84, 74, 75, 76, 89, 90, 89, 80, 82, and 83.

Find the mean percentage obtained by the class.

Solution: Mean = Total percentage obtained by 20 students in class/Total number of students.

= [88 + 82 + 88 + 85 + 84 + 80 + 81 + 82 + 83 + 85 + 84 + 74 + 75 + 76 + 89 + 90 + 89 + 80 + 82 + 83]/20

= 1660/20

= 83

Hence, the mean percentage of each student in the class is 83%.

1.8.6 Mean of Negative Numbers

Thus far, we have seen instances of determining the mean of positive values. What transpires, then, if the observation list contains negative integers? Let us illustrate with an example.

Example:1 Find the mean of 9, 6, -3, 2, -7, 1.

Solution: Add all the numbers first:

Total: 9+6+(-3)+2+(-7)+1 = 9+6-3+2-7+1 = 8

Now, divide the total by 6 to get the mean.

$$\text{Mean} = 8/6 = 1.33$$

1.8.7 Types of Mean

In statistics, you will learn about mean values in three main varieties.

1. Arithmetic Mean
2. Geometric Mean
3. Harmonic Mean

1.8.7.1 Arithmetic Mean

An "arithmetic mean" is calculated by dividing the total number of values by the total number of values. To calculate, multiply the total number supplied by the total number of numbers provided.

Example:1 What is the mean of 3, 5, 9, 5, 7, 2?

Solution: Now add up all the given numbers:

$$3 + 5 + 9 + 5 + 7 + 2 = 31$$

Now divide by how many numbers are provided in the sequence:

$$31/6 = 5.16$$

5.16 is the answer.

1.8.7.2 Geometric Mean

The x and y numbers have a geometric mean of xy. The geometric mean of three numbers, x, y, and z, is 3xyz.

$$\text{Geometric Mean} = \sqrt[n]{x_1 x_2 x_3 \ldots\ldots\ldots\ldots x_n}$$

Example: Find the geometric mean of 4 and 3.

$$\text{Geometric Mean} = \sqrt{4 \times 3} = 2\sqrt{3} = 3.46$$

1.8.7.3 Harmonic Mean

The x and y numbers have a geometric mean of xy. The geometric mean of three numbers, x, y, and z, is 3xyz.

$$\text{Harmonic mean (H)} = \frac{n}{\frac{1}{x_1} + \frac{1}{x_2} + \frac{1}{x_3} \ldots\ldots\ldots \frac{1}{x_n}}$$

Variance and standard Deviation are the two main ideas in statistics. It is a statistical data dispersion measurement. A distribution's dispersion is when values vary from the average. The magnitude of the fluctuation can be determined using several metrics, such as:

(i) Range

(ii) Quartile Deviation

(iii) Mean Deviation

(iv) Standard Deviation

The degree of dispersion is computed through the measurement of data point fluctuation. This article will lead you through discovering values with examples, explaining variance and standard Deviation, and presenting calculations.

1.9 VARIANCE AND STANDARD DEVIATION

Statistics has a relationship between variance and standard deviation since the square root of the variance yields the standard deviation for a given data set. Here are definitions of variance and standard deviation for you.

1.9.1 What is a Variance?

Variance quantifies the degree of noticeable dispersion in a set of data. If all data values are the same, there will be no variance. Favourable variances are all those that are not zero. A low variance indicates that the data points are near the mean and one another; a significant variance suggests that the data points are far from the mean. The squared average of the separations between each end and the mean represents the variance in its most basic form.

1.9.2 What is Standard Deviation?

The standard deviation indicates the degree of variation (dispersion, spread, etc.) from the mean. The standard deviation indicates a "typical" departure from the mean. Reverting to the original units of measurement in the data set makes it a popular measure of variability. Like variance, there is a substantial variance if the data points are widely scattered from the mean and a slight variation if the data points are close to the mean. The standard deviation determines the degree of variation of the numbers from the average.

Based on all values, the standard deviation is the most widely used method for evaluating dispersion. Because of this, even a tiny variation in a single statistic might affect the authoritative deviation figure. It is origin-independent but not scale-dependent. It also helps with some problematic statistical problems. The formula for Variance and Standard Deviation

The following are the formulas for standard deviation and variance:

Standard Deviation Formula

The population standard deviation formula is given as follows:

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(X_i - \mu\right)^2}$$

Here,

σ = Population standard deviation

N = Number of observations in population

Xi = ith observation in the population

μ = Population mean

Similarly, the sample standard deviation formula is:

$$s = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}$$

Here,

S = Sample standard deviation

n = Number of observations in sample

xi = ith observation in the sample

How is Standard Deviation calculated?

The standard deviation is computed using three variables. The first variable in a data set is the value of each point, and the sum number represents each subsequent variable (x, x1, x2, x3, etc.). The means of the values of the variable M and the amount of data assigned to the variable n are considered. Variance is the arithmetic mean squared departures from the mean divided by the total. The mean value can be found by adding the values of the individual data pieces and dividing the result by the total number of data entities involved.

The term "root-mean-square deviation" refers to the square root of the mean of the squares of all the values in a series derived from the arithmetic mean. The symbol σ, which stands for standard deviation, represents this measurement. The lowest value for the standard deviation is 0 since it cannot be negative. When a group of individuals deviates more from the mean, the standard deviation of the series rises.

The standard deviation is a statistical instrument that calculates the erraticism of the dispersion among the data through dispersion measurements. For instance, the mean, median, and mode are the metrics used to measure central tendency. Therefore, these are regarded as the centre first-order averages. Since they are averages of the deviations from the average values, second-order averages are the dispersion measurements that were previously discussed.

Standard Deviation Example

The goal is to determine the standard deviation of the quantity of gold coins on a pirate-run ship. The total number of pirates on the boat is one hundred. One hundred people make up the population, according to a statistical study. Utilizing the standard deviation equation, we can calculate the total number of gold coins every pirate holds for the population.

I'll use a sample of five persons to illustrate the statistical points. This situation can be handled using the sample group's standard deviation equation.

Using the standard deviation equation for a population sample suggests that the sample size is five.

Consider the number of gold coins five pirates have: 4, 2, 5, 8, 6.

Mean:

$$\bar{X} = \frac{\Sigma_X}{n}$$

$$\bar{X} = \frac{x_1 + x_2 + x_3 \ldots\ldots x_n}{n}$$

$= (4 + 2 + 5 + 6 + 8) / 5$

$= 5$

$x_n - \bar{x}$ for every valve of the sample

$x_1-\bar{x} = 4-5 = -1$

$x_2-\bar{x} = 2-5 = -3$

$x_3-\bar{x} = 5-5 = 0$

$x_4-\bar{x} = 8-5 = 3$

$x_5-\bar{x} = 6-5 = 1$

$$\Sigma \left(x_n-\bar{x}\right)^2$$

$$=(x_1-x)^2+ (x_2-x)^2+(x_3-x)^2 + (x_4-x)^2+ (x_5-x)^2$$

$= (-1)^2 + (-3)^2 + 0^2 + 3^2 +1^2$
$= 20$
Standard Deviation

$$S.D = \sqrt{\frac{\Sigma \left(x_i- \bar{x}\right)^2}{n-1}}$$

$$S.D = \sqrt{\frac{20}{4}}$$

$S.D = \sqrt{5}$

$S.D = 2.236$

Standard Deviation of Grouped Data

By considering the frequency of the data values, one can calculate the standard deviation when working with grouped data or grouped frequency distribution. You'll understand this better with an example.

Question: Calculate the mean, variance and standard deviation for the following data:

Class interval	0-10	10-20	20-30	30-40	40-50	50-60
Frequency	**27**	**10**	**7**	**5**	**4**	**2**

Answer :

Class interval	**Frequency (f)**	**Mid Value (x_i)**	**fx_i**	**fx_i^2**
0-10	27	5	135	675
10-20	10	15	150	2250
20-30	7	25	175	4375
30-40	5	35	175	6125
40-50	4	45	180	8100
50-60	2	55	110	6050
	$\Sigma f = 55$		$\Sigma fx_i = 925$	$\Sigma fx_i^2 = 27575$

$N = \Sigma f = 55$

Mean = $\Sigma fx_i / N = 925/55 = 16.818$

Variance = $1/ (N-1) [\Sigma fx_i^2 - 1/N (\Sigma fx_i)^2]$

$= 1/(55-1) [27575-(1/55) (925)^2]$

$= (1/54) [27575-15556.8182]$

$= 222.559$

Standard deviation = $\sqrt{}$variance = $\sqrt{}222.559$

= 14.918

1.1 SUMMARY

The summary of the present unit is as follows:

- This Unit covers the rules for calculations with significant figures in arithmetic. The goal is to determine the standard deviation of the quantity of gold coins on a pirate-run ship.
- In this unit, you clearly understand the types of errors, precision & accuracy, Significant figures, significant figures in Arithmatics addition, subtraction, multiplication and division, and Mean and standard deviation.

1.11 REFERENCES

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2. D. E., P. F. Velleman, and R. D. De Veaux. 2010. *Stats: Modeling the World*. Addison Wesley.

3. M. C. Bryson, 1976. "The Literary Digest Poll: Making of a Statistical Myth." *The American Statistician* 30 (4): 184–85.

4. https://byjus.com/physics/error-arithmetic-operations-significant-figures/

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1.12TERMINAL QUESTIONS

A. Short Answer Type:

Q1. What are significant figures?

Q2: In significant figures, which set of mathematical operations are used?

Q3. What is rounding off?

Q4. What are the dimensions of a physical quantity?

Q5. Define supplementary units.

B. Long Answer Type:

Q1. Find uot the mean and standard deviation for the following data.

Class interval (x)	60	61	62	63	64	65	66	67	68
Frequency (f)	**2**	**1**	**12**	**29**	**25**	**12**	**10**	**4**	**5**

Q2.Calculate the mean, variance and standard deviation for the following data:

Class interval	0-10	10-20	20-30	30-40	40-50	50-60
Frequency	**27**	**10**	**7**	**5**	**4**	**2**

Q3. In a class, there are 20 students, and they have secured a percentage of 88, 82, 88, 85, 84, 80, 81, 82, 83, 85, 84, 74, 75, 76, 89, 90, 89, 80, 82, and 83.Find the mean percentage obtained by the class.

Q4. The five students are the following heights: 161 inches, 130 inches, 145 inches, 156 inches, and 162 inches. Find out the students' average height.

Answer A

Q1. Significant figures are important integers between 0 and 9 that are used in the coefficient of an expression to characterize the precision of the expression. After the computations are finished, the expression is rounded to obtain these values.

Q2. The set of mathematical operations that are used in important figures is as follows.:

- Addition
- Subtraction
- Multiplication
- Division

Q3. When a number is rounded off, its value is preserved and it is brought closer to the next number, making it simpler. Whole numbers and decimals at different places of hundreds, tens, tenths, etc. are handled in this manner. The purpose of rounding off numbers is to keep the important numbers intact.

Q4. A physical quantity's dimensions pertain to its characteristics that provide a quantifiable definition for the quantity. The physical dimensions are denoted by the letters L, M, and T, which stand for length, mass, and time, respectively.

Q5. Physical values without dimensions that are employed in addition to fundamental units are called supplementary units.

UNIT 2: LABORATORY APPARATUS AND MEASURING EQUIPMENT

CONTENTS:

2.1 Introduction
2.2 Objectives
2.3 Location of Laboratory Equipments
2.4 Laboratory Note book
2.5 Laboratory Apparatus and Operation
2.6 Laboratory Safety
2.7 Summary
2.8 Terminal questions

2.1 INTRODUCTION

Introduction to basic laboratory techniques and procedures necessary for competent performance. Topics will include laboratory Reagents, apparatus, Glassware laboratory safety, volumetric and gravimetric measurements, titrations, critical evaluation of data, laboratory mathematics, preparing solutions and dilutions, and basic spectro photometric measurements. The purpose of this experiment is to introduce several of the tools and techniques necessary for success in this course.

Chemistry is an experimental science, and the laboratory is where you learn about "how we know what we know about it." The laboratory deals with the processes of scientific inquiry that organic chemists use. It demonstrates the experimental basis of what your textbook presents as fact. The primary goal of the laboratory is to help you understand how Chemistry is done by actually doing it. Learning how to obtain and interpret experimental results and draw reasonable conclusions from them is at the heart of doing science. Your laboratory work will give you the opportunity to exercise your critical thinking abilities, to join in the process of science.

2.2 OBJECTIVES

This Unit is designed to ensure that all the students regardless of their educational backgrounds are competent in necessary laboratory skills. These skills include but are not

limited to the use of an analytical balance, volumetric glassware, various pipettes, performing titrimetric and spectrophotometric determinations and learning the proper use and calibration of microscopes and centrifuges. Students should also become familiar with using laboratory apparatus.

Use the proper laboratory techniques to do the following;

- Pour liquids from a glass-stopper bottle.
- Transfer solids from a bottle.
- Heat liquids in a beaker.
- Heat liquids in a test tube.
- Light and adjust a Bunsen burner.
- Measure to 0.1 cm with a metric ruler.
- Use a graduated cylinder to measure volume.
- Use an analytical balance to measure mass.

2.3 LOCATION OF LABORATORY EQUIPMENT

(a) Chemicals and Solvents Organic and Inorganic:

Acids and Bases - under hood

Solvents - on shelves at end of benches

(b) Ovens and Refrigerators:

Each oven is designated for a specific purpose. Do not place any plastic items in the ovens. All samples must be clearly labeled with the identity of compound, your name and date. Ovens will be cleared weekly and improperly labeled samples will be removed. Refrigerators. Samples must be clearly labeled.

(c) Balances:

Abuse of balances and littering of the area will not be tolerated.

2.4 LABORATORY NOTE BOOK

2.4.1 General Guideline:

1. Use a ballpoint pen (press hard if duplicate pages).Write on one side only.

2. Do not erase or use whiteout. If you make a mistake, draw a single line through the error and write the correct entry on the top or side of it.
3. Do not remove an original page. If the entire page is incorrect, draw a single diagonal line through the page and state the reason for this line.
4. Record all data and results (with units) directly into your notebook.
5. Do not record data on scrap paper, your hand, etc., to be transferred later.
6. Start a new page for each new experiment.
7. Write the title of the experiment, date, and your name at the top of each page.
8. Indicate if a page is continued from the previous page.
9. Never skip a space for later additions.

2.4.2 Components

A. Pre-Lab – a detailed plan of the work that you will be doing:

Brief statement of purpose.

1. Paragraph discussion of the safety and environmental issues (ex. waste generation).
2. Step-by-step procedure in your own words. Be concise and complete, but do not cop the lab manual. Use diagrams and sketches when necessary. Reference all sources of Information.

   Note: The lab manual may not be brought into the laboratory or consulted during the laboratory session. However, the appendices are allowed.

B. Factual Record – what to record:

Keep a running account of all procedures carried out and observations made during experimental work.

1. Record observations such as physical appearance, color, odor, and physical properties.
2. Sketch apparatuses and label parts.
3. Use a table to record all information about reactants (see below).
4. Record all data and results, including the crude yield of products and mixtures. Use tables when possible.
5. All of the reactants must be accounted for in the factual record. For example, if you started with 1.0 mol of Reactant 1, you must account for the fate of all 1.0 mols at the end of the reaction. Simply describing the isolated 0.25 mol of product at the end (for example) will not be acceptable.

6. For calculations, show the formula and a sample calculation. If the calculation is repeated; use a table to report your results.
7. All graphs should be constructed with a graphing program. Label all axes and providea title for each graph.
8. Attach all spectra to your notebook, label the axes, and reference the spectra in the procedure section.

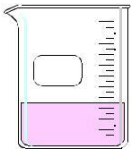
Data Analysis/Conclusions:

Examine and discuss the accuracy and precision of your data. Is the precision reasonable? Discuss possible systematic and random errors. Summarize the key results and provide a conclusion. Describe any difficulties that you had. Discuss which results are poor and provide explanations. Provide suggestions for improvement.

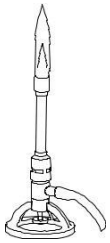
2.5 LABORATORY APPARATUS AND OPERATION

A. Common Laboratory Apparatus:

Beakers are useful as a reaction container or to hold liquid or solid samples. They are also used to catch liquids from titrations and filtrates from filtering operations.

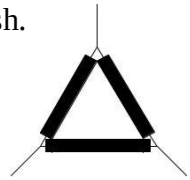


Bunsen Burners are sources of heat.



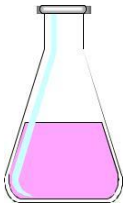
Burettes are for addition of a precise volume of liquid. The volume of liquid added can be determined to the nearest 0.01 ml. with practice.

Clay Triangles are placed on a ring attached to a ring stand as a support for a funnel, crucible, or evaporating dish.



Droppers are for addition of liquids drop by drop

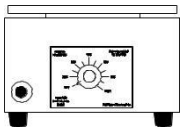
Erlenmeyer Flasks are useful to contain reactions or to hold liquid samples. They are also useful to catch filtrates.



Glass Funnels are for funneling liquids from one container to another or for filtering when equipped with filter paper.

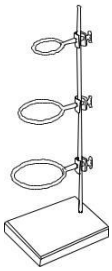
Graduated Cylinders are for measurement of an amount of liquid. The volume of liquid can be estimated to the nearest 0.1 ml with practice.

Hot Plates can also be used as sources of heat when an open flame is not desirable.



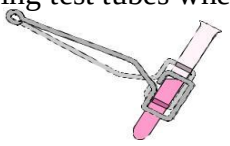
Pipets are used to dispense small quantities of liquids.

Ring stand with Rings are for holding pieces of glassware in place.

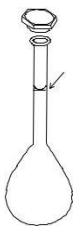


Test Tubes are for holding small samples

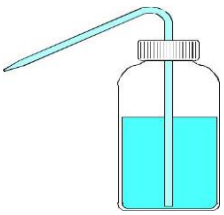
Test tube holders are for holding test tubes when tubes should not be touched



Volumetric Flasks are used to measure precise volumes of liquid or to make precise dilutions.

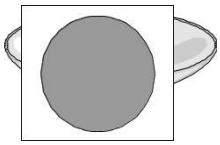


Wash bottles are used for dispensing small quantities of distilled water.



Watch glasses are for holding small samples or for covering beakers or evaporating dishes.

Wire Gauze on a ring supports beakers to be heated by Bunsen burners

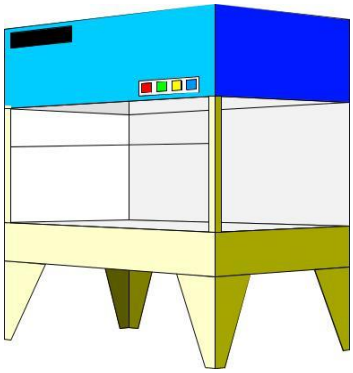


B. Laboratory equipment:

Balances are used to determine the mass of a reagent or object.

Spectrophotometers are used to measure the absorbance or transmittance of a liquid sample.

Fume Hoods are used to ventilate noxious or harmful gases



2.5 COMMON LABORATORY REAGENTS

Name	General Description
Acetic acid	An organic acid; is one of the simplest carboxylic acids.
Acetone	An organic compound: simplest example of the ketones
Acetylene	A hydrocarbon and the simplest alkyne; widely used as a fuel and chemical building block

Ammonia	Inorganic; the precursor to most nitrogen-containing compounds; used to make fertilizer.
Ammonium hydorixde	Aqueous ammonia; used in traditional qualitative inorganic analysis
Ammonium hydoride	Aqueous ammonia; used in traditional qualitative inorganic analysis
Azobisisobutyron trile	Organic compound; often used as a foamier in plastics and rubber and as a radical initiator
Baeyer's reagent	An alkaline solution of potassium permanganate; used in organic chemistry as a qualitative test for the presence of unsaturation, such as double bonds;
N-Bromosuccinimide	Used in radical substitution and electrophilic addition reactions in organic chemistry
Butanone(methyl ethyl ketone)	Organic compound; similar solvent properties to acetone but has a significantly slower evaporation rate.
Butylated hydroxytoluene	A fat soluble organic compound that is primarily used as an antioxidant food additive
n-Butyllithium	An organolithium reagent; used as a polymerization initiator in the production of elastomes such as ploybutadience or styrene-butadiene-styrene(SBS)
Carbon disfulifde	A non-polar solvent; used frequently as a building block in organic chemistry
Carbon	Toxic, and its dissolving power is low; consequently, it has been largely
Tetrachloride	Supersede by deneuterated solvents
Carbonylidiimidazole	Often used for the coupling of amino acids for peptide synthesis and as a reagent in organic synthesis
Ric ammonium nitrate	An organic compund; used as an oxidising agent in organic synthesis and as a standard oxidant in quantitative analysis

Chloroform	Organic compound; often used as CDC13 (deuterated chloroform) as a solvent for NMR spectroscopy and as a general solvent.
Chromic acid	A strong and corrosive oxidisig agent; an intermediate in chromium plating
Chromium trioxide	The acidic anhydride of chromic acid; mainly used in chrome-plating .
Chromium trioxide	The acidic anhydride of chromic acid; mainly used in chrome-plating
Colloins reagent	Used to selectivley oxidize primary alchols to an aldehyde
Copper(I) iodide	Useful in a variey of applications ranging from organic sysnthesis to cloud seeding
Dess-martin periodinane	Chemical reagent used to oxidize primary alcohols to aldehydes and secondary alcohos to ketones
Diborance	The central organic synthesis reagent for hydroboration
Diethyl azodicarboxylate	A valuable reagent but alos quite dangerous and explodes upon heating
Diethyl ether	Organic compound; a common laboraory solvent
Dihydropyran	A heterocyclic compound; used as a protecting group for alcools in organic synthesis.
Disobutlyaluminum hydride	An organoaluminium compound; a redcing agent; converts esters and nitriles to aldehydes
Diisopropyl azodicarboxylate	The diisorpropyl ester of azodicarboxylic acid; a reagent in the production of many organic compounds
Dimethyl ether	The simplest ether, a useful precursor to other organic compounds and an aerosol propellant
Dimethylformamde	Organic compound; a common solvent for chemical reactions
Dimethylsulfide	Organosulfur compund; used in petroleum refinint and in petrochemcal production processes; a

	reducing agent in ozonolysis reactions.
Dimethyl sulfoxide	An organosulfur compound; an important polar aprotic solvent that dissovles both polar and nonpolar compounds
Dioxane	A heterocyclic organic compound; classified as an ether
Ethanol	A powerful psychoactive drug; used in alcoholic beverages, in thermometers, as a solvent, and as a fuel.
Fehling's reagent	Used to differentiate between water-soluble aldehyde and ketone functional groups
Fentons' reagent	A solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or waste waters.
Formaldehyde	The simplest aldehyde; an important precursor to many other chemical compounds; such as ploymers and polyfunctional alcohols
Formic acid	The simplest caroxylic acid; often used as a source of the hydride ion
Grignard reagents	The most common application is for alkylation of aldehydes and ketones;
Hydrazine	It's a good reducing agent and is used in the wolff-kishner reaction for reducing carbonyls to its corresponding alkanes. Used as a foaming agent in preparing polymer foams; also a precursor to polymerization catalysts and pharmaceuticals; also as an oxygen scavenger in power plants.
Hydrazoic acid	Used primarily for preservation of stock solutions, and as a reagent
Hydrochloric acid	A highly corrosive, strong mineral acid with many industrial uses
Hydrofluoric acid	Valued source of fluorine, precursor to numerous pharmaceuticals; highly corrosive

Hydorgen peroxide	Commonly used as a bleach
Imidazole	An organic compound; this aromatic heterocyclic is a diazole and is classified as an alkaloid
Isopropyl alcohol	Simplest example of a secondary alcohol; dissolves a wide range of non-polar compounds
Lime	Used in flue gas desulphurization in power plants.
Limestone	Used in Flue Gas Desulphurization in power plants
Manganese dioxide	Used as a pigment and as a precursor to other manganese compounds; used as a reagent in organic synthesis for the oxidiation of allylic alcohols
Methyl tert-butyl ether	A gasoline additive; also used in organic chemistry as a relatively inexpensive solvent.
Millon's reagent	An analytical reagent used to detect the presence of soluble proteins
Nitric acid	Highly corrosive and toxic strong acid; used for the production of fertilizers, production of explosives, and as a component of aqua regia
Osmium tetroxide	In organic synthesis, is widely used to oxidise alkenes to the vicinal diols
Oxalyl chloride	Used in organic synthesis for the preparation of acid chlorides from the corresponding carboxylic acids
Palladium(II) acetate	A catalyst for many organic reactions by combining with many common classes of organic compounds to form reactive adducts.
Perchloric acid	A powerful oxidizing agent; readily forms explosive mixtures; mainly used in the production of rocket fuel
Phosphoric aicd	A mineral acid with many industrial uses; commonly used in the laboratory preparation of hydrogen halides
Phosphorus	One of the most important phosphorus chlorides; a

	chlorinating reagent.
Pentachloride	Also used as a dehydrating agent for oximes which turn them into nitriles.
Pposphorus trichloride	Most important of the three phosphorus chlorides; used to manufacture organophosphorus compounds; used to convert primary and secondary alcools into alkyl chlorides, or carboxylic acids into acyl chlorides.
Phosphoryl chloride	Used to make phosphate esters such as tricresyl phosphte.
Potassium dichromate	A common inorganic chemical reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications
Potassium hydroxide	A strong oxidizing agent; can be used to quantitatively determine the total oxidisalbe organic material in an aqueous sample. A reagent for the synthesis of organic compounds
Raney nickel	An alternative catalyst for the hydrogenation of vegetable oils; in organic synthesis, used for desulfurization
Silver oxide	Used to prepare other silver compounds; in organic Chemistry, used as a mild oxidizing agent.
Silver nitrate	Precursor to man othe silver compounds; commonly used in organic chemistry to abstract halides
Sodium amide	Used in the industrial production of indigo, hydrzine, and sodium cyanide; used for the drying of ammonia; used as a strong base in organic chemistry
Sodium azide	Gas-forming component in airbag systems; used in organic synthesis to introduce the azide functional group by displacement of halides
Sodium	A versatile reducing agent; converts ketones and

	aldehydes to alcohols
Sodium chlorite	In organic synthesis, used for the oxidation of aldehydes to caroxylic acids.
Sodium hydride	A strong base used in organic synthesis.
Sodium hydroxide	Strong base with man industrial uses; in the laboratory, used with acids to produce the corresponding salt, also used as an electrolyte
Sodium nitrite	Used to convert amines into diazo compounds
Sulfuric acid	Strong mineral acid; major industrial use it the production of phosphoric acid
Tert-Butyl hydroperoxide	Used in variety of oxidation processes, industrially, is used as a starer of radical polymerization
Tetrahydrofuran	One of the most polar ethers; a useful solvent; its main use is as a precursor to polymers
Tetramethylsilane	The simplest tetraorganosilane; a building block in organometallic chemistry
Thionyl chloride	An inorganic compound; used in chlorination reactions; converts carboxylic acids to acyl chlorides
Thiophenol	An organosulfur compound; the simplest aromatic thiol
Titanium tetrachloride	An intermediate in the production of tiatnium metal and titanium dioxide
Tollens' reagent	A chemical test most commonly used to determine whether a known carbonyl-containing compound is an aldehyde or a ketone
Triphenylphosphine	Used in the synthesis of organic and organometallic compounds.

2.6 LABORATORY SAFETY

General Safety Rules:

1. The safe way is the right way to do your job. Plan your work. Follow instructions. If you do not know how to do the experiment safely, ask your teaching assistant.
2. Be able to use all safety devices and protective equipment provided for your use and *know their location* (eyewash fountain, shower, fire blanket, fire extinguisher).
3. Safety goggles must be worn at all times.
4. *Do not* eat or drink in the laboratory (and do not store food in the refrigerators). Smoking in the laboratory is absolutely forbidden.
5. Horseplay in any form is dangerous and prohibited. Do not run in laboratory areas.
6. Report to your TA all unsafe conditions, unsafe acts, and "near misses" that might cause future accidents. Report any accident or fire, no matter how trivial, to the TA.

Hazardous Chemicals:

(a) Be especially mindful of fire hazards when you or your lab neighbors are working with flammable liquids.

(b) Hazardous Substances: Know common explosive, toxic, and carcinogen materials and use them only with adequate safeguards.

(c) Never leave a reaction or experiment running unattended, unless you have told your lab partners enough about it to deal with potential hazards while you are away.

(d) Keep hood and bench top areas clean and workable space maximized.

Disposal of solvents, chemicals and other materials:

Never pour solvents or reactive chemicals down a drain. Such careless handling of flammable or toxic liquids presents a serious hazard in the laboratory. Also, never keep an open beaker of such solvents outside a hood. Chlorinated solvents are poured into solvent waste containers kept inside the hoods. When in doubt about how to dispose of something, ask a TA. If drain disposal is necessary and acceptable, always flush the drain before, during, and afterwards with a lot of water, always using the drains in the hoods. All glass must be discarded in the specially designed containers. A dustpan and brush for broken glass can be checked out of Lab Supplies. Spilled mercury is a special safety hazard and should be reported to your TA for cleanup.

2.7 SUMMARY

This course introduces the introduction about lab techniques to students. The whole material contains the following information.

- Location of laboratory equipment in the laboratory.
- General Guideline of the laboratory.
- A detailed plan of the work that students will be doing.
- Laboratory apparatus and operation.
- Common Laboratory Apparatus used in the Experiments.
- Common Laboratory Reagents used in the Experiments.
- General safety rules.

2.8 TERMINAL QUESTIONS

1. Define various precautions of Chemistry lab.
2. What is the difference between burette & graduated pipette?
3. Name of all apparatuses used.

UNIT 3: CHEMICAL CONCENTRATION

CONTENTS

3.1 Introduction
3.2 Objectives
3.3 Normality
3.4 Molarity
3.4.1 Relationship between normailiy and molarity
3.5 Preparation of solution of defined normality / molarity of a given compound and from a given solution of different strength.
3.5.1 Preparation of solution of defined normality of a given compound
3.5.2 Preparation of solution of defined molarity of a given compound
3.6 Percent compostion
3.7 Part per million (ppm)
3.8 Part per billion (ppb)
3.9 Summery
3.10 Terminal Questions
3.11 References and further studies

3.1 INTRODUCTION

In chemistry, **concentration** refers to the amount of a substance in a defined space. Another definition is that concentration is the ratio of solute in a solution to either solvent or total solution. Concentration is usually expressed in terms of mass per unit volume. However, the solute concentration may also be expressed in moles or units of volume. Instead of volume, concentration may be per unit mass. The unit of concentration are g/cm^3, kg/l, M, m, N, kg/L etc. It may be expressed both qualitatively ('informally') and quantitatively ('numerically').

3.2 OBJECTIVES

Concentration is a very common concept used in chemistry and related fields. It is the measure of how much of a given substance there is mixed with another substance. This can apply to any sort of chemical mixture, but most frequently is used in relation to solutions,

where it refers to the amount of solute dissolved in a solvent. The main Objectives of this unit are to introduce, different concentrations like, Normality, Molarity, how to prepare the different strength of solution, percentage compostion, ppm, and ppb. At the end of this chapter, you will be able to understand, explain and calculate the various types of concentrations.

3.3 NORMALITY

Normality is used to measure the concentration of a solution. It is define as follows:The concentration of the given solution during the specific chemical process is determined by normality. In other words, "The number of gram equivalents of the solute dissolved per litre of a solution at a particular temperature is called normality of the solution.'' Normality of the solution is represented by N.It actually expresses the contraction of a solution in gram equivalents per liter (g eq.L^{-1}). Mathematically,

$$\text{Normality} = \frac{\text{Number of equivalents of solute}}{\text{Volume of solution in litre}}$$

$$= \frac{\text{Weight of solute(w)/equivalent weight of solute(E)}}{\text{Volume of solution in litre(V)}}$$

$$\text{Equivalent weight} = \frac{\text{Molecular weight}}{\text{n factor}}$$

$$N = \frac{w/E}{V/1000}$$

$$\text{or ,} \qquad w = \frac{ENV}{1000}$$

An Normal solution consists of one gram equivalent of a substance dissolved per liter of the solution. Some common terms used in reference are given in table 3.1.

Table 3.1: Commonly used Normality terms

Normality	Solution known as	Composition
N	Normal	1 g eq / litre
$\frac{N}{10}$	Decinormal	$\frac{1}{10}$ g eq / litre
$\frac{N}{100}$	Centinormal	$\frac{1}{100}$ g eq / litre
$\frac{N}{2}$	Seminormal	$\frac{1}{2}$ g eq / litre
2N	Binormal	2 g eq / litre

Normality of binary solution on mixing two solutions:

Normality of a solution is also a function of temperature and varies change in temperature.

When volume V_1 of a solution of normality N_1 is mixed with the volume V_2 of another solution of normality N_2 then the resulting solution is calculated by the given equation:

$$N_1 \times V_1 = N_2 \times V_2$$

Steps to Calculate Normality: The following steps are used in order to calculate normality:

i) Firstly to collect information on the equivalent weight of the reacting substance or Solute to used the molecular weight and valency.

ii) To determine the volume of the solution in liters.

iii) Finally, the formula is used to calculate normality.

Example:

1. Calculate the normality of 1liter HCl solution made by dissolving 36.5 gram of HCl.

Solution: Molecular Mass of HCl= 36.5

So equivalent Weight = Molecular mass / Valency(Acidity) = 36.5 / 1 =36.5

No. of Gram Equivalent of Solute = Mass of Solute / Equivalent Weight

= 36.5 /36.5 = 1

Volume here is given as 1 L

Normality will be calculated as: Normality = $\frac{\text{Number of equivalents of solute}}{\text{Volume of solution in litre}}$

$= \frac{1}{1} = 1N$

2. **When 19.0 ml of the citric acid solution is titrated with 30.09 mL of 0.1811 N KOH, what is the citric acid concentration?**

Solution:

According to the normality equation:

$$N_a \times V_a = N_b \times V_b$$

Therefore,

$$N_a \times 19.0 = 0.1811 \times 30.09$$

$$N_a = (0.1811 \times 30.09) / 19.0$$

$$= 5.4492 / 19.0$$

= 0.2868 N

3.4 MOLARITY

The most common way to express solution concentration is molarity (M), which is defined as "The number of moles of solute dissolved per liter of the solution at a particular temperature is called the molarity of the solution at that temperature".In other words The number of moles of a solute dissolved in 1L (1000 ml) of the solution is known as the molarity of the solution.Molarity of the solution is represented by M. Molarity of the solution refers to solution which contains one mole of a substance dissolved per liter of the solution. Mathematically ,

$$\text{Molarity} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in liter}}$$

$$= \frac{\text{Weight of solute(w)} / \text{ Molar mass of solute}(M')}{\text{Volume of solution in litre(V)}}$$

$$= \frac{w}{M' \times V}$$

Where, M' = Molar mass of solute

Molarity represented the concentration of a solution in mol L^{-1} .

If we have percentage by mass and specific gravity or density , the molarity is calculated by the experession,

$$\text{Molarity} = \frac{\%\ \text{by weight x specific gravity x 10}}{\text{Molar mass(Solute)}}$$

Molarity of binary solution on mixing two solutions:

In case of dilution , the equation given below is used to determine the volume of an unknown solution from a known molarity solution:

$$\mathbf{M_1 \times V_1 = M_2 \times V_2}$$

where,

$\mathbf{M_1}$ is the initial molarity of the given solution

$\mathbf{V_1}$ is the initial volume of the given solution

$\mathbf{M_2}$ is the molarity of the new solution

$\mathbf{V_2}$ is the volume of the new solution

In Molarity involves volume which is dependent on temperature, the molarity of a solution changes with temperature.

Commonly used molarity terms are given in **table 3.2:**

Table 3.2: Commonly used Molarity terms

Molarity	Solution known as	Composition
M	Molar	1 mole / liter
$\frac{M}{10}$	Decimolar	$\frac{\mathbf{1}}{\mathbf{10}}$ mole / liter
$\frac{M}{100}$	Centimolar	$\frac{\mathbf{1}}{\mathbf{100}}$ mole / liter
$\frac{M}{2}$	Semimolar	$\frac{\mathbf{1}}{\mathbf{2}}$ mole / liter
2M	Bimolar	2 mole / liter

In Molarity involves volume which is dependent on temperature, the molarity of a solution changes with temperature.

Steps to Calculate Molarity:

Step 1: Calculate the moles of the solute present in the solution.

Step 2: Mark the volume of solution in liters.

Step 3: Use the formula for finding molarity of the solution'

Molarity = Number of Moles of Solute / Volume of Solution in liters

Step 4: Substitute all the values in the above formula to get the Molarity of the solution.

Example:

1. Calculate molarity of 5.3 g anhydrous sodium carbonate dissolved in 100 mL of solution.

Solution:

Molar mass of (Na_2CO_3) = 23 g x 2 + 12 g x 1 + 16 g x 3 = (46 + 12 + 48) g = 106 g

Number of moles of (Na_2CO_3) = given mass / molecular mass = 5.3 g/ 106 g = 0.05

$$\text{Molarity of solution} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in liter}}$$

= 0.05 / 0.1 = 0.5 M

2. Calculate molarity of pure water if its density is 1 g/mL.

Solution: Let us consider 1000 mL of water

Mass of water = volume x density = 1000 mL x 1 g/mL = 1000 g

Molar mass of water = 1 g x 2 + 16 g x 1 = (2 + 16) g = 18 g

$$\text{Molarity of water} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution in liter}}$$

= 1000 / 18 g = 55.5M

3.4.1 Relationship between Normailiy and molarity:

The Normality and molarity of a solution are related as :

Molarity x Molecular mass of solute = Normality x Equivalent mass of solute

$$\text{Molarity} = \text{Normality} \times \frac{Equivalent\ mass\ of\ solute}{Molecular\ mass\ of\ solute}$$

$$\text{Normality} = \text{Molarity} \times \frac{Molecular\ mass\ of\ solute}{Equivalent\ mass\ of\ solute}$$

For acids the normality can be calculated with the following formula:

Normality = Molarity x Basicity

To know the value for basicity, count the number of H^+ ions an acid molecule can give.

For bases the normality can be calculated with the following formula:

Normality = Molarity x Acidity

To know the value for acidity, count the number of OH^- ions a base molecule can give.

3.5 PREPARATION OF SOLUTION OF DEFINEDNORMALITY/ MOLARITY OF A GIVEN COMPOUND AND FROM A GIVEN SOLUTION OF DIFFERENT STRENGTH.

3.5.1 . Preparation of solution of defined Normality of a given compound

Normality (N) expressing the concentration of solute in the solution.In Normal solution consists of " gram equivalent weight (Eq.Wt)" (formula weight) of a solute or substance in per liter. it is defined as "number of gram equivalents of solute per litre of the solution". To obtain gram equivalent weight one should know the no of hydrogen atoms that can be added or removed from the given substance. When you divide the GMW of the substance with no of replaceable hydrogens we get EW:

$$\frac{GMW}{Number\ of\ replaceble\ hydrogen\ atoms} = \text{Eq. Wt (EW)}$$

For example: Molecular weight of NaOH is Na = 23, O= 16 ,H= 1,

$$=23 +16+1 =40u$$

NaOH possess 1 hydrogen atom that can be replaced, hence Eq Wt of NaOH is :

$$\frac{40}{1} = 40$$

For example: How to prepare 500 mL of 0.5N solution of NaOH.

$$\text{Weight in grams} = \frac{desired\ normality\ x\ volume\ required\ in\ liters\ x\ GMW}{Valence}$$

$$\text{Weight in grams} = \frac{0.5\ x\ 500ml\ x\ 40\ GMV}{1EW} = 10\text{g of NaOH}$$

10 grams of NaOH is needed to prepare 500 ml of 0.5N solution of NaOH

3.5.2 . Preparation of solution of defined Molarity of a given compound: A molar solution consists of "gram molecular weight" (formula weight) of a solute or substance in grams. Gram Molecular weight (GMW) is obtained by combining the atomic weights of all atoms present in that particular solute molecule. Molarity is defined as "the number of moles of solute per litre (L) of solution"

$$\text{The mole is expressed as moles} = \frac{Weight\ of\ solute\ in\ grams}{Gram\ molecular\ weigh}$$

Like ,Number of moles of NaOH present in 40 gm is = $\frac{40}{40}$ = 1

Molecular weight of NaOH = 23 + 16+1 = 40

For example: How to prepare 1 L of 1M solution of NaOH .

Since molecular weight of NaOH is 40, dissolve 40 grams of NaOH in 1 liter of water to make 1 M NaOH solution per 1 L.

3.6 PERCENT COMPOSTION

The percentage composition of a given compound is defined as the ratio of the amount of each element to the total amount of individual elements present in the compound multiplied by 100.

Mass percent: Mass percent of a solution may be define as:

"The number of parts by mass of one component (solute or solvent) per 100 parts by mass of the solution.

$$\text{Mass percent} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \text{ x } 100$$

Like 10% (w/ W) solution of NaCl means that 10g of NaCl is present in 90g of water so that the total mass of the solution is 100g.

Volume percent: Volume percent of a solution define as the volume of the component per 100 parts by volume of the solution. Like if V_A and V_B are the volumes of two components A and B respectively in a solution, then,

$$\text{Volume percent of A} = \frac{\text{Volume of A}}{\text{Volume of A} + \text{Volume of B}} \text{ x } 100$$

$$\text{Volume percent of B} = \frac{\text{Volume of B}}{\text{Volume of A} + \text{Volume of B}} \text{ x } 100$$

This may be expressed as *v* / V

Mass / Volume percent: It may be define as , the number of parts by mass of one component to the total volume of the solution.

Mathematically, Mass / Volume percent of A = $\frac{WA}{VA+VB}$ x 100

$$\text{Mass / Volume percent of B} = \frac{WB}{VA+VB} \times 100$$

Note: Both mass percent and volume percent are simply ratios and have no units.

Example:

1. **A solution is prepared by dissolving 15 g of cane sugar in 60 g of water. Calculate the mass percent of each component of the solution.**

Solution: $$\text{Mass percent(\%)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

Mass of solution = mass of solute + mass of solvent = 15 g + 60 g = 75 g

Mass percent of solute (cane sugar) = $\frac{15}{75}$ x100 =20%

Mass percent of solvent (water) = 100 – 20 = 80%

2. **12.8 cm^3 of benzene is dissolved in 16.8 cm^3 of xylene. Calculate percentage by volume of benzene.**

   Solution: Volume of solution = Volume of solute + Volume of solvent

   Volume of solution = 12.8 cm^3+ 16.8 cm^3 = 29.6 cm^3

   $$\text{Percentage by volume} = \frac{\text{Volume of solute}}{\text{Volume of solution}} \times 100$$

   $$\text{Percentage of benzene by volume} = \frac{12.8\ cm3}{29.6\ cm3} \times 100 = 43.24\ \%$$

3.7 PARTS PER MILLION (ppm):

For a dilute solution in which a very small amount of the solute is dissolved in large excess of the solvent, the values of the mass percent and volume percent will be very small. In order to magnify the same, the concentrations are expressed as parts per million or ppm . It may be define as : the number of parts by mass (or by volume) of one component per million parts by mass (or by volume) of the solution. ppm can b expressed according to the type of solutions as follows:

a) Solid solid solution : Such as an element in a alloy ,

Mathematically, Concentration in ppm = $\frac{\text{Mass of component(g,mg.....)}}{\text{Total mass of solution(g,mg....)}} \times 10^6$

b) Liquid – liquid solution : Such as solute and solvent in liquid phase (like alcohol in water).

Mathematically, Concentration in ppm = $\frac{\text{Volume of solute(mg,µg...)}}{\text{Volume of solution(kg,g...)}} \times 10^6$

c) Solid – liquid solution: Such as solute is solid and solvent in liquid phase.

Mathematically, Concentration in ppm = $\frac{\text{Weight of solute(mg,µg...)}}{\text{Volume of solution(L,ml...)}} \times 10^6$

- Atmospheric pollution in cities due to harmful gases is generally expressed in ppm through in this case the values refer to volumes rather than masses .Like the concentration of SO_2 in Delhi has been found to be as high as 10 ppm . This means that 10 cm^3 of SO_2 are present in 10^6 cm^3 (10^3) of air.

Example:

1.Air contains about 0.03% of carbon dioxide. Calculate its concentration in parts per million units.

Solutions: Number of parts of CO_2 in 100 parts of air = 0.03

$$\text{Concentration in ppm} = \frac{\text{Mass of component}}{\text{Total mass of solution}} \times 10^6$$

$$= \frac{0.03}{100} \times 10^6$$

$$= 300 \text{ ppm}$$

2.If 0.025 gram of $Pb(NO3)_2$ is dissolved in 100. grams of H_2O, what is the concentration of the resulting solution, in parts per million?

Solutions: Concentration in ppm = $\frac{\text{Mass of component}}{\text{Total mass of solution}} \times 10^6$

$$= \frac{0.025}{100+.025} \times 10^6$$

$$= 250 \text{ ppm}$$

3.8 PART PER BILLION (ppb)

Parts per billion (ppb) is a term that expresses the number of units (parts) of a given substance that exist as a portion of a greater substance comprised of one billion parts. "Parts-per" notations such as ppb are referred to as "volume in volume" measurements.

PPB stands for parts per billion. "One part per billion is one part of solute per one billion parts solvent". PPB is a commonly used unit of concentration for very small values. The "parts per" notation is not part of the SI system of units. The notation describes dimensionless quantities.

The same as mentioned in the above ppm term, but instead of using 10^6 we use 10^9 or we use a unit for the solution is equal to one billion unit used for the solute as can be seen in the following formulas:

a) Solid-solid solution:

$$\text{Concentration in ppb} = \frac{\text{Weight of solute(g,mg,µg,ng....)}}{\text{Weight of solution(g,mg,kg...)}} \times 10^9$$

b)Liquid-liquid solution:

$$\text{Concentration in ppb} = \frac{\text{Volume of solute(L,ml....)}}{\text{Volume of solution(L,ml...)}} \times 10^9$$

c) Solid-liquid solution:

$$\text{Concentration in ppb} = \frac{\text{Weight of solute(g,kg,µg....)}}{\text{Volume of solution(L,ml...)}} \times 10^9$$

Example:

1.A sea water sample contains $8\times10-3$ g of dissolved oxygen per kilogram. What is the concentration of oxygen in parts per billion?

Solutions: 1000 g of sea water contains $8\times10-3$ g of oxygen

$$\text{Concentration in ppb} = \frac{\text{Weight of solute(g,mg,µg,ng....)}}{\text{Weight of solution(g,mg,kg...)}} \times 10^9$$

$$= \frac{8\times10-3\ \text{g}}{1000\text{g}} \times 10^9$$

$$= 8000$$

2.How many milligrams are required to prepare 500ml solution of substance B of each of the following concentration units? a) 2000 ppb b) 5g /L

Solutions: a) Concentration in ppb = $\frac{\text{Weight of solute(g,mg,µg,ng....)}}{\text{Weight of solution(g,mg,kg...)}} \times 10^9$

$$2000 \text{ ppb} = \frac{\text{Weight of solute(µg)}}{500(\text{ml})\text{x}10-3(\text{L})}$$

Weight of solute (µg) = $2000 \times 500 \times 10^{-3}$

= 1000 µg = 1mg

b) Concentration in ppb = $\frac{\text{Weight of solute(g,mg,µg,ng....)}}{\text{Weight of solution(g,mg,kg...)}} \times 10^9$

$$5(\text{g/ l}) = \frac{\text{Weight of solute(g)}}{500(\text{ml})\text{x}10-3(\text{L})}$$

Weight of solution (g) = $5\text{x } 500 \text{ x } 10^{-3}$

= 2.5 g = 2500 mg

3.9 SUMMERY

This chapter provides with the concise description of various types of concentration in chemistry.The description on topices such as normality molarity, how to prepare normal and molar solution, percentage composition, ppm, ppb and calculation based on these topices.These topic are significantly very important to find out out concentration of components individually.

We also understand how molarity and normality are related to each other and how molarity and normality of binary mixture become calculated.

3.10 TERMINAL QUESTIONS

A.Multiple choice questions:

1.The equivalent weight of H_2SO_4 is:

a) 98 b) 49 c) 32 d)90

2. Unit of molarity is:

a) kg / L b)g/ L c)mole/ L d) Mole x L

3.The number of gram equivalent weight of solute dissolved in per liter of solution known as:

a)Normality b)Molarity c)ppm d) Mass percent

4) What does ppm stand for?

a)Parts per million b)Percentage per million

c)Parts per metric d)Parts percentage of metric

5) " M'' shown by the:

a)Molarity b) Molality c) mass d)Mass percentage

6) Unit of mass percent is:

a) Percent b) gm/L c) mole/ L d) Unitless

7)Concentration 1ppm = ____ ppb

a)10^{-6} b) 10^{3} c) 10^{-3} d) 10^{-2}

8) How many ml of water are needed to dilute 65ml, 7M ,KCl to 2M?

a) 18.75 ml b)227.5L c) 227.5ml d)0.0044ml

9) The unit of normality is :

a) gram/liter b) mole c) Mole x L d) per L

10) The Molecular weight of $CuSO_4$ is :

a) 160 b) 180 c) 162 d) 278

B. Long Question:

Q.1. Write a short notes on: a) Normality b) ppm c) ppb

Q.2. What is the molarity of 20% H_2SO_4 solution?

Q.3.A solution is prepared by dissolving 0.63 g of oxalic acid in 100 cm^3 of water. Find the normality of the solution.

Q.4.Out of 1 M H_2SO_4 and 1N H_2SO_4 , Which is more concentrated and why?

Q.5.Calculate the molarity of each of the following solutions:

a)30g of $Co(NO_3)_2$ 6H2O in4.3 of solution

b) 30ML OF 0.5 M H_2SO_4 diluted to 500Ml

Q.6. Calculate the mass percentage of benzene and carbon tetrachloride if 22 g of benzene is

dissolved in 122 g of carbon tetrachloride.

Q.7 If 40g of hydrochloric acid (HCl) is present in 100mL of solution. Calculate the mass by volume percentage of (HCl) in solution.

Q.8. What are the steps for finding the mass percentage?

Q.9. How many grams of hydrogen chloride (HCl) are required to prepare 4 Litre of 5M HCl in water?

Q.10. What are the steps for finding the Normality of the solution?

ANSWERS:

1) b 2) c 3) a 4) b 5) a 6) d 7) b 8)c 9) a 10)a

3.11REFERENCES AND FURTHER STUDIES

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UNIT 4: TITRATION

CONTENTS:

4.1 Introduction
4.2 Objectives
4.3 Types of Titration
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4.5 Methods to determine the equivalence point
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4.1 INTRODUCTION

Titration is a process of mixing of two solutions in order to react in a conical flask. One solution is with known strength or standard while the other solution is unknown solution or solution whose strength is not known. The solution which is to be titrated is taken in a conical flask with the help of a pipette and other solution is taken in a burette. Indicator is added to the conical flask in order to detect the end point or equivalence point. Two solutions are mixed dropwise by opening the tap of the burette. A sharp change in color indicates the end point. At this point, the reaction between two solutions is just completed.

4.2 OBJECTIVES

In this chapter you will learn about general introduction of titration, types of titration, general idea about indicators, titrimetric experiments, Equivalence point, titration between strong acid with strong base and weak acid strong base.

4.3 TYPES OF TITRATION

There are generally four types of titration depending on the reaction taking place between the two solutions. These are as follows:

1. Neutralization titration:

These titrations are also known as acid- base titration as it involves two solution, one is of acid while the other is of base. For example, mixing of sodium hydroxide (base) with oxalic acid. This titration is further classified into acidimetry and alkalimetry. In acidimetry, the strength of an acid is determined by titrating it with standard alkali solution. In alkalimetry, the strength of an alkali is determined by titrating it against standard solution of an acid.

2. Redox titration:

As the name indicates, redox titration are those titration in which on mixing two solutions, one solution undergoes oxidation while the other solution undergoes reduction or in simple words we can say that redox reaction occurs on mixing. These are also known as reducation-oxidation titration. The substance which undergoes oxidation is known as reducing agent while the substance that undergoes reduction is known as oxidizing agent. In redox reaction, both oxidation and reduction takes place simultaneously. For example, mixing of ferrous ammonium sulphate (FAS) and acidified KMnO4, in which FAS undergoes oxidation and and KMnO4undergoes reduction. Redox titration includes iodine titration where iodine is used as an oxidizing agent. There are two types of iodine titration, one is iodimetric and another is iodometric titration. In iodimetric titration, standard iodine solution is directly titrated against some reducing agent. The reducing agent used is generally hypo solution, Na2S2O3. In iodometric titration, iodine is liberated from iodine solution by using some oxidizing agent and then the liberated iodine is titrated with a standard solution of a reducing agent.

3. Precipitation titration:

As the name indicates, on mixing two solutions there is a formation of precipitate. Precipitate is a solid mass which get accumulate at the bottom of the solution. For example, on mixing of sodium chloride (NaCl) with silver nitrate solution (AgNO3), there is a formation of precipitate of silver chloride (AgCl). Precipitation titration is also known as Argentometric titration viz; AgNO3 is used as one of the solution during titration for the estimation of chloride content in water using K2CrO4

4. Complexometric titration:

As the name indicates, on mixing two solutions there is a formation of a complex. Complexes are formed by metals and ligands; in which ligand donate lone pair of electrons to metal mainly transition elements. For example, in the determination of hardness present in given water sample, there is a formation of a complex between Ca2+/ Mg2+ with EDTA. EDTA is a hexadentate ligand. One of the solution is of ligand and the other is of a metal containing compound.

4.4 EQUIVALENCE POINT

The **equivalence point**, or **stoichiometric point**, of a chemical reaction is the point at which chemically equivalent quantities of reactants have been mixed. For an acid-base reaction the equivalence point is where the moles of acid and the moles of base would neutralize each other according to the chemical reaction. This does not necessarily imply a 1:1 molar ratio of acid:base, merely that the ratio is the same as in the chemical reaction. It can be found by means of an indicator, for example phenolphthalein or methyl orange.

4.5 METHODS TO DETERMINE THE EQUIVALENCE POINT

Different methods to determine the equivalence point include:

1. pH indicator:

A pH indicator is a substance that changes color in response to a chemical change. An acid-base indicator (e.g., phenolphthalein) changes color depending on the pH. Redox indicators are also frequently used. A drop of indicator solution is added to the titration at the start; when the color changes the endpoint has been reached, this is an approximation of the equivalence point.

2. Conductance:

The conductivity of a solution depends on the ions that are present in it. During many titrations, the conductivity changes significantly. (For instance, during an acid-base titration, the H_3O^+ and OH^- ions react to form neutral H_2O. This changes the conductivity of the solution.) The total conductance of the solution depends also on the other ions present in the solution (such as counter ions). Not all ions contribute equally to the conductivity; this also depends on the mobility of each ion and on the total concentration of ions (ionic strength). Thus, predicting the change in conductivity is harder than measuring it.

3. Color change

In some reactions, the solution changes color without any added indicator. This is often seen in redox titrations, for instance, when the different oxidation states of the product and reactant produce different colors.

4. Precipitation

If the reaction forms a solid, then a precipitate will form during the titration. A classic example is the reaction between Ag^+ and Cl^- to form the very insoluble salt AgCl. Surprisingly, this usually makes it difficult to determine the endpoint precisely. As a result, precipitation titrations often have to be done as back titrations.

Isothermal titration calorimeter

5. Spectroscopy

Spectroscopy can be used to measure the absorption of light by the solution during the titration, if the spectrum of the reactant, titrant or product is known. The relative amounts of the product and reactant can be used to determine the equivalence point. Alternatively, the presence of free titrant (indicating that the reaction is complete) can be detected at very low levels. An example of robust endpoint detectors for etching of semiconductors is EPD-6, a system probing reactions at up to six different wavelengths.[1]

6. Amperometry

Amperometry can be used as a detection technique (amperometric titration). The current due to the oxidation or reduction of either the reactants or products at a working electrode will depend on the concentration of that species in solution. The equivalence point can then be detected as a change in the current. This method is most useful when the excess titrant can be reduced, as in the titration of halides with Ag^+.

4.6 INDICATORS

Indicators are those chemical substances that indicate the end point during titration by color change. There are three types of indicators:

1. **Internal indicators**:

Indicators which are added in the conical flask containing on of the solutions are known as internal indicators. For example, phenolphthalein, methyl orange etc.

2. External indicators:

Indicators which are used outside the conical flask (in a white tile) are known as external indicators. For example, potassium ferricyanide, K3[Fe(CN)6].

3. Self-indicators:

In titration, two solutions are used. When one of the solutions itself acts as an indicator, it is known as self-indicator viz;, potassium permanganate (KMnO4).

4.7 SAMPLE TITRIMETRIC EXPERIMENTS

There are several experiments based on the type of titrations i.e. acid- base titration, redox titration, precipitation titration and complexometric titration. Let us discuss the determination of strength of given sodium hydroxide solution.

4.7.1 Determination of strength of given sodium hydroxide solution:

As we know that NaOH is a secondary standard chemical. Exact weighing of NaOH is not done as it is hygroscopic in nature (it can absorb moisture from the atmosphere). Hence an approximate weight of NaOH is taken in 500 mL volumetric flask. Distilled water is added in a flask. First 50 mL and then allow NaOH to dissolve. After complete dissolution of NaOH, additional distilled water is added up to the mark, thereby making the solution 500 ml. We have simply dissolve NaOH without weighing. Now in order to determine its exact strength, we mix two solutions, one of the solutions is NaOH solution and the other solution is standard solution generally the primary standard solution. NaOH solution is taken in a burette and standard solution of known volume say 10 ml solution of N/10 oxalic acid is taken in a conical flask. Two or three drops of indicator (phenolphthalein) are added into the conical flask. Now by opening the tap of the burette, both solution one in the burette and another in the conical flask containing the indicator are mixed drop wise in order to react until light pink color appears at the end point indicating completin of reaction. When there is change in color, close the tap of the burette and record the volume of the burette. Repeat the titration for two concordant readings and the repeating volume be V2 mL. Using law of equivalence (N1V1 = N2V2), the exact normality of NaOH is calculated.

(Oxalic acid) N1V1 = N2V2 (NaOH)

Where N1 is normality of oxalic acid that is 1/10, V1 is volume of oxalic acid that is 10 ml and N2 is normality of NaOH which is to be calculated. The N2 is the exact normality of

NaOH. In this way, the normality of NaOH is determined and is now become standard. The strength of NaOH is calculated by multiplying N2 with the equivalent weight. For NaOH, equivalent weight is 40.

Strength(S) = Normality × equivalent weight

4.7.2 Instrumental determination of an equivalence point:

There are different instruments used for determining the end point or equivalence point like pH meter, conductivity meter. Using pH meter, we can determine the end point by measuring the pH of the solution while in conductivity meter, we can measure conductance of the solution. Let us discuss the method of determining equivalence point using conductivity meter. It is provided with a conductivity cell which is dipped in a solution for measuring the conductance. There is a display which shows conductance in Siemens or ohm–1. A fixed volume of standard solution is taken in a beaker and its conductance is measured by dipping the conductivity cell. Burette is filled with the solution whose strength is to be determined. The solution is titrated and after every 2 ml addition from the burette, the conductance of the solution is recorded. In this way, we obtain a series of conductance value with similar trend in first half and with different trend in second half. Then these conductance values are plotted against the volume of solution added from the burette. The graph will show two straight lines and their point of intersection represents the equivalence point.

4.7.3 Acid base titrations:

Acid base titrations are basically neutralization titrations. Acids and bases ionize in water.

$$HA \longrightarrow H^+ + A^-$$

$$ABOH \longrightarrow B^+ + OH^-$$

$$H^+ + A^- + OH^- + B^+ \longrightarrow B^+ + A^- + H_2O$$

The extent of hydrolysis of the salt BA formed from neutralization between the acid and base decides the pH of the solution at equivalence point. The pH of a solution is given as

pH = - log [H+]

pH titration is the process of adding either base from the burette to a known volume of acid (alkalimetry) in a beaker and measuring the pH of the solution at each addition or vice versa (acidimetry). In a titration of an acid with a base, the pH of the solution before titration is low. On addition of aliquots of base to the acid, the pH starts increasing. Near the end point a sharp increase in pH occurs. When a plot of pH versus volume of base is constructed you

obtain a pH curve. After the end point, addition of the base does not change pH and results in a plateau in the curve. The pH curves for strong acid-strong base, strong acid-weak base, weak acid-strong base and weak acid-weak base are depicted in Fig 1. However, it is difficult to locate the end point in weak acid-weak base titrations by potentiometric method.

4.8 TITRATION OF STRONG ACID (HCL) WITH STRONG BASE (NAOH)

In titration of a strong acid (HCl) with a strong base (NaOH) the salt formed by neutralization reaction does not hydrolyse in water. Hence the solution at the equivalent point is neutral. Initially the pH keeps increasing slowly as the base is added. After the end point the concentration of the base (NaOH) is in excess and a sharp increase in pH is noted.

[H+] = [HCl]

The pH is given by

pH = 14 – pOH

In the case of a strong acid versus strong base, at equivalence point [H+] = [OH-]

The ionic product of water = Kw = [H+] [OH-] =10^{-14}

Kw = $[H+]^2$

$(Kw)^{1/2}$ = [H+]

[H+] = [HCl]

pH = -log $[H^+]$ = -log $(Kw)^{1/2}$ = - ½ log K_w = -1/2 log 10^{-14} = ½ x 14 x log 10 = 7

(log 10 = 1)

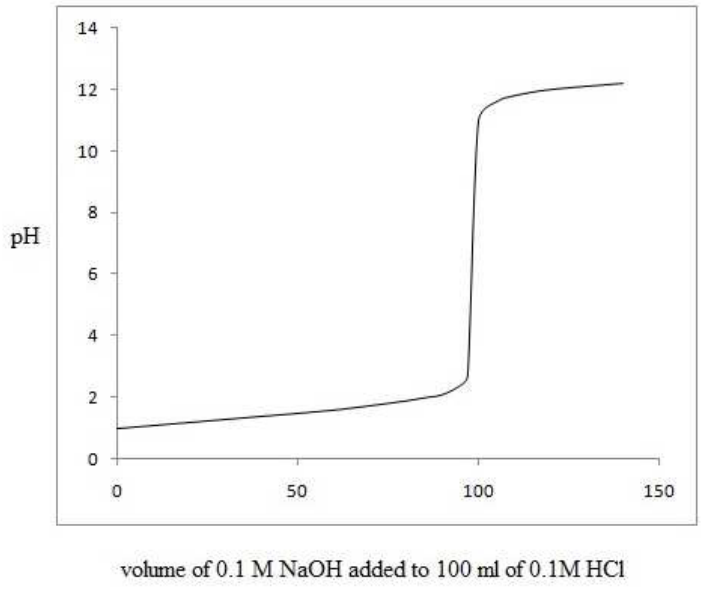

Figure 4.1. pH titration curve of strong acid (HCl) vs strong base (NaOH)

4.9 TITRATION OF WEAK ACID (CH_3COOH) VS STRONG BASE (NAOH)

In case of weak acid

$[H^+] = \{K_a [\text{acetic acid}]\}^{1/2}$

$CH_3COOH + OH^- \rightleftharpoons H_2O + CH_3COO$

Addition of NaOH converts a portion of acetic acid to its conjugate base. This solution of a weak acid and its conjugate base forms a buffer for which the pH of the solution is calculated by Hendersen equation. At equivalence pH is more than 7

pH = pKa + log [Conjugate base] / [Weak acid]

After the equivalence point, NaOH is present in excess and pH rises to about 12..

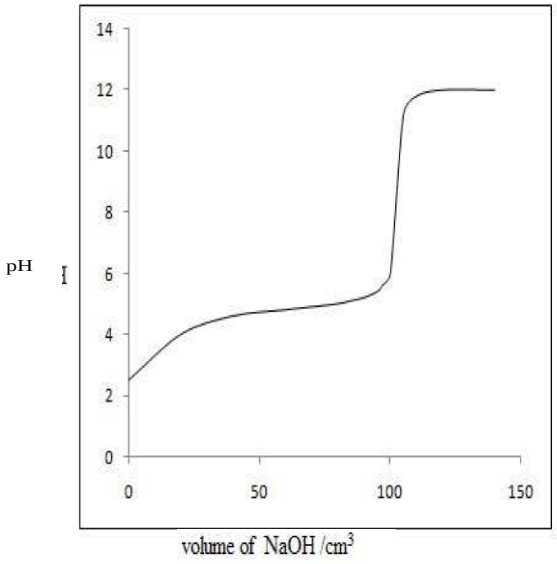

Figure.4. 2 pH titration curve of weak acid (CH3COOH) vs strong base (NaOH)

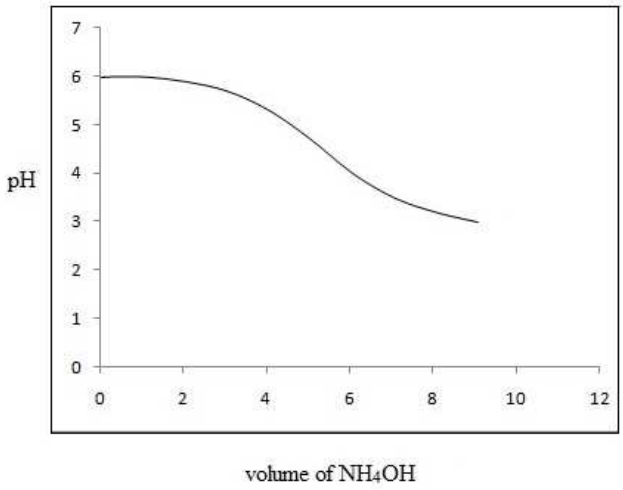

Figure 4.3. pH titration curve of weak acid (CH3COOH) vs weak base (NH4OH)

4.10 SUMMARY

Quantitative analysis by potentiometric titration method for an acid base neutralization reaction involves recording the pH after each addition of a standard solution of a base to a known volume of an acid of unknown strength. The pH of the solution depends on the ionisability of the acid and base in water and the extent of hydrolysis of the salt formed from the neutralization of the acid by the base. A graph of pH versus volume of base added to the acid is constructed. The end point is located from the point of inflexion which is a point where the pH of the solution changes rapidly. A perpendicular drawn from point of inflexion to X axis gives the volume of base required to neutralize the volume of acid taken in the beaker. This value is incorporated in the equation $V_1N_1=V_2N_2$ to determine the normality of the acid. The strength of the acid is calculated by the formula, Strength of acid =Normality of Acid x Equivalent weight of acid.

4.11 TERMINAL QUESTIONS

1. Define acidimetry and alkalimetry.
2. What is a standard solution?
3. Give two examples of a primary standard.
4. What is equivalence point in an acid base titration?
5. How do you express acidity of a base and basicity of an acid?
6. What factors affect the form of a pH curve?
7. When will be the pH =0, < 7 and > 7 at equivalent point in an acid base reaction?
8. How do you express the pH of acetic acid?
9. Calculate the weight of NaOH required neutralizing 25 cm^3 of 1N HCl.
10. In an experiment 50 cm^3 of 0.1N HCl is titrated against 0.1N NaOH. Calculate the pH of the solution after addition of 40 cm^3 of NaOH.

UNIT 5: SOLUBILITY AND EXTRACTION

CONTENTS:

5.1 Introduction
5.2 Objectives
5.3 Solubility product
5.4 Types of solubility
    5.4.1 Solubility of liquids in liquids
    5.4.2 Solubility of Solids in Liquids
    5.4.3 Solubility of Gases in Liquids
5.5 Solubility of organic compounds
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    5.6.1 Liquid Liquid Extraction
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    5.6.3 Solid-phase extraction
5.7 distribution coefficient
5.8 Separation and Drying agents
5.9 Summary
5.10 Terminal Questions
5.11 References

5.1 INTRODUCTION

The maximum amount of solute that can dissolve in a known quantity of solvent at a certain temperature is its solubility. A solution is a homogeneous mixture of one or more solutes in a solvent. Sugar cubes added to a cup of tea or coffees are a common example of a solution. The property which helps sugar molecules to dissolve is known as ***solubility***. Hence, the term solubility can be defined as a property of a substance (solute) to dissolve in a given ***solvent***. A ***solute*** is any substance which can be either solid or liquid or gas dissolved in a solvent.

5.2 OBJECTIVES

In this chapter you will learn about definition of solubility, behavior of solubility, water as a solvent nature of organic solvent, and also about the extraction, theory of extraction, distribution

coefficient, separation and drying agents. Apart from this in this chapter we will understand about extraction, theory of extraction, distribution coefficient, separation and drying agents**.**

5.3 SOLUBILITY PRODUCT

The term solubility product is generally applicable for sparingly soluble salts. ***It is the maximum product of the molar concentration of the ions (raised to their appropriate powers) which are produced due to dissociation of the compound.*** At a given temperature the solubility product is constant. Lesser the value of solubility product indicates lower solubility and higher value of solubility product indicates greater solubility.

5.4 TYPES OF SOLUBILITY

On the basis of solubility, the factors affecting solubility vary on the state of the solute:

1. *Liquids in Liquids*
2. *Solids in Liquids*
3. *Gases in Liquids*

5.4.1 Solubility of Liquids in Liquids:

Water is known as a universal solvent as it dissolves almost every solute except for a few. Certain factors can influence the solubility of a substance. Solubility is the new bond formation between the solute molecules and solvent molecules. In terms of quantity, solubility is the maximum concentration of solute that dissolves in a known concentration of solvent at a given temperature. Based on the concentration of solute dissolves in a solvent, solutes are categorized into highly soluble, sparingly soluble or insoluble. If a concentration of 0.1 g or more of a solute can be dissolved in a 100ml solvent, it is said to be soluble. While a concentration below 0.1 g is dissolved in the solvent it is said to be sparingly soluble. Thus, it is said that solubility is a quantitative expression and expressed by the unit gram/litre (g/L).

Based on solubility, different types of solution can be obtained. A saturated solution is a solution where a given amount of solute is completely soluble in a solvent at a given temperature. On the other hand, a supersaturated solution is those where solute starts salting out or precipitate after a particular concentration is dissolved at the same temperature.

Factors Affecting Solubility:

The solubility of a substance depends on the physical and chemical properties of that substance. In addition to this, there are a few conditions which can manipulate it.

Temperature, pressure and the type of bond and forces between the particles are few among them.

1. Temperature:

By changing the temperature we can increase the soluble property of a solute. Generally, water dissolves solutes at 20° C or 100° C. Sparingly soluble solid or liquid substances can be dissolved completely by increasing the temperature. But in the case of gaseous substance, temperature inversely influences solubility i.e. as the temperature increases gases expand and escapes from their solvent.

2. Forces and Bonds:

Like dissolves in like, the type of intermolecular forces and bonds vary among each molecule. The chances of solubility between two unlike substances are more challengeable than the like substances. For example, water is a polar solvent where a polar solute like ethanol is easily soluble.

3. Pressure:

Gaseous substances are much influenced than solids and liquids by pressure. When the partial pressure of gas increases, the chance of its solubility is also increased. A soda bottle is an example of where CO_2 is bottled under high pressure.

5.4.2 Solubility of Solids in Liquids:

It has been observed that solid solubility depends on the nature of the solute as well as the solvent. We often see that substances like sugar, common salt (NaCl), etc readily dissolve in water while substances like naphthalene do not dissolve in water. From the various observations and experimental results, it has been seen that only polar solutes tend to dissolve in the polar solvent and non-polar solvents dissolve only non-polar solutes. Hence, the nature of the solvent can be seen as one of the prominent factors affecting solubility. The above observation led to the statement that like dissolves like, that is polar solvents will dissolve polar solutes and non-polar solvents dissolve non-polar solutes.

Now let us understand the process by which a solid dissolves in a solvent. Once a solid solute is added to a solvent, the solute particles dissolve in the solvent and this process is known as dissolution. Solute particles in the solution collide with each other and some of these particles get separated out of the solution, this process is called crystallization. A state of dynamic

equilibrium is established between these two processes and at this point, the number of solute molecules entering the solution becomes equal to the number of particles leaving the solution. As a result, the concentration of the solute in the solution will remain constant at a given temperature and pressure.

A solution in which no more solute can dissolve in the solvent at a given temperature and pressure is said to be a saturated solution as the solution contains the maximum amount of solute. The concentration of solute in such a solution is called its solubility at that temperature and pressure. If more solute can be added to a solution then it is called an unsaturated solution.

Factors Affecting Solubility

1. Effect of Temperature:

Apart from the nature of solute and solvent, temperature also affects solid solubility considerably. If the dissolution process is endothermic then the solubility should increase with an increase in temperature in accordance with Le Chateliers Principle. If the dissolution process is exothermic the solid solubility should decrease.

2. Effect of Pressure:

Solid solubility hardly gets affected by changes in pressure. This is due to the fact that solids and liquids are highly incompressible and practically do not get affected by changes in pressure.

5.4.3 Solubility of Gases in Liquids:

Gas solubility in liquids deals with the concept of gas dissolving in a solvent. Let us first define solubility. For any substance, solubility is the maximum amount of solute that can be dissolved in a given solvent at a particular temperature. Now our concern is gas solubility in liquids. The gas solubility in liquids is greatly affected by temperature and pressure as well as the nature of the solute and the solvent.

Factors Affecting Solubility

1. Effect of Pressure:

It has been found that the gas solubility in liquids increases with increase in pressure. To have a better understanding of the effect of pressure on gas solubility let us consider a system of a gas solution in a solvent in a closed container in a state of dynamic equilibrium. Now the

solution is in equilibrium and hence the rate of gaseous molecules entering the solution is equal to the rate of gaseous molecules leaving the solution.

2. The solubility of gases in liquids:

Henry's Law gives a quantitative relation between pressure and gas solubility in a liquid. It states that:

The solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution.

The most general way of using Henry's Law is that the partial pressure of a gas above a solution is proportional to the mole fraction of the gas in the solution.

$$\mathbf{P = K_H x}$$

Where, p = partial pressure of the gas x = mole fraction of the gas in solution K_H = Henry's law constant

3. Effect of Temperature:

Gas solubility in liquids is found to decrease with increase in temperature. The gas molecules in a liquid are dissolved by the process of dissolution. During this process, heat is evolved. According to Le Chatelier's Principle which states that when the equilibrium of a system is disturbed, the system readjusts itself in such a way that the effect that has caused the change in equilibrium is countered. So, as we know that dissolution is an exothermic process, the solubility should decrease with an increase in temperature to validate Le Chatelier's Principle.

5.5 SOLUBILITY OF ORGANIC COMPOUNDS

The principle outlined above under polarity that *like dissolves like*, is the usual guide to solubility with organic systems. For example, petroleum jelly will dissolve in gasoline because both petroleum jelly and gasoline are non-polar hydrocarbons. It will not, on the other hand, dissolve in ethyl alcohol or water, since the polarity of these solvents is too high. Sugar will not dissolve in gasoline, since sugar is too polar in comparison with gasoline. A mixture of gasoline and sugar can therefore be separated by filtration or extraction with water.

5.6 EXTRACTION

Extraction depends on the process of selective removal of one or several compounds or components from a mixture of liquid or solid sample or substance with an organic solvent,

known as extraction. Extraction of solid with a liquid (liquid solid extraction) is also known as selective dissolution. Extraction from liquid (liquid liquid extraction) or solvent extraction is more often employed and here one of the liquid is commonly water.

When two mutually insoluble or only, partially soluble liquids are brought in contract together the species to be extracted will partition between them in a definite way, concentrating predominantly in one of them. Extraction arises from differential solubility of such substance in two mutually immiscible liquids.

The process of extraction takes place according to the laws of diffusion and equilibrium distribution and is described by the mass transfer equation. In analytical practice extraction is typically achieved in reparatory funnel (Fractional extraction).

A mixture of two solvents and a substance being extracted is shaken, the phase after complete separation in to layers are separately withdrawn. The unknown substance is removed from the extract thus obtained by evaporation, trying, distillation and crystallization.

5.6.1 Liquid-Liquid Extraction:

The most important application of distribution law is in the process of extraction which is of great importance both the laboratory as well as in industry. In the laboratory often substances dissolved in water, have to be separated by means of organic solvents like, ether, carbon tetrachloride, chloroform, benzene etc. In the separation, the advantage is taken of the fact that the distribution ratio of most inorganic substances is in the favour of water, while those of organic compounds is in favour of organic solvents.

This is due to the organic compounds are generally more soluble in organic solvents like benzene, ether, chloroform etc. than in water and those solvents are immiscible with water. Organic compounds are then easily separated from the mixture with inorganic compounds in aqueous medium by adding benzene, chloroform, ether etc. because organic compounds have their distribution ratio largely in favour of organic solvents, more of them would pass in to non-aqueous layer. Finally, this non-aqueous layer is removed and distilled to obtained the purified compound.

The type of extraction discussed above is known as liquid extraction. The liquid extraction is a technique in which a substance dissolved in one phase is more or less completely transferred to the second phase essentially immiscible with the first i.e., an organic liquid such as benzene, chloroform, etc.

5.6.2 Acid–base extraction:

Acid–base extraction is a subclass of liquid–liquid extractions and involves the separation of chemical species from other acidic or basic compounds. It is typically performed during the work-up step following a chemical synthesis to purify crude compounds and results in the product being largely free of acidic or basic impurities. A separatory funnel is commonly used to perform an acid-base extraction.

Acid-base extraction utilizes the difference in solubility of a compound in its acid or base form to induce separation. Typically, the desired compound is changed into its charged acid or base form, causing it to become soluble in aqueous solution and thus be extracted from the non-aqueous (organic) layer. Acid-base extraction is a simple alternative to more complex methods like chromatography. It is not possible to separate chemically similar acids or bases using this simple method.

5.6.3 Solid-phase extraction:

Solid-phase extraction (SPE) is a solid-liquid extractive technique, by which compounds that are dissolved or suspended in a liquid mixture are separated, isolated or purified, from other compounds in this mixture, according to their physical and chemical properties. Analytical laboratories use solid phase extraction to concentrate and purify samples for analysis. Solid phase extraction can be used to isolate analytes of interest from a wide variety of matrices, including urine, blood, water, beverages, soil, and animal tissue.

SPE uses the affinity of solutes, dissolved or suspended in a liquid (known as the mobile phase), to a solid packing inside a small column, through which the sample is passed (known as the stationary phase), to separate a mixture into desired and undesired components. The result is that either the desired analytes of interest or undesired impurities in the sample are retained on the stationary phase. The portion that passes through the stationary phase is collected or discarded, depending on whether it contains the desired analytes or undesired impurities. If the portion retained on the stationary phase includes the desired analytes, they can then be removed from the stationary phase for collection in an additional step, in which the stationary phase is rinsed with an appropriate eluent.

5.7 DISTRIBUTION COEFFICIENT

In the physical sciences, a **partition coefficient** (***P***) or **distribution coefficient** (***D***) is the ratio of concentrations of a compound in a mixture of two immiscible solvents at equilibrium.

This ratio is therefore a comparison of the solubility's of the solute in these two liquids. The partition coefficient generally refers to the concentration ratio of un-ionized species of compound, whereas the distribution coefficient refers to the concentration ratio of all species of the compound (ionized plus un-ionized).

In the chemical and pharmaceutical sciences, both phases usually are solvents. Most commonly, one of the solvents is water, while the second is hydrophobic, such as 1-octanol. Hence the partition coefficient measures how hydrophilic ("water-loving") or hydrophobic ("water-fearing") a chemical substance is. Partition coefficients are useful in estimating the distribution of drugs within the body. Hydrophobic drugs with high octanol-water partition coefficients are mainly distributed to hydrophobic areas such as lipid bi layers of cells. Conversely, hydrophilic drugs (low octanol/water partition coefficients) are found primarily in aqueous regions such as blood serum.

If one of the solvents is a gas and the other a liquid, a gas/liquid partition coefficient can be determined. For example, the blood/gas partition coefficient of a general anesthetic measures how easily the anesthetic passes from gas to blood. Partition coefficients can also be defined when one of the phases is solid, for instance, when one phase is a molten metal and the second is a solid metal, or when both phases are solids. The partitioning of a substance into solid results in a solid solution.

Partition coefficients can be measured experimentally in various ways (by shake-flask, HPLC, etc.) or estimated by calculation based on a variety of methods (fragment-based, atom-based, etc.). If a substance is present as several chemical species in the partition system due to association or dissociation, each species is assigned its own K_{ow} value. A related value, D, does not distinguish between different species, only indicating the concentration ratio of the substance between the two phases.

5.8 SEPARATION AND DRYING AGENTS

A Separation is defined as, where your product and any by-products are at any point during the isolation of your final product from a chemical reaction. Whenever there is the physical separation of two immiscible layers, a solid from a solid/liquid mixture or the removal of a solvent from the final product, the Separation Scheme details where each product or by-product is (or should be). It is a useful guide to you or anyone else performing the same experiment that shows how to get the final product in pure form, devoid of any of the by-products or solvents. The start of any Separation Scheme is typically the end of the reaction,

when all of the ingredients are still in the reaction flask, but the reaction is considered complete. Typical physical manipulations of the reaction mixture at the end of the reaction include, extracting, washing, rinsing, filtration, evaporation of solvent, and drying.

Drying agents: When a solution of an organic compound is dried using a drying agent (such as anhydrous Na_2SO_4 or $MgSO_4$), the resulting mixture is similar to that from a Precipitation process – the resulting mixture is an organic compound in solution and a solid (the hydrate) that requires removal by filtration. In this case the solid is not the desired material, but rather the filtrate, in which the compound of interest is still in solution. In this case, the filtrate is usually obtained by either decanting or by gravity filtration and the solute (hydrates, $Na_2SO_4.10H_2O$ or $MgSO_4.7H_2O$) is discarded.

(Note that the drying agent never "dissolves" in an organic solvent, but simply goes from anhydrous to hydrate).

5.9 SUMMARY

In this chapter we are understand how we will check the solubility of different mixture, solubility of various organic solvents etc. In this chapter we will learnt about extraction process, types of extraction, about distribution coefficient and Separation and drying agents.

5.10 TERMINAL QUESTIONS

1. What solvent extraction or liquid extraction.
2. Describe various types of solubility.
3. What is the solubility of organic compounds? Explain.
4. Define the extraction.
5. Describe types of extractions.
5. What is distribution coefficient? Explain.
6. Write a short note on the followings:

(a) Separation

(b) Drying agents

(c) Solid-phase extraction

(d) Solubility product

5.11 REFERENCES

1. https://en.wikipedia.org/wiki/Partition_coefficient

UNIT 6: PHYSICAL CONSTANTS

CONTENTS:

6.1 Introduction
6.2 Objectives
6.3 Melting points
6.3.1Explanation of Melting Point
6.3.2 Factors Affecting Melting Point
6.4 Melting point theory
6.5 Mixture melting point
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6.7 Determination of melting point
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6.10.1.Ion Exchange method for water softening
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6.1 INTRODUCTION

Substances can change phase often because of a temperature change. At low temperatures, most substances are solid; as the temperature increases, they become liquid; at higher temperatures still, they become gaseous. This unit are to introduce, phase change are always accompanied by a change in the energy of a system. Like, converting a liquid , in which molecules are close together, to a gas in which molecules are far apart , required an input of

heat to give the molecules enough kinetic energy to allow them to overcome the intermolecular attractive forces. The term ***sublimation*** refers to a physical change of state and is not used to describe the transformation of a solid to a gas in a chemical reaction and this technique used by chemists to purify compounds. This unit topic the Mixed melting point" is a technique used to identify chemical compounds. It is particularly used for organic compounds, where a sample with a known identity and melting point is mixed with an unknown purified sample to determine the melting point.

6.2 OBJECTIVES

The main Objectives of this unit are to introduce, phase change are always accompanied by a change in the energy of a system. In this unit we learn about melting point, melting point theory, mixture of melting point theory, also explain the boiling point and its theory.This unit mainly define , the melting point of a chemical is the temperature where it transitions from a solid to a liquid state and the temperature at which the equilibrium vapour pressure of the liquid equal to the atmospheric pressure known as boiling point.In sublimation process,we learn about how , a substance transforms from a solid to a gas without ever going through a liquid phase.

The chapter is developed to stimulate interest of the reader into phase transfer and at the same time to built the deep understanding of the phase transfer process. To offer students an easy and interesting experience, each of the topics covered is depicted with diagram and figures also.

6.3 MELTING POINTS

The melting point is usually defined as the point at which materials changes from a solid to a liquid. The temperature at which solid changes its state to liquid at atmospheric pressure is called the melting point of that liquid. This is the point at which both liquid and solid phase exists at equilibrium.

As heat is applied to a solid, its temperature will increase until the melting point is reached. More heat then will convert the solid into a liquid with no temperature change. When the entire solid has melted, additional heat will raise the temperature of the liquid. The melting temperature of crystalline solids is a characteristic figure and is used to identify pure compounds and elements. Most mixtures and amorphous solids melt over a range of temperatures.

Different solids display varying melting points like the melting point of ice is 0 °C at atmospheric pressure.

6.3.1Explanation of Melting Point:

Melting or fusion is the process by which a solid substance changes into a liquid on heating. On heating a substance, the particles vibrate with greater intensity and move more vigorously. Heat energy is produced. The particles gain sufficient kinetic energy to overcome the strong forces of attraction. They gain energy to break through to form small groups of particles. Solids, therefore, melt to form a liquid state and the energy supplied to melt a system is known as **Enthalpy of fusion** or **Entropy of fusion**.

Melting point of some common organic compound are given below:

Compound	Melting Point (°C)	Compound	Melting Point (°C)
Phenol	42	α-Naphthylamine	50
α-Naphthol	96	Acetamide	82
β-Naphthol	123	Benzamide	128
Oxalic Acid	101	Urea	132
Benzoic Acid	122	Fructose	103
Cinnamic Acid	133	Glucose	146
p-Toludine	43	Sucrose	186
Naththalene	80	Acetanilide	114.3

6.3.2 Factors Affecting Melting Point:

The following factor affecting the melting points are given below:

a) **Bonding:** The melting point depend upon the type of bonding between the compound.

The compound which having ionic bonding have more melting points than compounds have covalent bonding.

b) **Molecular Weight and Size:** Larger the molecule, the more area it has for intermolecular interactions, hence a much stronger force of attraction between molecules and melting point as well. Therefore, larger molecules have greater melting

points than smaller molecules. Other than size, shape also affects the melting point as linear-shaped molecules can be packed much more efficiently than branched or spherical-shaped molecules.

c) **Impurities :**The presence of impurities in a substance can lower its melting point. Impurities disrupt the regular packing arrangement of molecules or ions, making it easier for the substance to transition from the solid to the liquid phase. This phenomenon is known as "melting point depression."

d) **Pressure:** Increase in pressure increase the melting point of the compounds which expands on melting and it decreases with an increases in pressure for the compound which contracts on melting.

e) **Bonding:** The bonding between the compound,also affected the melting point of compounds.The compounds having ionic bonding have more melting points than covalent compounds. This is because in ionic compounds opposite ions have strong electrostatic force of attraction between the ions, and to breaking the bond large amount of energy , which result in a high melting point.

6.4 MELTING POINT THEORY

The melting point (m.p) 0C of a compound is the temperature at which it changes from a solid to a liquid. Since this requires that the intermolecular forces that hold the solid together have to be overcome. The melting point is a physical property (melting point, boiling point, density, solubility, etc.) often used to identify compounds . Usually, chemists can only obtain a melting range of a 2-3 ^{0}C accuracy. A pure, nonionic, crystalline organic compound usually has a sharp and characteristic melting point (usually 0.5-1.0 0C range). A mixture of very small amounts of miscible impurities will produce a depression of the melting point and an increase in the melting point range . Melting point range: The interval between the temperature at which a solid sample just begins to turn to liquid and the temperature at which the entire sample becomes liquid. or range of temperatures in which the first crystal starts to melt until the temperature at which the last crystal just disappears.

6.5 MIXTURE MELTING POINT

If Two substance melt at the same temperature , a mixed melting point determination can reveal if they are one and the same substance.The phenomenon of melting point depression can be applied to the identification of unknown pure substances.

In other world " Mixed melting point'' is a technique used to identify chemical compounds. It is particularly used for organic compounds, where a sample with a known identity and melting point is mixed with an unknown purified sample to determine the melting point.

For the identification of a compound by determining a mixed melting point.At first prepare a mixture of unknown chemical and in which one may be suspected and measure the melting point of the mixture then there are two possibilities:

a) If melting point of the mixture is the same as the pure compound, which shown that known and unknown compound are the same.
b) If the melting point of the mixture lower than either of the two pure components, but melting range is large. This is because the two components are different with the result that one is an impurity in the other.

For example, both benzoic acid and mandelic acid are white crystalline solids which melt at 121°C. However a 1: 1 mixture of the two compounds begins to melt at about 80°C.

The usefulness of mixed melting points is limited in that you must have some idea of the chemical nature of your unknown compound and a sample of the suspected compound must be available.

6.6 PACKING OF MELTING POINT TUBE

For melting point analysis, preparation is straight forward. The sample must be thoroughly dried and relatively pure (<10% impurities). The dry sample should then be packed into a melting point analysis capillary tube, which is simply a glass capillary tube with only one open end. Only 1 to 3 mm of sample is needed for sufficient analysis. The sample needs to be packed down into the closed end of the tube. This may be done by gently tapping the tube or dropping it upright onto a hard surface **(**Figure 6.1**).** Some apparatuses have a vibrator to assist in packing the sample. Finally the tube should be placed into the machine.

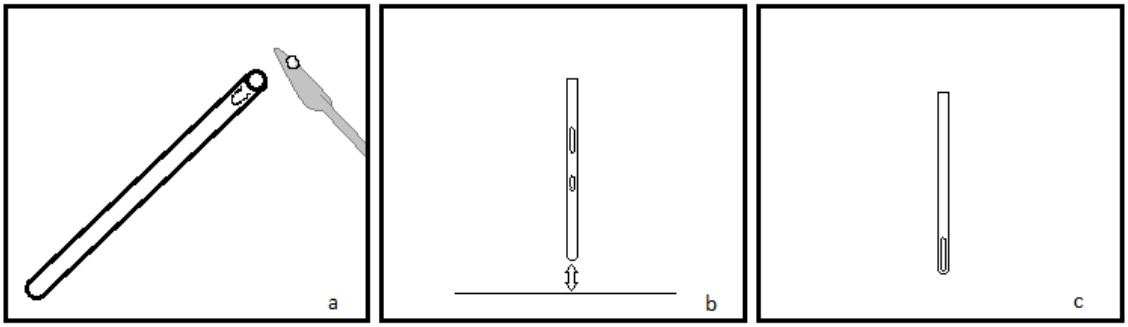


Figure 6.1: Schematic showing how to pack dried sample into a melting point analysis capillary tube: (a) using a spatula, push a sufficient amount of sample into the tube opening, (b) using a tapping motion or dropping the tube, pack the sample into the closed end, (c) the sample is ready to be loaded into the apparatus.

6.7 DETERMINATION OF MELTING POINT

To determine the melting point of a solid, at first take a capillary tube and seal it from on end. After that fill the capillary tube with given finely powdered organic solid substance from the non sealed end whose melting point is to be determined. Fasten this capillary tube to the thermometer using a rubber band/ thread.On the other hand thermometer partly immerse in the paraffin liquid taken in a Thiele's tube **(Figure 6.2),** taking care to see that thread is above the level of the liquid bath i.e. it is not coming contact with liquid bath.Heat the Thiele's tube gently at the lower bent arm and no stirring is required as convection currents maintain uniform temperature. Now we check that solid changing into liquid from the lower end of the capillary tube that is when we observed partly powdered compound changed to liquid and still some in the solid state. Note down this temperature, this is the melting point of the solid.

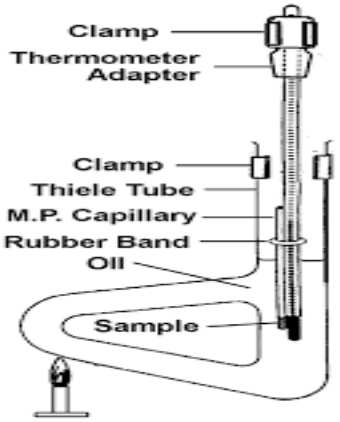


Figure 6.2 : Thiele's tube to determined the melting point of solid substance

6.8 DECOMPOSITION

Decomposition reaction define as "A decomposition reaction is a chemical process in which the molecule or reactant breakdown into simpler products. Thus, when one reactant breaks down into two or more products." General equation of decomposition reaction of any compound AB can be given as:

$$AB \longrightarrow A + B$$

In above reaction AB is the reactant chemical compound after decomposition A and B represent the products obtained by the decomposition of the reaction.

Some important example of decomposition reaction are given below:

a) $2\ KClO_3\ (s) \rightarrow 2\ KCl\ (s) + 3\ O_2\ (g)$

b) $CaCO_3\ (s) + heat \rightarrow CaO\ (s) + CO_2\ (g)$

Decomposition in chemistry means breaking a single reactant to form more stable products compared to the reactant. Decomposition is an essential process of chemistry as it results in the formation of new products.

Types of decomposition:

The decomposition is classified broadly into two types because changes can be of two types.Types of decomposition or changes, which are given below.

a)Physical decomposition or changes

b)Chemical decomposition or changes

a)Physical decomposition or changes:

Physical changes are generally reversible also irreversible and only the physical properties are changed in such changes. In a physical change, a substance undergoes a change of its physical properties. Some common examples of physical changes are melting an ice cube, boiling of water, breaking of a glass, freezing water etc.

b)Chemical decomposition or changes

Chemical changes are irreversible changes in which new products are formed. The product is different from the reactants and has entirely different properties. Chemical changes that occur are also considered chemical reactions.

Classification of decomposition reaction: Decompostion reaction classified into following types:

a) Thermochemical Decomposition Reaction: Heat-induced chemical reaction in which one material splits into two or more compounds is called a thermochemical decomposition reaction. This heat is necessary to dissolve the chemical link between the components. It is an endothermic process.

$$CaCO_3\ (s) \xrightarrow{heat} CaO\ (s) + CO_2\ (g)$$

b) **Electrolytic Decomposition Reaction:**In electrolytic decomposition electric current is passed in aqueous solution of substance.The decomposition of water is a good example of electrolytic decomposition.

$$H_2O \rightarrow H_2 + O_2$$

c) **Photo Decomposition**

It is a type of decomposition reaction in which light or photons are used to break the reactants to form several products. Light energy is used to break the bonds in the reactant. This reaction is also known as photolysis.

$$AgCl \xrightarrow{\text{sunlight}} Ag + Cl$$

6.9 DISCOLORATION

A discoloration is a change in something's color, usually for the worse. When the color of something gets dingier, duller, or faded, this process is called discoloration. Some types of materials subject to discoloration include paper, textiles, finishes, papier mâché, print media, fur, feathers, skin, leather, pigments, dyes, silk, velvet, lacquered surfaces, celluloid, and wood.

A chemical reaction isn't always visible to the human eye, but sometimes it results in an impressive color change and makes science experiments more fun to witness. When two or more substances combine, they create one or more new substances, which sometimes have different molecular structures from the original substances, meaning they absorb and radiate light in different ways, leading to a color change.

Some example of discoloration:

- To test whether starch is present in a foodstuff, mix a solution of iodine and potassium iodide in water. The solution has a light orange-brown color, but when you apply it directly to a sample that contains starch (such as potatoes or bread), it turns a blue-black color.
- When reaction occurs in rusting of iron,iron oxide forms on its surface (oxidation)causing the iron to turn a raddish brown color.

6.10 SOFTENING

Water softening, the process of removing the dissolved calcium and magnesium salts that cause hardness in water. The most common means for removing water hardness rely on ion-exchange resin or reverse osmosis. Other approaches include precipitation methods and

sequestration by the addition of chelating agents. Distillation and reverse osmosis are the most widely used two non-chemical methods of water softening.

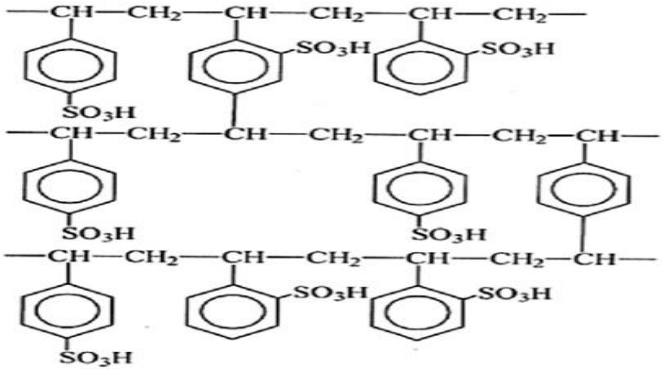
6.10.1.Ion Exchange method for water softening:

Ion- exchange or Deionization or Demineralization process recently ion- exchange resins have been used to remove all minerals from water. Ion – exchange resins are insoluble , cross – linked, long chained organic polymer having some ionisable group.The functional groups attached to the chains are responsible for the ion exchange properties . The ion exchange resins are classified as follows:

a) Cation exchange resins or Cation Exchanger
b) Anion exchange resins or Anion Exchanger

a)Cation exchange resins or Cation Exchanger :

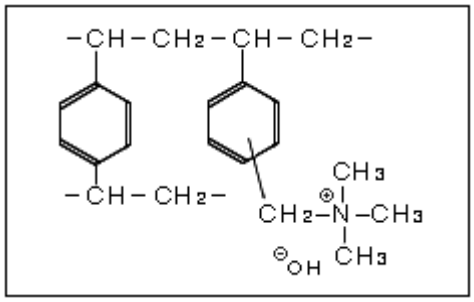
Such resins have $–SO_3H$, -COOH, -OH , group as the ionizable group.Since these resins exchange the cationic portion of minerals by their hydrogen atom , they are known as cation exchangers.



Strong acid cation exchange resine

b) Anion exchange resins or Anion Exchanger :

These resins have $–NH_2$, $-NHCH_3$, $-N(CH_3)_2$, or –OH group. They exchange the anionic portion of the minerals and they are known as anion exchanger.



Anion exchange resine hydroxide form

Uses of Ion- exchange resin- water treatment by ion- exchange resin includes softening deionization and de- alkalization of water. Therefore, hard water can be converted into soft water by making use of ion – exchange resins.

Process: In this process hard water is passed first through cation exchange colomn which removes all the cations (like Ca^{2+} , Mg^{2+} etc) from it and equivalent amount of H^+ ions are released from this column to water.

Thus,

$$2RH^+ + Ca^{+2} \rightarrow R_2Ca^{+2} + 2H^+$$

$$2RH^+ + Mg^{+2} \rightarrow R_2Mg^{+2} + 2H^+$$

After this process, hard water is passed through anion exchange column , which removes all the anions (like SO_4^{-2}, Cl^- etc.) from it, and equivalent amount of OH^- ions are released from this column to water. Thus,

$$R'OH^{-2} + Cl^{-2} \longrightarrow R'Cl^- + OH^-$$

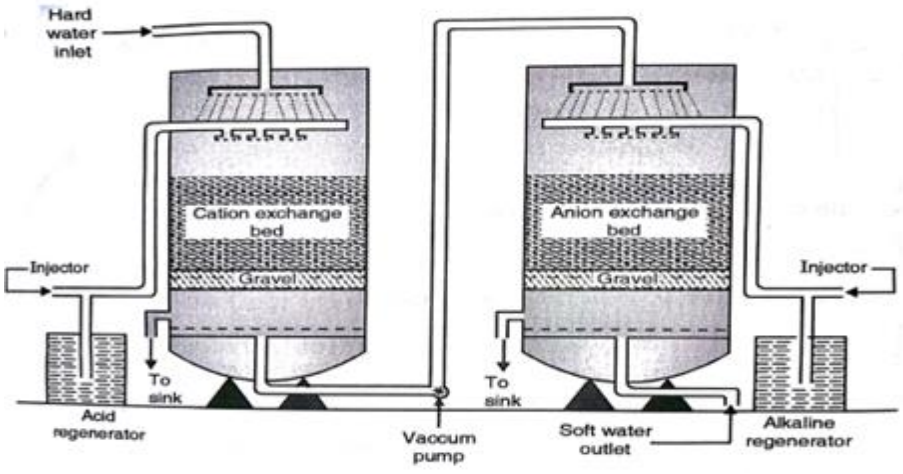
$$2R'OH^- + SO^{2-}{}_4 \longrightarrow R'_2\,SO_4^{-2} + 2OH^-$$

$$2R'OH^- + CO^{2-}{}_3 \longrightarrow R'_2\,CO^{2-}{}_3 + 2OH^-$$

H^+ and OH^- ions get combined to produce water molecule

$$H^+ + OH^- \longrightarrow H_2O$$

The water coming out from the exchanger is free from cations as well as anions. Ion-free water is known as a deionized or demineralized water.



Figuur 6.3: Demineralization of water

Advantages:

1. The process can be used to soften highly acidic or alkaline water.

2. It produces water of very low hardness. So it is very good for treating water for use in high pressure boilers.

Disadvantages:

1. The equipment is costly and more expensive chemicals are needed.
2. If the water contains turbidity. Then the output of the process is reduced. The turbidity must be below 7.00 ppm if it is more , it has to be removed first by coagulation and filtration.

6.10.2 .Some other Method Used for water softening:

a) By boiling the water: The temporary hardness of water can be easily removed by boiling of

hard water.On boiling, the soluble magnesium and calcium bicarbonate is decomposed into

insoluble carbonates.These insoluble carbonate can be removed by filtration and obtained

soft water. Thus:

$$Mg(HCO_3) \xrightarrow{\text{heat}} MgCO_3 + CO_2 + H_2O$$

Magnesium bicarbonate Magnesium carbonate

The permanent hardness of water cannot be removed by boiling because the salts of chloride and sulphates are stable to heat.

b) Washing soda method: In this method water is treated with washing soda or sodium

carbonate. Which converts calcium and magnesium chlorides and sulphates of calcium and magnesium into their respective carbonates . Which get precipitated and can be removed by filtration process to obtained soft water.

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2NaCl$$

$$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$$

c) **Reverse osmosis :** Reverse osmosis uses an applied pressure gradients across a semi permeable membrane to overcome osmotic pressure and remove water molecules from

the solution with hardness ions.The membrane has pores large enough to admit water molecules for passage hardness ions such as Ca^{2+} and Mg^{2+} will not fit through the pores. The resulting soft water supply is free of hardness ions without any other ions being added. Membranes are a type of water filter requiring regular cleaning / replacement maintence.

6.11 SHRINKING AND SUBLIMATION

6.11.1 Shrinking:

Chemical shrinkage is defined as the absolute internal volume reduction of the hydration products of binders compared to the volume of initial components caused by the hydration reaction of cement. A desaturation of pores is then caused after the setting of the cementations material. In short the volume changes in the concrete due to loss of moisture known as shrinking.

Types of shrinking:

A)Plastic Shrinkage:

- Plastic shrinkage happens soon after the concrete is poured in the form work , while the concrete is still in plastic stage.
- The water evaporates and results in a reduction of volume , this causes the concrets on the surface to collapse.
- The aggregate particles or the rainforcement comes in the way of subsidence due to which creaks may appear at the surface or internally around the aggregate or reinforcement.
- Plastic shrinkage can be reduced mainly by preventing the rapid loss of water from surface.
- It can be reduced by covering the surface with polyethylene sheeting immediately after it is poured.
- An effective method of removing plastic shrinkage cracks is to revibrate the concrate in a controlled manner.Use of small quantity of aluminium powder is also suggested to offset the effect of plastic shrinkage.

B) Drying Shrinkage:

- This shrinkage is mainly due to the deformation of the paste, though the aggregate stiffness also influences it. It takes place once the concrete has set is called as the drying shrinkage.
- Drying shrinkage take place after Contraction of hardened of concrete due to loss of capillary water in the concrete.Drying shrinkage occure in 3 to 4 days or several months after concreting.
- The loss of water held in gel pores that causes the decrease in volume.
- Under drying condition the gel water is lost progressively over a long time, as long as the concrete is kept ib drying conditions.
- Drying shrinkage is also a function of the fineness of gel. The finer the gel the more is the shrinkage.
- The higher pressure steam cured concrete with low specific surface of gel, shrinks much less than that of normally cured cement gel.

Factors Affecting Drying Shrinkage: The following are the main factors that affect the drying shrinkage:

a)Material Selection: Ingredients that are chosen for the concrete mix must be good quality to ensure chances of drying shrinkage.

b)Water cement Ratio Higher the water /cement ratio of the concrete mix, more is the chances for drying shrinkage. As the water/cement ratio increases, the strength of the paste and the whole stiffness will decrease. Hence shrinkage increase with the increase of water.

c)Aggregates Type used in the Mix: Size of aggregate will influence the cause of drying shrinkage. The increase in the maximum size of aggregates will decrease the shrinkage.

d)Environmental Conditions The relative humidity of the site plays an important role on the drying shrinkage of the concrete structure. With the increase in humidity in the environment, there is a decrease in the decrease of shrinkage.

e) Size and Shape of the Specimens The surface to the volume ratio is a factor that can influence the rate of shrinkage..

C)Autogeneous Shrinkage : Autogenous shrinkage is a phenomenone that occurs in concrete without any external drying or thermal effects.It refers to the volume reduction or contraction of concrete due to the self- desiccation process, which is caused by the chemical rections between cement and water during hydration.When cement react with water form gel like substance called calcium sillicate hydrate if this process done continously , if this gel

continous to absorb water leading to a decrease in water content within the concrete materix. As a result, the volume of gel decreases , causing autogenous shrinkage.

Factors Affecting Autogenous Shrinkage :

- **Temperature** With the increase in temperature the rate of autogenous shrinkage the autogenous shrinkage is related to the hydration process, the volume change will be higher.
- **Cement Content** More the cement content in the mix, higher will be the autogenous shrinkage.
- **Mineral Admixtures** The addition of mineral admixtures will increase the hydration process and hence the autogenous shrinkage

D) Carbonation Shrinkage :

Carbonation shrinkage occurs when the calcium hydroxide will react with the atmospheric carbon dioxide to give calcium carbonates. This will lead to the conversion of the concrete surface to get carbonated or acidic in nature. This process is called as carbonation. The carbonation shrinkage is observed in areas that have intermediate humidity conditions. The carbonation process will result in the decomposition of some of the cement compounds. The carbonates that are formed by the carbonation will result in filling up of the pores and hence decrease the permeability. As the permeability is decreased, the strength will increase.

Effects of Carbonation: Following are some of the effects of carbonation:

- **Shrinkage in concrete**: The volume of products of carbonation reduces causing shrinkage in concrete.
- **Increase in weight of concrete**: Products of carbonation increase the weight of concrete.
- **Reduced permeability**: Formation of $CaCO_3$ fills up the voids in concrete, thus reducing permeability.
- **Increased strength**: Water released during carbonation promotes the hydration reaction leading to increased strength.

6.11.2 Sublimation:

Sublimation, in physics, conversion of a substance from the solid to the gaseous state without its becoming liquid. An example is the vaporization of frozen carbon dioxide (dry ice) at ordinary atmospheric pressure and temperature. The phenomenon is the

result of vapour pressure and temperature relationships. The opposite process of sublimation- where a gas undergoes a phase change into solid form is called deposition or desublimation.

Example of sublimation:

- Naphthalene, a chemical commonly used in mothballs, readily sublimates at room temperature and pressure.
- At the right temperature, the elements iodine and arsenic will sublimate from solid form into gaseous form.
- Air fresheners used in washrooms and cars sublime into gaseous state. The particles of gas , on moving through the room brings about a good smell.
- Dry ice is the best example of sublimation . When dry ice get exposed to air , it is directly changes solid –state to gaseous state which is visible as fog.Frozen CO_2 in its gaseous state is more stable than in its solid- state.

6.12 BOILING POINT

The temperature at which liquid vapour pressure equals atmospheric pressure is referred to as boiling point. The boiling point is defined as the temperature at which a liquid's saturated vapour pressure equals the atmospheric pressure surrounding it.

The boiling point of a liquid varies depending upon the surrounding atmospheric (environmental) pressure.A liquid in a partial vacuum,under low pressure has lower boiling point than that liquid is at atmospheric pressure.Like water boils at 99.7 ^{0}C under standard pressure at sea level but 93.4 ^{0}C at 1,905 (high altitude) altitude.Normally , boiling points are determined at standard pressure760 mm Hg (torr) or 1 atmospheric pressure. For a given pressure , different liquids will boil at different temperatures.

When all the particles in the liquid phase have been transformed into the gas phase,the

temperature begins to rise again, as long as heat is still being applied to the surrounding system. As the temperature starts to increase, so does the particle's kinetic energy.

In terms of intermolecular interaction the boiling point represents the energy required to overcome the various intermolecular attractions binding the molecules as a liquid (dipole-dipole attraction and hydrogen bonding) and therefore undergo a phase change into the gaseous phase. Therefore the boiling point of a liquid is also an indicator of the strength of the attractive forces between the liquid's molecules.

6.12.1 Factors Affecting Boiling Point:

a) Pressure: The biggest determinant of a liquid's boiling point is the surrounding pressure . If extranal pressure is lower than the atmospheric pressure then the boiling point is less than the normal boiling point. It increases when the pressure is more than the atmospheric pressure.

b) Effect of impurities: On adding an impurity, the vapor pressure of solution decreases. With an increase in concentration of solute, vapour pressure decreases, hence boiling point increases. This phenomenon is known as 'elevation of boiling point'. For example – adding salt to water will lead to increase in its boiling point.

c) Intermolecular forces: Intermolecular forces (IMFs) can be used to predict relative boiling points. The stronger the IMFs, the lower the vapor pressure of the substance and the higher the boiling point. Therefore, we can compare the relative strengths of the IMFs of the compounds to predict their relative boiling points.

d) Molecular weight: Larger molecules have higher boiling points than smaller molecules of the same kind.

e) Branching : As branching increases, the surface area of the molecule decreases which results in a small area of contact. As a result, the Van der Waals force also decreases which can be overcome at a relatively lower temperature. Hence, the boiling point of an alkane chain decreases with an increase in branching.

6.13 DETERMINATION OF BOILING POINT

Take a small tube (usually sodium fusion tube) and fill it two – third by pure organic liquid whose boiling point is to be determined. Seal a capillary tube at one end and place it in the liquid with the sealed end above the surface of the liquid. Fasten the glass tube to the thermometer using a thread or a rubber band. Immerse partly the thermometer in the paraffin liquid taken in a small beaker or Thiele's tube taking care to see that thread is above the level of the liquid bath i.e. it is not coming in contact with liquid bath. Heat the Thiele's tube gently at the lower bent arm and no stirring is required as convection currents maintain uniform temperature. As rapid and continuous stream of air bubbles start coming out from the lower end of the capillary tube, remove the burner but continue stirring note down the temperature at which the air bubble stop and the liquid rushes into the capillary tube. The mean of these two temperatures gives the boiling point of the liquid.

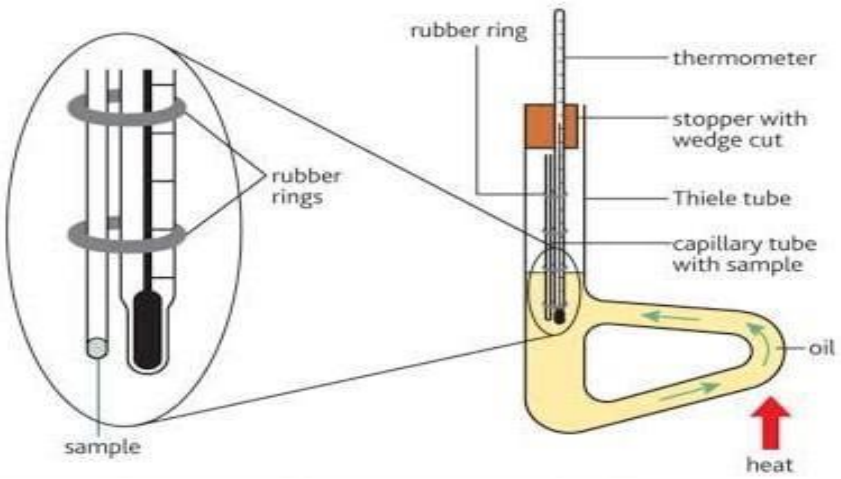


Figure 6.4: Thiele's tube to determine the Boiling point of liquid

6.14 SUMMERY

In this unit physical constant of different states is briefly discussed. This unit define in brief What is melting and boiling point? How it is determine and what factor affecting the melting and boiling point of different stages. In a simpler terms, this unit explain mixed melting point techniques used to identify the chemical compounds. If any sample with known identity and melting point is mixed with unknown purified sample to determine the melting point. This unit also covered the decomposition and type of decomposition used in various type of reactions and discoloration , softening process.

6.15 TERMINAL QUESTIONS

A.Multiple choice questions:

1.The temperature at which solid and liquid coexist in equilibrium is called :

a)Melting point of liquid b) Freezing point of liquid

c) Freezing point of solid d) All of these

2.Melting point of ice is :

a) 0^0C b) -4^0C c) 4^0C d) 100^0C

3.When the solid and liquid phase are in equilibrium, the temperature become:

a) Increases b) Decreases c) Remains constant d) None of these

4. The temperature of water vapour released from the solution after facing boiling point elevation is _____:

a) Equal to 100 ^{0}C b) Below 100 ^{0}C

c) Above 100 ^{0}C d) Much larger than 100^{0}C

5. Which of the following state is not formed during sublimation?

a) Solid b) Liquid c) Gas d) None of these

6. Which of the following undergo sublimation?

a) Naphthalene balls b) Ammonium chloride

c) Carbon dioxide d) All of the above

7. What is the remainder product of sublimation called?

a) Subliment b) Solute c) Solvent d) Sublimate

8.Brass gets discolored in air due to the presence of:

a) Oxygen b) Nitrogen c) Hydrogen sulphite d) Carbon dioxide

9.Electrolysis of water is a decomposition reaction. The mole ratio of hydrogen and oxygen gases liberated during electrolysis of water is:

a) 2:1 b) 1:1 c) 4:1 d) 1:2

10.On heating lead nitrate (by decomposition reaction) to gives;

a) PbO_2 and NO_2 b) PbO and NO_2 c) PbO and NO d) PbO_2 and NO

11 How many types of shrinkages, caused due to loss of water?

a)1 b) 2 c) 3 d) 4

12.Reduction in the volume due to shrinkages causes_____.

a) low volume b) Volumetric strain c) Volumetric stress d) w/c ratio

B.Long Question:

Q.1. Define melting point? How to determined the melting point of solid substance with the help of Thiele's tube?

Q.2.Explain melting point theory ? What factor affected the melting point of solid substances?

Q.3.What do you understand by decomposition reactions? Define the type of decomposition.

How we classified various decomposition reactions?

Q.4. Define boiling point of liquid? What factor affected the boiling point of liquid?

Q.5.How to determined the boiling point of liquid by Thiele's tube?

Q.6.Write a short notes on : a) Softening, b) Shrinking

Q.7.Explain ion-exchange Process for Softening of Hard water. What are its Advantages and Disdvantage?

Q.8. Define Shrinking ? Explain the types of shrinking?

Q.9. What factor affecting the Autogenous and Drying Shrinkage?

ANSWERS:

1) b 2) a 3) c 4) c 5) b 6) d 7) d 8) c 9) a 10)b

11) c 12) b

6.16 REFERENCES AND FURTHER STUDIES

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UNIT 7: DISTILLATION

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7.1 INTRODUCTION

Distillation, process involving the conversion of a liquid into vapour that is subsequently condensed back to liquid form. It is exemplified at its simplest when steam from a kettle becomes deposited as drops of distilled water on a cold surface. Distillation technique is useful in obtaining a pure liquid from non-volatile impurities or to raise the absorption of the specific component in a mixture. It's a reversible process, i.e., a physical process which means the process can be returned to the original state of matter. But In dry distillation process that includes the destructive distillation of solid products to convert them into gaseous products.

In Raoult's Law explain the properties of ideal solutions. This law only applies to dilute solutions, yet it is followed by some liquid combinations over a wide concentration range. In column efficiency also refer to the design of a distillation column, it is necessary to determine the column diameter and the column height for economic considerations. Azeotrope, in chemistry, a mixture of liquids that has a constant boiling point because the vapour has the same composition as the liquid mixture. The boiling point of an azeotropic mixture may be higher or lower than that of any of its components.

7.2 OBJECTIVES

The main Objectives of this unit are to define the purifying of liquids by distillation methods. On the bases of types of impurities different distillation method will be applied. In this unit we learnt about the various distallation method ,distallation theory and difference between simple and fractional distallation.Mainly this unit define to purification of various liquids on the bases of present impurities in it.In this unit , in Raoults law we determine the bonding strength of liquids. Raoults law is useful in the determination of vapor pressure involving non-volatile solute. In this unit the topic Azeotropes have important practical applications in various industries, especially in separation processes where precise control of composition and boiling point is necessary.

For learners this chapter is developed to stimulate interest in purification of immesible liquid using by different distillation techniques. To offer students an easy and interesting experience , each of the topic covered is depicted with diagram and figures also.

7.3 DISTILLATION

In the most general sense, "distillation" means to purify something. In chemistry, distillation refers to a particular method of purifying liquids:

Distillation is the process of separating components from a liquid mixture by using selective boiling and subsequent condensation. It is a process in which water vapors convert into volatile liquids and separate through selective boiling. Distillation can be used to either increase the concentration of a particular component in the mixture or to obtain pure components from the mixture.

- **Distillation is physical reversible process.**
- **Distillation is carried out between liquids having different boiling points.**
- A plant that performs distillation is known as a **distillery**.
- The equipment used for distillation may be called a distillation apparatus or ***still*.**
- **The repetition of the process of distillation on the collected liquid to improve the purity of the product is called double distillation.**

  Example of distillation:

  a) Pure water can be separated from salt water through distillation.
  b) Alcohol can be separated from pure water by distillation process.

7.4 SIMPLE DISTILLATION

7.4.1. Principle : Simple distillation is the basic process of distillation it involves heating the liquid mixture to its boiling point and then condensing the resulting vapours immediately.This method of distillation is only applicable when the difference between the boiling points of the liquid is a considerably large minimum difference of 25°C is required at least. The simple distillation involves the heating of the liquid to its boiling point so that it is converted into vapors. On cooling the vapors' , pure liquid is obtained and collected separately.

7.4.2. Apparatus and procedures : To perform a simple distillation, you will need to set up the following apparatus: **Figure 7.1**

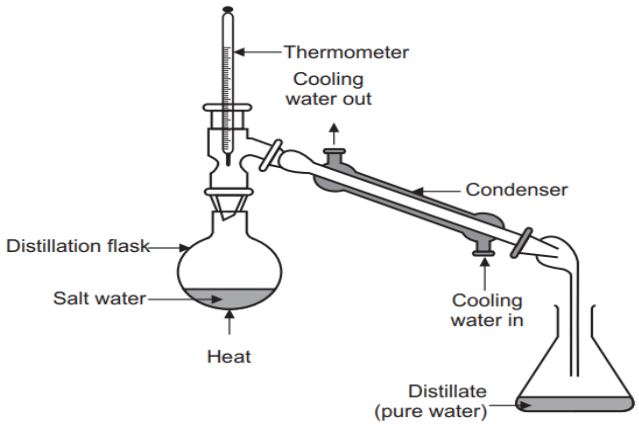


Figure 7.1

1. A heat source, which raises the mixture temperature.
2. A round-bottom boiling flask, which contains liquid mixture or "analyte".
3. A sand bath, which ensures even heating of your boiling flask.
4. A Vigruex column, which features internal "finger" structures that serve to collect vapors into liquid drops. These "fingers" primarily collect the trace vapors of the less volatile liquid(s), since they more easily condense. These drops then fall back into the analyte while the more volatile gas(es) pass into the condenser.
5. A thermometer, which allows close monitoring of the vapor temperature.
6. A condenser column, which features an external cold water jacket that cools the vapor, condensing it to a liquid. Importantly, this water jacket is completely separate from the vapor mixture, which flows through an internal tube.
7. A receiver joint, which delivers the condensed liquid to the receiving flask. It features an inlet that you can use to apply a vacuum, which is useful in some separations.
8. A receiving flask, into which the condensed liquid or "distillate" flows from the condenser.
9. The pure liquid is collected in the receiver kept at the open end of the condenser . The distillate contains pure liquid while impurities are left behind in the distallation flask.

   In this method mainly liquid mixture is taken in around bottom flask and heated carefully in an apparatus shown in figur 7.1.The liquid having lower boiling point will vapourize first and its vapours are condensed using a condenser and the liquid formed is collected. The vapours of higher boiling component form later and condensed seperately.

   The main object of simple distallation is to separate:

   - Volatile liquid from non – volatile impurities.
   - Liquid having sufficient difference in their boiling point.

This method can be used to separate a mixture of :

(i) Acetone (b.p 329 K) and water (b.p 373 K)

(ii) Chloroform (b.p 334 K) and aniline (b.p 457 K)

(iii) Benzene (b.p 353 K) and aniline (b.p 457 K)

(iv) Simple distillation is used to separate salt from seawater, to separate sugar from water and to separate ethanol from water in the production of hard liquor

7.5 DISTILLATION THEORY

Distillation is the process in which water vapors converts into volatile liquids and separate through selective boiling. It is carried out between liquids having different boiling points. This technique is useful in obtaining a pure liquid from non-volatile impurities or to raise the absorption of the specific component in a mixture. It's a reversible process, i.e., a physical process which means the process can be returned to the original state of matter. But dry distillation is a chemical process that includes the destructive distillation of solid products to convert them into gaseous products.

In this process the solution is heated at a selective boiling point where one of the components of the mixture turns into a gaseous state and is separated from the original solution. The condensed vapour is collected separately.

- A solution contained in a distillation flask with a thermometer to measure the temperature is heated till the boiling point.
- The vapours coming out of the flask are transferred to the condenser with entry and exit inlets for the water source as per requirement for the cooling process.
- As the vapours cool down through the condenser under the influence of a lower temperature due to cold water running around it, the distilled vapours are now known as distillate.
- This distillate is collected in a receiving flask to obtain the pure solution of the required material.

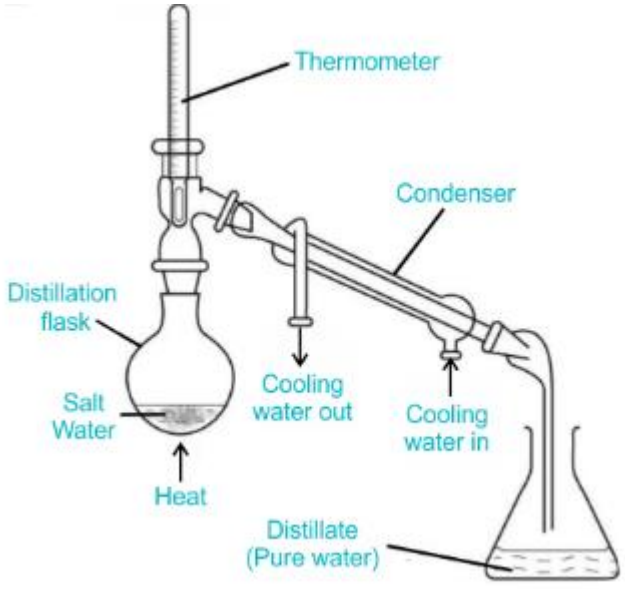


Figure 7.2

7.6 FRACTIONAL DISTILLATION

7.6.1 Principle : Fractional distillation is used to separate liquid mixtures where the compounds have similar boiling points and/or they are present in comparable amounts. If the boiling points of the two liquids are very close to one another, the separation cannot be achieved by a simple distillation method. It is because, with the boiling point of the more volatile liquid of the mixture, there will also be sufficient vapours of the less volatile liquid. As a result, both the liquids will distil together, and the separation will not be completed.The separation of such liquid mixture into individual components can be achieved by a process called fractional distillation, which involves repeated distillations and condensations.

7.6.2. Apparatus and procedures :

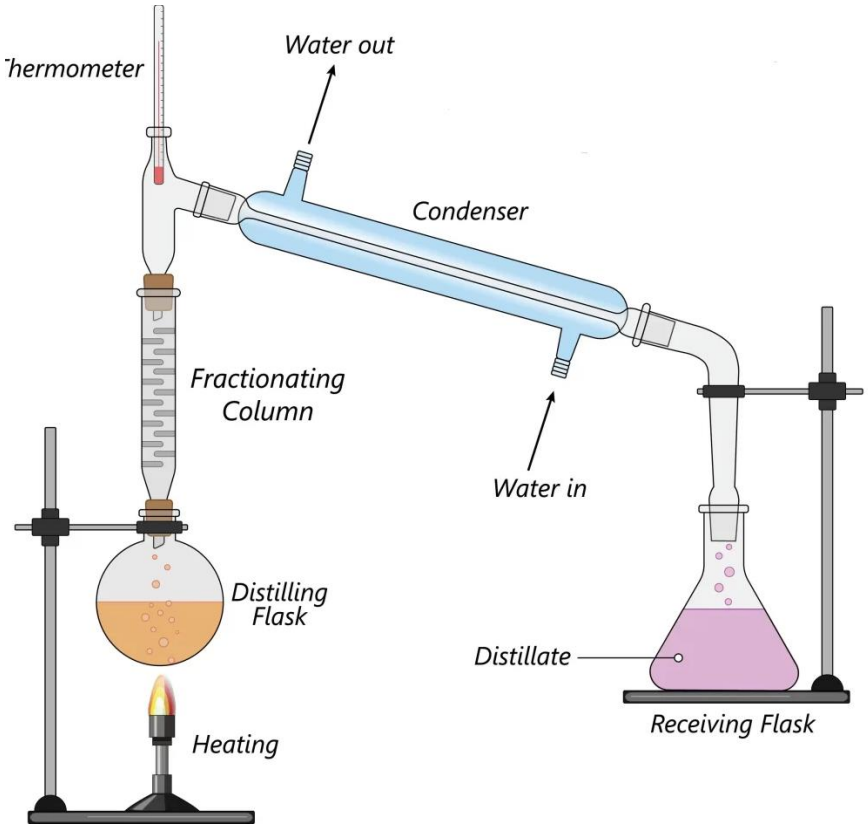


Figure 7.3 Fractional distillation

When the boiling point of two liquid close each other in this cases the process of simple distallation will fail because the vapour pressure of both liquids will be formed simultaneously and the distillate will also contain both of them.to solve the problem using fractionating columns. The fractionating column is along tube provided with obstructions to the passage of the vapours moving upwards and liquid moving downwards.

After setting the apparatus a mixture of two miscible liquids is prepared. In which one is more volatile liquid than other.The solution is added to the distilling flask while the fractionating column is is connected at the tip of the flask. A slow heat is applied to increase the solution temperature. In the flask vapours rise as the mixture then starts to boil. The vapour of the more volatile components (low boiling component) passing through the fractionating column .Due to the obstructions in the fractionating column, some of the condensing liquid in the fractionating column gets heat from the ascending vapours and vaporizes. As a result, the vapours become richer in low boiling component.These rise up in the fractionating column and condense while poassing through the condenser collected in the receiver .

Throughout the process, vaporization and condensation take place repeatedly until the two mixtures are separated completely.This method may be used to separate a mixture of :

i) Acetone (b.p 330 K) and methyl alcohol (b.p. 338 K)

ii) A mixture of Ammonia(239.8 K) and water (273 K).

7.6.3Advantages:

i) It is extremely easy to use.

ii) The liquids having very little difference in boiling points can be separated by this process.

iii) The fractionating column makes the separation of components easy.

iv) Readily purifies complex mixture.

7. 6.4 Disadvantages :

i) It consumes more energy, and the setup is complicated and costly.

ii) It cannot be used to separate miscible liquids, which form azeotropic mixtures.

iii) Takes longer time for liquids to distill.

7.7 DIFFERENCE BETWEEN SIMPLE DISTILLATION AND FRACTIONAL DISTILLATION :

The difference between Simple Distillation and Fractional Distillation is shown in the table added below:

Simple Distillation	Fractional Distillation
1. Simple distillation is used to separate a mixture of miscible liquids with sufficiently large differences in their boiling points.	1. Fractional distillation is used when the difference in boiling point is quite less.
2. It consists of simple apparatus with two flasks and a condenser.	2. It consists of more complex apparatus with a fractionating column.
3. Simple distillation process does not have to repeated.	3. Fractional distillation process has to be repeated several or many times to gets the pure liquid.
4.Solvent molecules can easily be separate from the solute.	4. Solvent molecules cannot be separate from the solute.
5.Purification of sea water	5. **Example:** Crude oil refining

7.8 VAPOUR PRESSURE LIQUID COMPONENT DIAGRAM

At any particular temperature the composition of the liquid phase is the same and the vapour phase composition shown the variability.Hence we find out different vapour pressure – vapoure composition curves for the two phases.At any particular temperature, these can be obtained by measuring the vapour pressure as well as the composition of the vapour phase corresponding to each of the liquid mixture.

For the real solution, there are following three types of vapour pressure- compostion diagrams :

Type I : Those in which total vapour pressure is intermediate between those of the pure components and do not show any maximum / minimum.

Type II : Those which show a maximum in total vapour pressure curve.

Type III : Those which show a minimum in total vapour pressure curve.

The vapour pressure liquid compostion curves as well as the vapour pressure- vapour composition curves of all the three types are given in **Figure 7.4**

It may be observed that in all three types , the vapour composition curve lies below the liquid composition curve.This is explained in each type :

- In type I , B is more volatile than A ,corresponding to composition a of the liquid phase, vapour phase will be richer in B i.e., corresponding to composition a′ .
- In type II, upon the point C, Behaviour is same as in Type I, at C , the liquid phase and the vapour phase have the same composition and after point C, the vapour phase is richer in A as seen from points c and c′ .
- In type III,upon the point D , the vapour phase is richer in A than the liquid phase, at the point D both have the same composition and after point D, the behaviour is similar to Type I.This can be seen from points d, d′, e, e′.

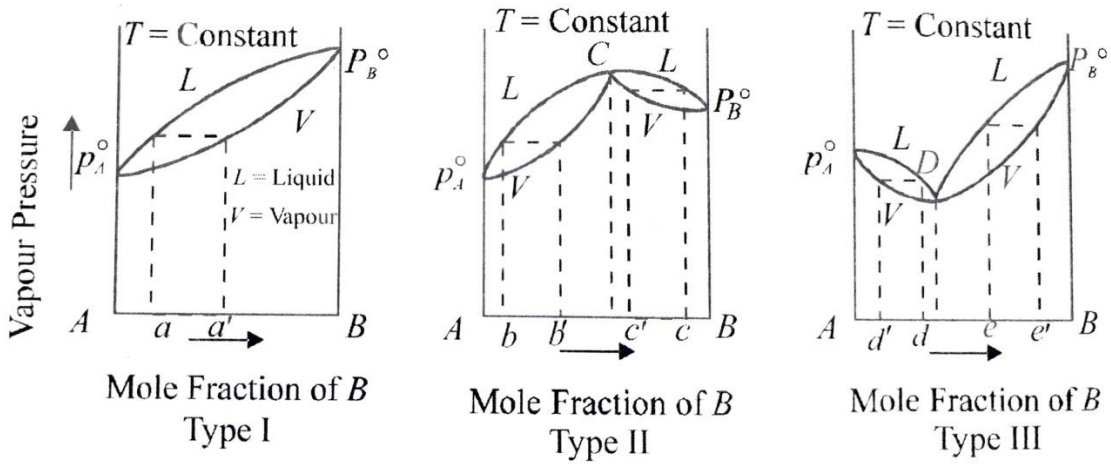


Figure 7.4 Vapour pressure composition diagram of binary miscible real solution at constant temperature.

7.9 RAOULT'S LAW

The term "ideal solution" refers to a solution that follows Raoult's law. This law only applies to dilute solutions, while some liquid combinations follow it throughout a wide range of concentrations. Raoult's (1886) gave a quantitative relationship between the partial pressures and the mole fraction of component. This relationship is known as Raoults law.

7.9.1 Raoults law for Volatile solutes:

According to this law , "The solvent's partial vapour pressure in a solution (or mixture) is equal or identical to the vapour pressure of the pure solvent multiplied by its mole fraction in the solution". Mathamatically, Raoult's law equation is expressed as :

$$P_{solution} = P^0_{solvent} . X_{solvent}$$

Where,

$P_{solution}$ = vapour pressure of the solution

$X_{solvent}$ = mole fraction of the solvent

$P0_{solvent}$ = vapour pressure of the pure solvent

Let us consider, a solution of volatile liquids A and B in a container and the mole fraction of A and B x_A and x_B respectively. If p_A and p_B are the vapour pressures of the components in the solution, then according to Roult's law,

$$p_A = p_A^0 x_A$$

$$p_B = p_B^0 x_B$$

where, p_A^0 p_B^0 is the vapour pressure of pure A and B at same temperature.

According to Dalton's law of partial pressure the total pressure exerted by a mixture is equal to the sum of the partial pressures of the component of the solution. This is given as:

$$P_{total} = p_A + p_B$$

Substituting the values of p_A and p_B , we get

$$P_{total} = p_A^0 x_A + p_B^0 x_B$$

We know that, $x_A + x_B = 1$, or $x_A = 1 - x_B$

Now, $P_{total} = p_A^0 (1 - x_B) + p_B^0 x_B$

$$P_{total} = p_A^0 + (p_B^0 - p_A^0) x_B$$

The above equation conclude that,

i) The total vapour pressure of the solution can be related to the mole fraction of any one component i.e . $(1 - x_B)$ or x_A

ii) The total vapour pressure of the solution varies linearly with the mole fraction of component B because p_A^0 and p_B^0 are constant.

Raoult's law equation shows that total vapour pressure is linear function of the mole fraction x_B (x_A as $x_A = 1 - x_B$) because p_A^0 and p_B^0 are constant at a particular temperature.This is shown in Graphical presentation of raoults law : **Figure 7.5**

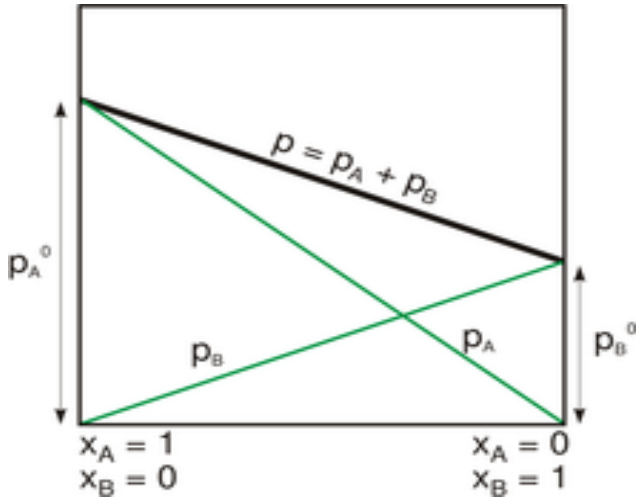


Figure 7.5: Vapour pressure behaviour of liquid – liquid solution of two volatile components obeying Raoult's law

Limitation of Raoult's law :

i) This law applicable to very dilute solution.

ii) This law is applicable to ideal solution.

iii) When the solute particles associate or dissociate this law is not applicable.

iv) This law applicable to solution , whose heat of dilution does not change.

7.9.2 Raoults law for Non-Volatile solutes: For solution containing non volatile solutes,only the solvent molecules are present in vapour phase ,Therefore, the vapour pressure of the solution will be the vapour pressure due to solvent only.

Vapour pressure of the solution = Vapour pressure of the solvent in the solution

If , p_A = Vapour pressure of the solvent

x_A = Mole fraction of non volatile solute

Then according , to Raoult's Law, the vapour pressure of the solvent in the solution ,

$$p_A = p_A^0 x_A$$

Thus for solution containing non volatile solute, the Raoult's Law stated as :

"At a given temperature, the vapour pressure of a solution containing non – volatile solute is directly proportional to the mole fraction of the solvent ."

The above relationship are rearranged then, we get ,

$$\frac{pA}{pA\,0} = x_A$$

Subtracting ach side of the equation from 1 , we have

$$1 - \frac{pA}{pA\ 0} = 1 - x_A$$

$$\frac{pA\ 0 - pA}{pA\ 0} = x_B \qquad (x_A + x_B = 1) \text{ or } (1 - x_A = x_B)$$

$$\frac{P\ 0\ Solvent - P\ 0\ Solution}{P\ 0\ Solvent} = x_{solute}$$

Hear, the difference between in vapour pressure of pure solvent and solution represent the lowering in vapour pressure on the formation of solution.Now lowering in vapour pressure with respect to vapour pressure of pure solvent, we get relative lowering in vapour pressure.Thus the Raoult's Law stated that,

" The relative lowering in vapour pressure of an ideal solution containing the non- volatile solute is equal to the mole fraction of the solute at a given temperature."

7.9.3 Deviation from Raoult's Law :

Deviation from Raoult's Law occure for non-ideal solutions.On the basis of nature of solution there are two types of deviation in Raoult's Law that is:

Positive Deviation From Raoult's Law : Consider a binary solution have two component A and B.When the attraction forces between A-A and B-B (same component) are stronger than A-B (Different component) .As a result escaping tendency of A and B component of the solution has a partial vapour pressure greater than expected on the basis of Raoult's Law. i.e

$$p_A > p_A^0 x_A \quad \text{,or} \quad p_B > p_B^0 x_B$$

Some example which shown the positive deviations:

Benzene (C_6H_6) and acetone (CH_3COCH_3)

a) Ethyl alcohol (C_2H_5OH) and Water (H_2O)
b) Acetone (CH_3COCH_3) and Ethyl alcohol (C_2H_5OH)

Negative Deviation From Raoult's Law: In such solution, when attraction forces between A-B (Different component) is stronger than between A-A and B-B pairs (same component).Due to stronger A-B interaction , the escaping tendency of A and B component from the solution becomes less than from pure liquids. i.e

$$p_A < p_A^0 x_A \quad \text{or,} \quad p_B < p_B^0 x_B$$

Some example which shown the negative deviations:

a) Acetone (CH_3COCH_3) and Chloroform ($CHCl_3$)

b) Water (H_2O) and Nitric acid (HNO_3)

c) Water (H_2O) and Acetaldehyde (CH_3CHO)

7.10 TYPES OF FRACTIONATING COLUMNS

A fractionating column or fractional column is an essential item used the distillation of liquid mixtures to separate the mixture into its component parts, or fractions, based on the differences in volatilities.There are two main types of industrial fractionating columns:

a) Tray (Plate) columns

b) Packed columns

a)Tray (Plate) columns :

i) In plate column , liquid flows downward via gravity and gas flows upward (countercurrent flow)

ii**)** In the simplest case, there is only one feed stream and two product streams(top and bottom)

iii)Trays (Plates) divide the column into stages. The process is a stagewise contact operation.

iv) The most common types of trays are bubble- cap, sieve and valve trays.

v)Liquid flows through downcomers from one tray to the lower one.

vi)Gas liquid contact occurs in the trays.

b) Packed columns :

i)In a packed column, the gas and liquid flow up and down in continuous (not stagewise) way.

ii)Column is filled with suitable packing materials to provide a lage contacting area between the phases.

iii)Packung materials can be divided into three catagories:

- Random packing (Just dumped into the shell)
- Structured packing
- Grid packing

7.10.1. Advantage of Plate and Packed column:

Plate column :

1.Plate column can handle wide range of gas and liquid flow rates.

2.Plate column operation is considerably smooth.

3. Plate column can be provided cooling arrangements.

4.Plate efficiency can be predicted more accurately.

5. Plate column provide stage wise contact.

Packed column:

1. Packed column provides continuous contact between the vapor and liquid phases.
2. Packed columns are particularly useful in the field of vacuum distillation.
3. Packed columns are more suitable for low capacity operations.
4. Total weight of packed column is less due to use of low weight and high capacity packing.
5. Packed columns are useful For separating heat sensitive materials

7.10.2 Disadvantage of Plate and Packed column :

Plate column :

1.For corrosive liquids, cost of plate column is too high.

2.Liquid hold up is very high. Therefore pressure drop is very high.

3. Supporting structure is very costly.

Packed column:

1.Packed columns are not suitable for very low liquid rates.

2. Removal of side stream is not possible in packed column.

3. Provision of cooling arrangement is difficult in packed columns.

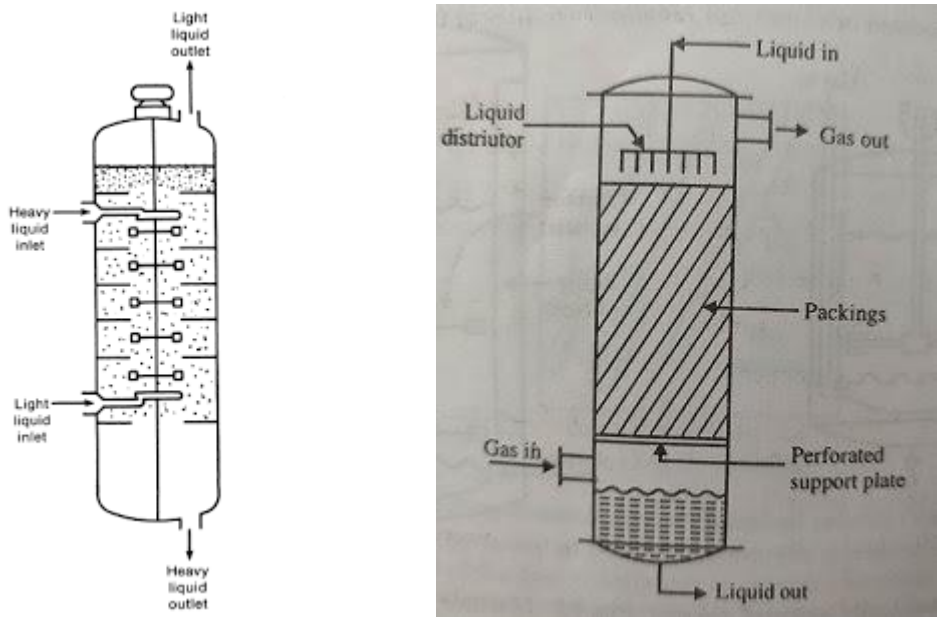


Figure 7.6

7.11 COLUMN EFFICIENCY

In the design of a distillation column, it is necessary to determine the column diameter and the column height for economic considerations. When determining the column height, the required theoretical number of stages is generally determined from the results of vapor-liquid equilibrium calculations, but in order to determine the actual column height, it is necessary to determine the column efficiency and the stage efficiency.

- Efforts have been made to estimate this efficiency empirically or theoretically (semi- theoretically), but highly accurate correlations have not yet been established.
- In the case of a tray-type distillation column, vapor-liquid contact occurs on the tray, and heat and mass transfer occur.
- However, since the contact time of the vapor and liquid is short, the number of stages required is greater than the theoretical number of stages obtained by assuming that equilibrium is reached.
- A measure of the deviation from such vapor-liquid equilibrium is the stage efficiency (plate efficiency, tray efficiency), and the following three types are generally used

  1)Overall stage efficiency (column efficiency)

  2) Point efficiency

  3) Murphree efficiency

  Column efficiency (EO) is expressed as the ratio of the number of theoretical stages to the number of actual stages, and if this value is known, the number of actual stages can be determined.

$$E0 = \frac{Number\ of\ theoretical\ stages}{Actual\ Number\ of\ Stages}$$

- Although it is extremely convenient for practical use and widely employed, it is in fact given empirically without any theoretical basis.

- The column efficiency of industrial tray columns is said to be about 60 to 90% for light hydrocarbons and water systems, and about 10 to 20% for gas absorption and diffusion.
- In particular, as a rough guideline, in the case of bubble-cap columns, the following values have been considered: 80% for high pressure columns, 60% for normal pressure columns, and 40% for vacuum columns.

Importance of column efficiency : The efficiency of a distillation column directly impacts the purity of the products obtained. Higher efficiency means better separation, resulting in purer products.

7.12 AZEOTROPES

An azeotrope is the mixture of the vapor phase and liquid phase that exhibits the same concentration. In simple words, it is a liquid containing a mixture of two liquids that contain the same concentration of liquid phase and vapor phase. Azeotropes are known to have either a low boiling point or high boiling point for one of their components. This liquid mixture also has a constant boiling point, and the fraction of mixed liquids cannot be altered by simple distillation..

Thus , The solution (Liquid mixtures) which boil at constant temperature and can distil unchanged in composition are called azeotropes or azeotropic mixtures (Greek meaning boiling without change). Thus the azeotropes distil over as if they were pure liquids.

For Example: Some compounds like Toulene, Benzene and Cyclohexane foem azeotropes with the mixture.

7.12.1.Types of azeotropes :

The azeotropes are mainly following types :

a)Minimum boiling azeotropes : In minimum boiling azeotropes :

i) The solution shown positive deviation through Raoult's Law.

ii) In this solution shows a boiling point lower than of all its constituents.

iii)They exhibit the highest vapour pressure and have the lowest boiling point.

iv) An example mixture of ethanol and water has shown positive deviation , minimum boiling azeotropes with large concentraction of ethanol (96%) and a lower concentration of water(4%).

v) Ethanol boils at 351.5 K , water boils at 373K , but the azeotrope boils at , which is lower than either of its constituents.It shown 351 K is the minimum temperature at which any ethanol/water solution can boil at atmospheric pressure , is the example of minimum boiling azeotropes.

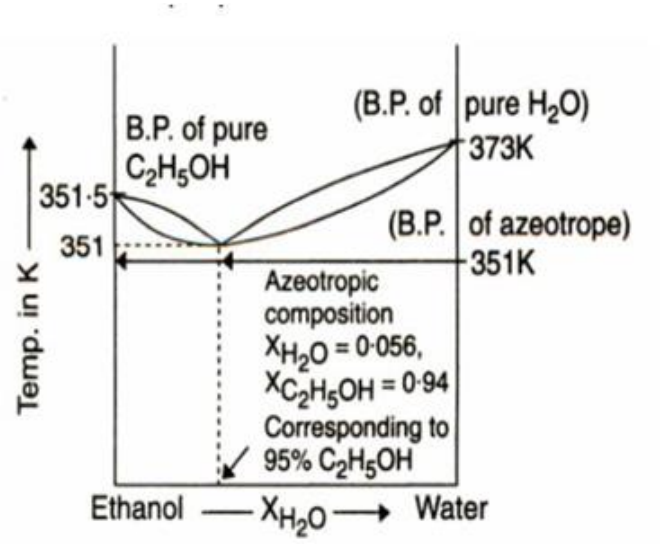


Figure 7.7: Boiling point diagram of ethanol water mixture

b) Maximum boiling azeotropes : In maximum boiling azeotropes:

i) The solution shown negative deviation through Raoult's Law.

ii) In this solution shows a boiling point higher than of all its constituents.

iii) They exhibit the lower vapour pressure and have the highest boiling point.

iv) An example mixture of HCl and H_2O has shown negative deviation , maximum boiling azeotropes at a concentration of 20.3%of HCl and 68.8% HNO_3 (by mass).

v) Nitric acid boils at 359K and water at 373K , but the azeotrope boils at 393.5K, which is higher than either of its constituents. The maximum boiling point of any nitric acid acid solution is 393.5K, is the example of maximum boiling azeotropes.

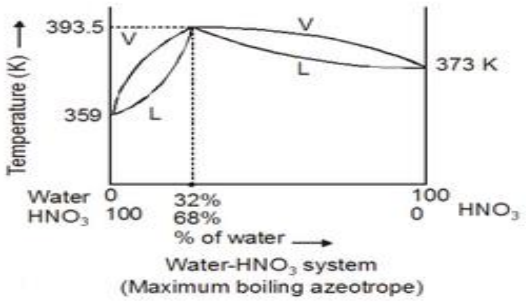


Figure 7.8: Boiling point diagram of nitric acid water mixture

c) Heterogeneous Azeotropes : If constituents of azeotropic mixtures not completely mixed each other , and can also be found inside the miscibility gap.

For example: When the mixture of chloroform and water are shaken together and left to stand then form two separate layers.This mixture boils at 326 K while the boiling point of water is 373K and chloroform is 334 K.

d) Homogeneous Azeotropes : Homogeneous Azeotrope is an azeotropic mixture in which the constitutions of mixtures are completely miscible. For example, any amount of ethanol can be mixed with any amount of water to form a homogeneous azeotropic mixture.

e) Binary azeotrope : It is an azeotropic mixture which containing two constituents.

For example: The mixture of 1.2% water and 98.8% diethyl ether.

The mixture of ethyl alcohol 96% and water 4%

f) Ternary Azeotropes – Azeotropes consisting of three constituents are called ternary azeotropes. For example, an azeotropic mixture of acetone, methanol, and chloroform.

7.13 SUMMERY

In this unit briefly discuss about Distillation process. Distillation is a very effective method of separating the constituent parts of a mixture.In this chapter we learnt about, If the boiling points of the two liquids are very close to one another, the separation cannot be achieved by a simple distillation method , in this case fractional distillation must be used.We also understand how many types of packing column are used for distillation process.With the heip of Roults law we are find out *the nature as well as the properties of a solution*. In simple term this unit also explain the , azeotrope mixture of liquids has an identical composition to the liquid mixture, despite the constant boiling point for both liquid and vapour.

7.14 TERMINAL QUESTIONS

A.Multiple choice questions:

1. What are the two processes in distillation?

a) Distilling and freezing b) Distilling and condensation reflux

c) Freezing and condensation reflux d) Only condensation reflux

2. What is the distillate in distillation?

a) Vapor collected from the mixture b) Liquid present in the distillation column

c) Vapor introduced during distillationprocess d) Liquid introduced during distillation process

3. Fractional distillation method is used for purification of liquids when there is a :

a)Small difference (less than 25^0C) in their boiling points.

b) large difference (greater than 25^0C) in the boiling points of liquid.

c) Small difference in their Melting points.

d)None of the above

4. According to Raoult's law the partial vapour pressure of each component in the solution is directly proportional to its :

a)Volume b) Density c)Molality d) Mole fraction

5. Raoult's law work only on:

a) Atoms b) Molecules c) Ideal mixtures d)Perfect gas

6. Azeotropic mixture are:

a) Boil at different temperature b)Mixture of solid

c) Constant boiling mixture d) Gaseous mixture

7. An azeotropic solution of two liquids has boiling point lower than either when it :

a) Shows a negative deviation from Raoult's law

b) Shows a no deviation from Raoult's law

c) Shows a positive deviation from Raoult's law

d) Solution is saturated.

8. Which of the following solution shows positive deviation from Raoult's law :

a) Acetone + Aniline b) Acetone + Ethanol

c)Water + Nitric acid d) Chloroform + Benzene

9. Which of the following solution shows positive deviation from Raoult's law :

a) Acetone and chloroform b)Benzene and Toluene

c) Acetone and carbondisulphite d) Ethanol and cyclohexane

10) Solutions which show positive or negative deviation from the Raoult's law are called

a)Ideal solutions b) Non ideal solutions

c True solutions) d)Homogenous solutions

11) Relative lowering of vapour pressure of a solution containing a non – volatile solute is equal to the mole fraction of ;

a) Solute b)Solvent c) Solvent minus solute d) Solvent plus solute

12) What apparatus is used in distillation?

a) Distillation flask, column b) Distillation flask, condenser

c) Condenser, collection vessel d) Distillation flask, condenser, collection vessel

13) What is the distillate in distillation?

a)) Liquid present in the distillation column

b Vapor introduced during distillation process

c) Liquid introduced during distillation process

d) Vapor collected from the mixture

14) Distillation does not involve in one of the following processes

a) Evaporation b) Extraction c) Purification d) Separation

15) Which part in the distillation apparatus represents the heat exchanger?

a) Condenser b)Adapter c)Receiver d)Still

B.Long Question:

1. Draw the fundamental setup for fractional distillation also explain the methods by which two liquid will be fractionalily distilled ?
2. What are fractional column ? Explain the Plate and Packed column with suitable diagram?
3. Define the advantage and disadvantage of Plate and Packed column ?
4. Define Raoult's Law for (a)Volatile solute (b) Non volatile solute

   Also write down the limitation of Raoult's Law?

5. Calculate the vapor pressure of a mixture containing 252 g of n-pentane (Mw = 72) and 1400 g of n-heptane (Mw = 100) at 20°C. The vapor pressure of n-pentane and n-heptane are 420 mm Hg and 36 mm Hg respectively. (Ans = 112.8 mm)
6. What are azeotropic mixture ? Define its type with suaitable example.
7. Define the positive and negative deviation according to Raoult's Law?
8. Explain the vapour pressure liquid component diagram of binary miscible real solution
9. Define the theory of distillation with suitable diagram ?

ANSWERS:

1) b 2) a 3) a 4) d 5) c 6) c 7) c 8) b 9) a 10) b

11) a 12) d 13) d 14) b 15) a

7.15 REFERENCES AND FURTHER STUDIES

1. Chemistry for Degree Students B.Sc. Third Year By R. L. Madan 2010, S Chand & Company pvt.
2. Principles of Mass Transfer and Separation Process Internet Archive https://ia800602.us.archive.org › B.K Dutta.pdf
3. Wikipedia https://en.wikipedia.org › wiki › Azeotrope .
4. Essentials of Physical ChemistryB.S. Bahl, G.D. Tuli, Arun Bahl.

BLOCK 2: SEPERATION TECHNIQUES

UNIT 8: GENERAL ASPECTS OF CHROMATOGRAPHY

CONTENTS:

8.1 Introduction
8.2 Objectives/Learning outcomes
8.3 Chromatography
8.4 General Principles
8.5 Classification of chromatography
8.6 Theory of chromatography
8.7 Efficiency of chromatographic techniques
8.8 Mechanism of seperation
8.9 Summary
8.10 Bibliography
8.11 Terminal questions

8.1 INTRODUCTION

In this unit we will cover the general aspects of chromatography. The unit will begin with a discussion on general principle and classification of chromatographic methods. We will also explain the theory of chromatography as well as the efficiency of the chromatochraphic technique. The mechanism of seperation will also be discussed and the development of the chromatograms will be explained. We will also discuss the characteristics of the stationary, mobile phase and other terminology used in the chromatography.

8.2 OBJECTIVES

After studying this unit you should be able to

- Understand the fundamental concepts of separation technique-Chromatography
- General principles behind chromatographic separations
- Various types of chromatography
- Efficiency of chromatographic techniques
- Method involved in the development of chromatogram

8.3 CHROMATOGRAPHY

Chromatography is one of the most widely used methods of separation in the analytical chemistry. It allows the components in a mixture to be separated based on their interaction

properties with stationary phase and mobile phase. The name “chromatography” comes from two Greek words: chroma, which means color, and graphein, which means to write. It was originally used to separate and identify the pigments in plants, hence the name.

The basic principle of chromatography involves the distribution or partition of components between two phases: a stationary phase and a mobile phase. The stationary phase is typically a solid or a liquid supported on a solid, while the mobile phase is a liquid or gas. As the mixture is introduced into the system, the different components interact differently with the stationary and mobile phases, leading to their separation over time. “Thus chromatography may be defined as a method of separating a mixture of components into individual components through equlibrium distribution between two paases”.

It is an analytical method used to separate and analyze complicated mixtures, identify individual molecules, and purify substances. It is used in many different fields of science, such as Chemistry, Biochemistry, Pharmacology, Environmental Science, and Food Science.

8.3.1 History of Chromatography

The history of chromatography dates back to the early 20th century, and its development has been a result of contributions from various scientists. Chromatography is a technique used for separating and analyzing mixtures of compounds based on their differential affinities for a stationary phase and a mobile phase. Here is a brief overview of the key milestones in the history of chromatography:

- **Michael Tswett (1903):** Russian scientist Michael Tswett is credited with the discovery of chromatography. In 1903, he separated plant pigments using a column of calcium carbonate, marking the first application of chromatography. He called the technique "chromatography" from the Greek words "chroma" (color) and "graphein" (to write), emphasizing its application to separate pigments.
- **Richard Synge and Archer Martin (1940s):** British biochemists Richard Synge and Archer Martin developed paper chromatography, for which they were awarded the Nobel Prize in Chemistry in 1952. Paper chromatography involved using a strip of paper as the stationary phase, and gas-liquid chromatography utilized a liquid stationary phase coated on a solid support.
- **Colin F. Poole and Paul J. W. Dearden (1950s-1960s):** Their work focused on the development of high-performance liquid chromatography (HPLC), which involves the use of a liquid mobile phase and a solid stationary phase. This method greatly improved the speed and efficiency of chromatographic separations.

- **Martin and James (1952):** Raymond D. Martin and A. T. James introduced a technique known as partition chromatography, which laid the foundation for liquid-liquid chromatography. This technique uses a liquid stationary phase coated on a solid support.
- **Gas Chromatography (1950s):** The development of gas chromatography, which uses a gaseous mobile phase and a liquid or solid stationary phase, was a significant advancement. This technique became widely used for the separation and analysis of volatile compounds.
- **Advancements in Instrumentation (1960s-1970s):** The development of more sophisticated instrumentation, including detectors and columns with improved resolution, greatly enhanced the capabilities of chromatography. This period saw the widespread adoption of gas chromatography and the continued refinement of HPLC.
- **Liquid Chromatography-Mass Spectrometry (LC-MS) (1970s):** The combination of liquid chromatography with mass spectrometry (LC-MS) became a powerful tool for identifying and quantifying compounds in complex mixtures. This hybrid technique is widely used in various scientific disciplines.
- **Advancements in Column Technology (1980s-1990s):** Continued improvements in column technology, including the development of new stationary phases and column geometries, further enhanced the efficiency and selectivity of chromatographic separations.
- **Ultra-Performance Liquid Chromatography (UPLC) (2000s):** UPLC represents a more recent advancement in liquid chromatography, offering higher resolution and faster analysis times compared to traditional HPLC.

8.3.2 General terms used in chromatography

- **Chromatography:** A physical separation method in which the components to be separated are distributed between two phases, one stationary (stationary phase) and the other (mobile phase) moving in a specific direction.
- **Chromatogram:** A chromatogram is a graphical representation of eluents, concentration of analytes or other quantity versus volume or time. It can be used to identify compounds and determine their relative concentrations in a mixture.
- **Stationary phase**: Stationary phase is the phase over which the mobile phase passes in the technique of chromatography. It may be solid (e.g., glass, silica, or alumina),

liquid that is packed into a glass or metal tube or that constitutes the walls of an open-tube capillary.

- **Mobile phase:** A fluid which flows through or along the stationary phase, in a specific direction. It may be a liquid (liquid chromatography) or a gas (gas chromatography) or a supercritical fluid (supercritical-fluid chromatography)
- **Analyte:** Analyte is the substance that is to be separated from the mixture during chromatography
- **Eluent:** Eluent refers to the fluid that enters and passes through the chromatographic column.
- **Elute:** Elute is the fluid containing the sample that exits the chromatographic column
- **Elution:** Elution is the process of removal or extraction of a solid by washing out it with a suitable solvent in a chromatographic column.
- **Column:** The column is the part of the chromatographic system where the separation of components occurs. It contains the stationary phase.
- **Retention factor (R_f):** The Rf is a ratio that represents the distance traveled by a compound relative to the distance traveled by the solvent (mobile phase).
- **Retention time (t_R):** Retention time refers to the time it takes for a particular compound to travel through a chromatographic column and reach the detector.
- **Peak:** A peak is a distinct raised portion of a chromatogram that corresponds to a specific component of the sample.
- **Peak width:** Peak width refers to the width of a peak at its base and is an important parameter in evaluating the efficiency of a chromatographic separation.
- **Resolution**: Resolution is the ability of a chromatographic method to separate and distinguish between different components in a mixture. Resolution is typically assessed by considering the separation of adjacent peaks in a chromatogram. The higher the resolution, the better the separation of components.
- **Detector:** The detector is the instrument that measures the concentration of the separated components as they elute from the chromatographic column.

8.4 GENERAL PRINCIPLES

Chromatographic separation involves a dynamic and rapid equilibrium of analyte molecules between stationary phase and mobile phase. Analyte molecules can be found in two states: bound state, where they are adsorbed on the surface of the solid stationary phase, or free state,

where they are completely dissolved in the liquid or distributed in the gaseous mobile phase (Figure 8.1). The equilibrium between the free and absorbed states depends on polarity and size of the molecule, stationary phase and solvent.

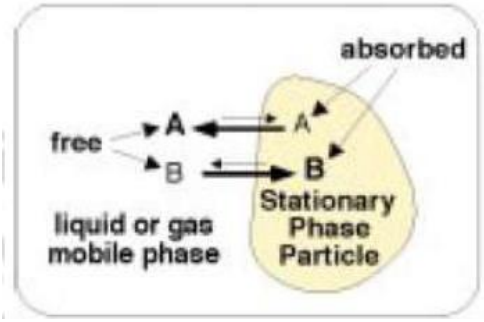


Figure 8.1: Distribution of analyte molecules A and B between stationary phase and mobile Phase

The size, shape and polarity of the molecules is their characteristic feature and is determined by their chemical structures. The equilibrium between the free and absorbed states of analyte molecules can be changed by selecting different stationary and mobile phases. From Figure 8.2, if the molecules of A compound dissolve faster, they tend to spend more time in the mobile phase. These molecules are thus carried faster through the stationary phase and move to larger distance in the given time. Conversely, the molecules of compound B are bound to the stationary phase with greater strength than A and they spend lesser time in the mobile phase. Therefore B molecules migrate through the stationary phase slowly and will not move as far as A in the same time.

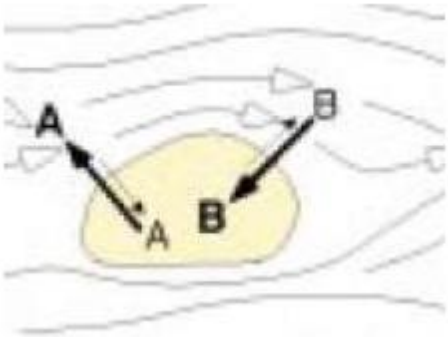


Figure 8.2: Dynamic equilibrium of A & B between mobile and stationary phase

Chromatography is a dynemic separation technique used to separate and analyze mixtures of compounds/analyte based on their differential distribution or partition between a stationary phase and a mobile phase. An analyte is in equilibrium between the stationary and mobile phase, then equlibrium represented as:

$$A_{mobile} \rightleftharpoons A_{stationary}$$

$$K = \frac{Cs}{Cm}$$

Where

K= Concentration of the analyte in the stationary and mobile phase (equilibrium constant)

Cs=Concentration of the analyte in stationary phase

Cm= Concentration of the analyte in mobile phase

The equilibrium constant, K is defined as the ratio of analyte in the stationary phase in molar concentration to the analyte in the mobile phase in molar concentration. This is also known as the distribution/ partition coefficient. The partition coefficient/ distribution cofficient is a measure of the distribution of an anylyte between the stationary phase (often a solid or liquid) and the mobile phase (usually a liquid or gas).

A higher partition coefficient indicates a greater affinity of the solute for the stationary phase, resulting in slower movement through the chromatographic system. Conversely, a lower partition coefficient suggests a stronger affinity for the mobile phase, leading to faster migration

Summarizing it all, higher the adsorption to the stationary phase, the slower will the molecule move through the column. Conversely, higher the solubility in the mobile phase, the faster will the molecule move through the column. Adsorption and solubility of molecules can be manipulated by choosing the appropriate stationary phase and mobile phase to obtain good separation. The differential distribution of different components of the sample mixture, between the mobile and stationary phases, determines the rate of migration of these compounds and results in their separation from each other.

8.5 CLASSIFICATION OF CHROMATOGRAPHY

Chromatographic methods are analytical techniques widely employed in various scientific and industrial fields, including chemistry, biochemistry, pharmaceuticals, environmental science, and more. There are several types of chromatography, and they can be classified based on various criteria, listed as follows:

- Purpose of chromatography experiment
- Shape/ Geometry of stationary phase and support used
- Physical states of stationary phase and mobile phases.
- Mechanism of separation used

- Polarity of stationary phase and mobile phase used

Chromatographic methods classified on each basis are:

1. On the basis of purpose of chromatography experiment

(a) Preparative chromatography: This type of chromatography is meant to separate the components of a mixture for further use and is thus a form of purification. The separated compounds are often pure and may be used for quantification or other applications. Thus the preparative chromatography is used to purify and isolate larger quantities of individual components for further use. Example: High Performance liquid chromatography (HPLC) and Supercritical fluid chromatography (SFC)

(b) Analytical chromatography: This type of chromatography is used to separate, identify and quantify the analytes in the given sample. The sample size applied to the chromatographic system is very small. It is basically used for qualitative and quantitative analysis of chemical or biological compounds in industry and academia. Example: HPLC, Thin layer chromatography (TLC), Gas chromatography (GC)

2. On the basis of shape of stationary phase and support

Depending upon the type of stationary support or more accurately the shape of the stationary support, chromatographic technique can be twodimensional or three-dimensional.

(a) Planar chromatography (Two dimensional chromatography): In this type of chromatography, the stationary phase is a planar surface and the chromatogram development is a two dimensional. The stationary phase may be the paper or the adsorbent/solvent coated on a glass plate. It is form of liquid chromatography in which the mobile phase moves through the stationary phase by capillary action and/or by gravity. Example: Paper chromatography and Thin layer chromatography (TLC).

(b) Column chromatography (Three dimensional chromatography)- In this chromatographic techniques stationary phase is filled in a tube or column which is three dimensional in shape and the separation is achieved on the basis of different retention time or differential partition of analytes between mobile phase and stationary phase. The stationary phase may be packed inside the column completely (packed column) or may stick to the walls of the column allowing the passage for mobile phase (open tubular column). Column chromatography is used to purify compounds depending on their polarity or hydrophobicity. Examples: HPLC and GC.

3. On the basis of physical state of stationary phase and mobile phases

Depending upon the physical state of stationary phase and moblie phases are soild, liqiud or supercritical fluid, and gas the chromatographic techniques can be classified as:

(a) Solid-Liquid Chromatography: In this chromatography, the stationary phase is an active solid (e.g. silica, alumina or a polymer) and mobile phase is liquid, and the separation is based on adsorption affinities between the sample molecules and the surface of the active solid. The sample/analyte is adsorbed on the solid stationary phase material and separation occurs on the basis of differential solubility of analytes in the mobile phase. Example: Ion exchange chromatography (IEC), Thin layer chromatography (TLC), High Performance liquid chromatography (HPLC), High Performance Thin layer chromatography (HPTLC).

(b) Liquid-Liquid Chromatography: In this chromatographic method, both the stationary and mobile phase is liquid but differs in their polarities/immiscible liquid. In which one phase being the mobile carrier and the other being the thin liquid layer supported on the inert stationary phase. The separation occurs on the basis of difference in partition coefficients of analytes in the two phases. Example: Partition chromatography, Paper chromatography

(c) Gas-Solid Chromatography (GSC): In this chromatographic technique the stationary phase is an active solid adsorbent and inert gas like helium is used as the mobile phase or carrier gas. It is used for the seperation and identification of volatile component in a mixture, gases and small polar molecule. Example: Gas chromatography (GC)

(d) Gas-Liquid Chromatography (GLC): In this chromatographic technique the mobile phase is the gaseous state (inert gas) and stationary phase is in the liquid state (nonvolatile liquid) coated as a thin layer on an inactive solid support or on the inside walls of the capillary tube. The compounds are separated according to their partition-coefficients. GLC is used for the analysis of sterols, hydrocarbons, pesticides.

4. On the basis of principle of separation/mechamism of separation:

According to mechanism involved in the seperation or interaction of analyte with stationary and mobile phase the chromatographic techniques classified as:

(a) Adsorption Chromatography: In adsorption chromatography, the stationary phase is a solid and mobile phase is either a liquid or a gas. The seperation is based on the

differential adsorption of solute/molecule onto the soild stationary phase (silica, alumina) and the solubility in mobile phase (polarity of mobile phase). The compounds are adsorbed on the solid stationary phase through various interactions like covalent bonding and electrostatic attraction. Example: Coulmn chromatography, HPLC, GC, TLC

(b) Partition Chromatography: In partition chromatography the mobile phase is either or gas while stationary phase is a liquid supported on an inert solid. The separation occurs as the components/compounds of the sample partition between the mobile and stationary phases based on their relative affinities for each phase. Example: Paper chromatograhy, GLC.

(c) Ion Exchange Chromatography: This chromatographic technique used for separating and purifying charged molecules based on their interactions with charged groups immobilized on a solid stationary phase. The separation is achieved through reversible exchange of ions between the stationary phase (resin or gel functionalized with cationic or ionic groups) and the mobile phase (buffer solution). The buffer serves to weaken the electrostatic interactions between the analyte and the resin and elutes it out at a particular pH.

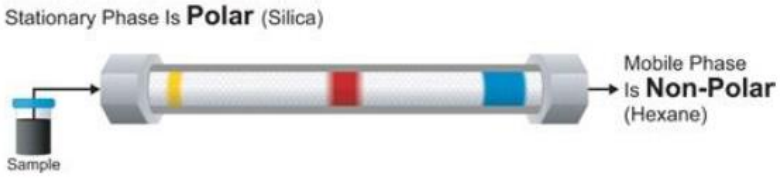
(d) Molecular Exclusion Chromatography: It is also known as size exclusion chromatography or gel filtration chromatography and the separation ocuurs on the basis of molecular size of the molecule. The stationary phase is a porous matrix of beads or gel with specific pore size. As the mobile phase (buffer solution) passes through a porous gel, larger solute molecules pass through the pores while smaller molecules are entrapped in the pores of gel beads. Consequently larger molecules to pass through the column at a faster rate than the smaller ones, and thus the compounds are separated on the basis of their molecular size. It used for the molecule like proteins, nucleic acids, and polysaccharides.

(e) Affinity Chromatography: It is highly selective type of chromatography that is based upon the specific interaction between the analyte molecule and another compatible molecule immobilized on a stationary phase. For example, for separation of antigens, an antibody may be immobilized on a matrix that forms a stationary phase. When sample consisting of a mixture of proteins is passed through the column, only the specific antigen is bound to the antibody immobilized on the stationary phase. This antigen can be extracted either by changing the ionic strength / pH or through dialysis.

5. On the basis of polarity of stationary phase and mobile phase used

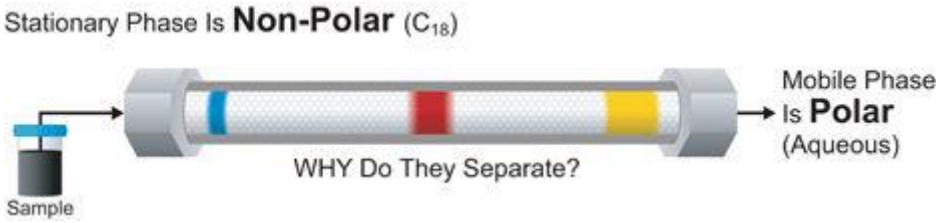
According to polarity of stationary and mobile phase the chromatographic techniques classified as:

(a) Normal phase chromatography: In this chromatographic technique, mobile phase is in non-polar solvent (hexane, chloroform, diethyl ether) and the stationary phase is polar in nature (silica gel or alumina).The polar compounds have greater affinity (interact more strongly) to the polar stationary phase, thus their mobility is slow in the system, therefore they eluted later and non-polar compounds are eluted first. It is useful for separating polar compounds such as carbohydrates, amino acids, peptides, and some natural products.



(https://i.stack.imgur.com/GzU3n.jpg)

(b) Reverse phase chromatography: This chromatographic method is reverse to the normal phase chromatography. The stationary phase is non-polar such as hydrophobic alkyl chains (e.g., C18) attached with soild surface and mobile phase is polar in nature like water and organic solvent like methanol and acetonitrile, therefore polar compounds are eluted first and non-polar are eluted later. This technique is used especially in the analysis and purification of organic compounds, pharmaceuticals, peptides, proteins, and nucleic acids.



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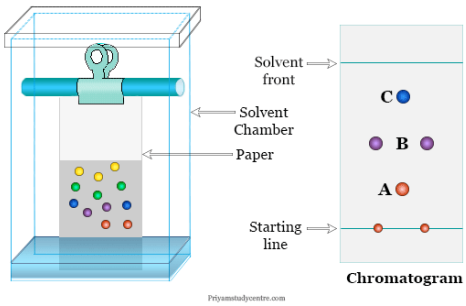
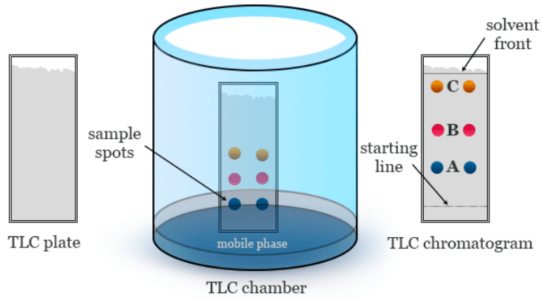
6. Based on the Technique Used for Detection:

In the recent advancement of technologies there is different detection techniques used for the analysis of analytes According to detection techniques the chromatographic techniques classified as:



(a) Paper Chromatography
(https://medium.com/study-chemistry/paper-chromatography-c7f97e5a4360)



(b) Thin Layer Chromatography
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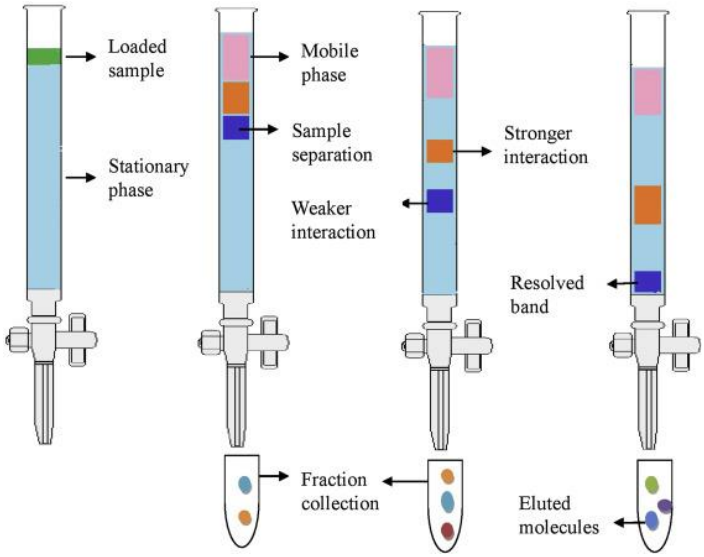

(c) Column Chromatography
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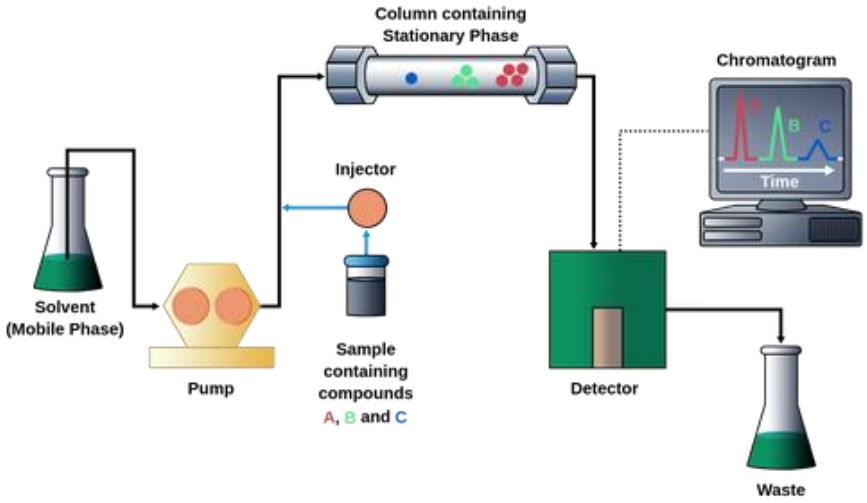

(d) High Performance Liquid Chromatography
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Figure 8.3: Types of chromatography

(a) Gas Chromatography-Mass Spectrometry (GC-MS): The combination of gas chromatography and mass spectrometry provides a highly selective and sensitive method for the identification and quantification of a wide range of compounds in a sample. GC-MS is widely used in various fields such as environmental analysis, forensic science, pharmaceuticals, food and beverage testing, and many others. It allows researchers to identify unknown substances, determine the concentration of known substances, and study complex mixtures of compounds. Thus GC-MS combines two different analytical techniques to provide detailed information about the composition of a substance.

(b) Liquid Chromatography-Mass Spectrometry (LC-MS): LC-MS is a versatile and powerful technique that combines the separation capabilities of liquid chromatography with the sensitivity and specificity of mass spectrometry, making it an essential tool in modern analytical chemistry. This technique used in the fields of chemistry, biochemistry, biology, pharmaceuticals, environmental analysis, metabolomics, proteomics, and forensic science for the identification, quantification, and characterization of chemical compounds, such as drugs, metabolites, and proteins.

8.6 THEORY OF CHROMATOGRAPHY

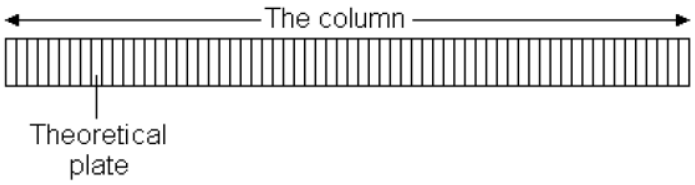
The plate theory and rate theory these two major theories have been used for the rate of migration of solute/anylyte, development of peaks in the chromatogram and the column efficiency.

1. Plate theory:

The plate theory, also known as the theoretical plate theory explains the measurement of column efficiency and performance in separating different components of a sample. This theory was developed by Archer J.P. Martin and R.L.M. Synge in 1941. The plate theory can be explained on the basis of following key point:

(a) Theoretical Plates:

- The column is conceptually divided into hypothetical stages/thin sections or plates called theoretical plates and each theoretical plate represents equilibrium between the mobile phase (eluent) and the stationary phase
- Each plate has a finite height (height of effective theoretical plate, HETP, H). The solute spends a finite time in this plate and at this time solute equilibrated between the mobile and stationary phases.



(b) Number of Theoretical Plates (N):

- The efficiency of a chromatographic column is often quantified by the number of theoretical plates (N). The more theoretical plates a column has, the better its ability to separate components.
- The equation to calculate the number of theoretical plates is

$$N = \left(\frac{t_R}{\sigma}\right)^2 = 16\left(\frac{t_R}{W}\right)^2 = 5.54\left(\frac{t_R}{W_{1/2}}\right)^2$$

Where

t_R is the retention time of the peak;

σ is the standard deviation as a measure for peak width;

W is the peak width measured in time units as the distance between the intersections of the tangents to the peak inflection points with the baseline and $W_{1/2}$ is the peak width at half height.

(c) Plate Height (H):

- Plate height (H), also known as the height equivalent to a theoretical plate (HETP), is a measure of the column's efficiency.

$$H = \frac{L}{N}$$

Where

L is the column length and N is the number of theoretical plates.

- The greater the number of theoretical plates (N) or the smaller the plate height, the more efficient the analyte exchange between two phases and the greater is the efficiency of the column, which means the better the separation. That is why column efficiency is measured by N. Thus A lower plate height indicates better efficiency.

(d) Relationship with Resolution (Rs):

- The number of theoretical plates is directly related to the resolution (Rs) between two peaks in a chromatogram.
- A higher number of theoretical plates contribute to better resolution.

- Resolution can be calculated by using this formula

$$Rs = 2 * (t_{R2} - t_{R1}) / (W_1 + W_2)$$

Where,

t_{R1} and t_{R2} are the retention times, and W_1 and W_2 are the peak widths at their bases.

(e) Optimization for Efficiency:

By optimizing the number of theoretical plates and variables such as column length, particle size, temperature, and flow rate can be adjusted to improve efficiency of seperation.

2. Rate theory:

The rate theory was developed by Van Deemter, Zuiderweg and Klinkenberg in 1956. This theory used to measure the contributions to band broadening and there by optimize the efficiency. According to the rate theory, some analytes pass through the column rapidly due to their incorporation in the mobile phase while others lag behind as they are accumulated in the stationary phase. This results in a Gaussian peak with widened velocities. Thus, as analyte moves down the column the width of the peak increases because of the enhanced space for broadening.

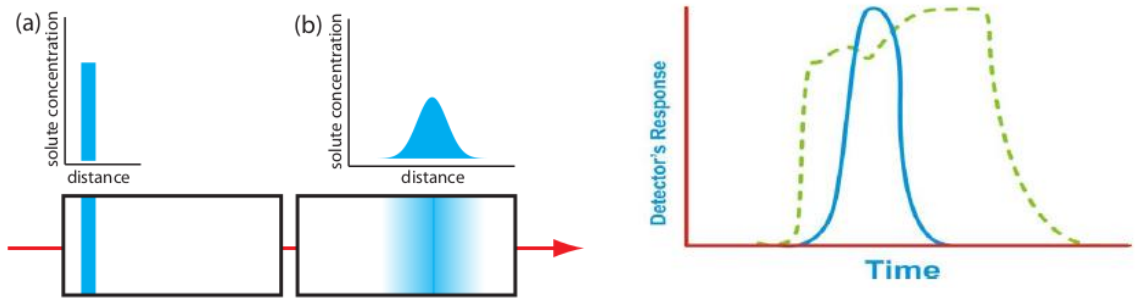


Figure 8.4: Band Broadening
(https://agora.cs.wcu.edu/~huffman/lectures/figures/chrom_opti_ld.png)

(a) Van Deemter equation:

The optimal separations are depicted by sharp and symmetrical chromatographic peaks. Inappropriate separation leads to band broadening in the chromatogram. Thus the peak width is also a measure of efficiency of the column. The shape of chromatographic peak or band is affected by several factors such as the rate of elution; different paths take by solute molecules as they travel through the column between particles of stationary phase. Considering various mechanisms that contribute to band broadening, the HETP in a column is given by Van Deemter equation.

The Van Deemter equation is a fundamental equation in chromatography that describes the relationship between the plate height (H), linear velocity (u), and the contributions of

different processes (A, B, and C) affecting chromatographic efficiency. The general form of the van Deemter equation is as follows:

$$H=A+(B/u)+Cu$$

Where,

H is the plate height (height equivalent to a theoretical plate, HETP),

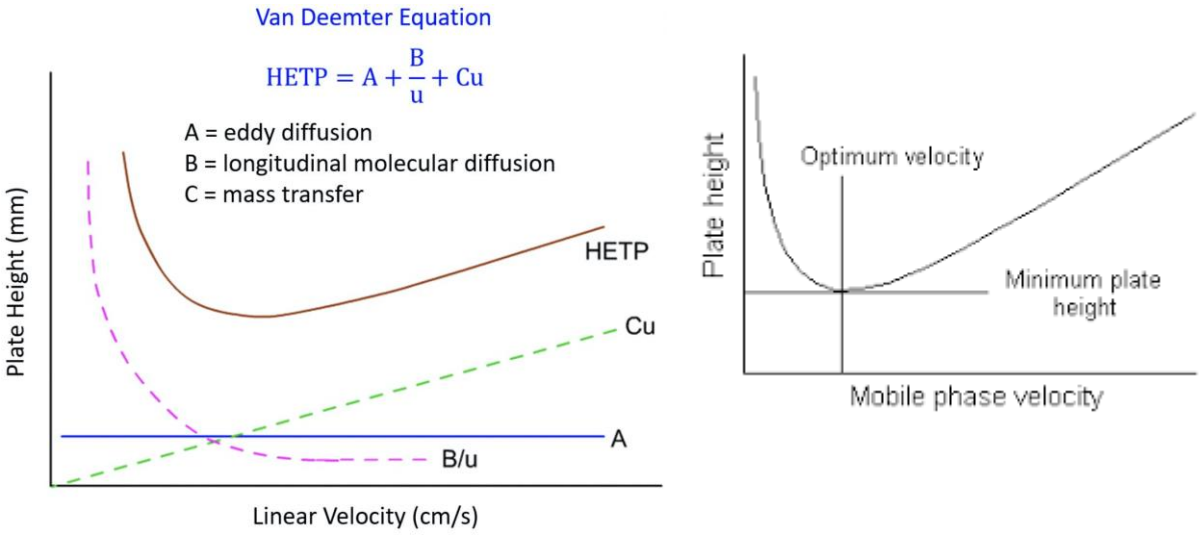
u = average velocity of the mobile phase.

A = Eddy diffusion: That accounts for random movement of analyte molecules through the column

B - Longitudinal diffusion: Due to the concentration of analyte more in the center than the walls of the column.

C - Resistance to mass transfer: Due to the time taken by the analyte to equilibrate between the stationary and mobile phase

The relationship between HETP and average linear velocity of mobile phase can be given by Van Deemter plot (Figure 8.4). This plot suggests that slight increase in mobile phase velocity or flow rate decreases the HETP and thereby increases the column efficiency. Thus the plot can be used to determine the optimum mobile phase flow rate.



(a) **(b)**

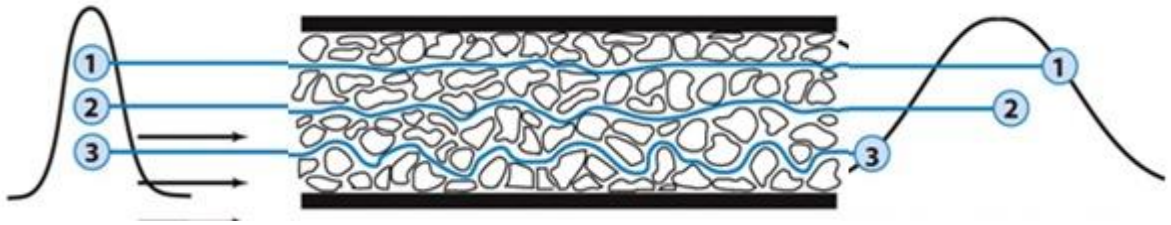
Figure 8.5: Van Deemeter plot
(https://cs-temp.imgix.net/media/wysiwyg//Technical/Tech-Tips/2020/April/Van-Deemter-equation.jpg)

(b) Factors affecting the band broadening:

The three major factors eddy's diffusion, longitudinal diffusion and resistance to mass transfer which contribute to band broadening due to uneven rate of migration of analyte through the column.

Eddy's diffusion:

The phenomenon of peak broadening due to different paths of different lengths is known as Eddy's diffusion.



Molecule enter the column at same time

Molecule exit the column at different time because of the different path

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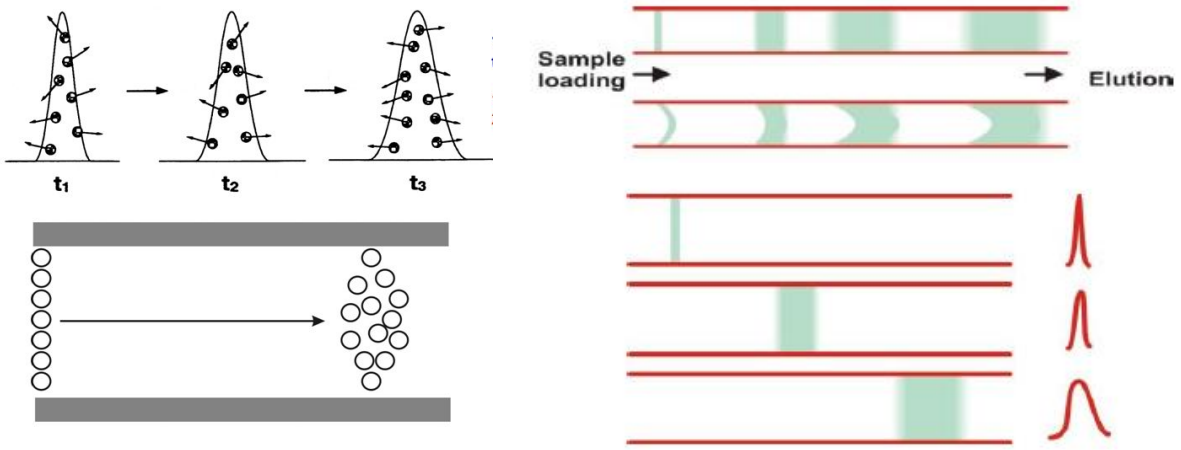
Figure 8.6: Band broadening due to Eddy's diffusion

Longitudinal diffusion:

The analyte concentration at the edges is lesser than at the center, due to this it spreads out from the centre to the boundaries, resulting in band broadening. This phenomenon is known as longitudinal diffusion or axial diffusion. When the velocity of the mobile phase is high, therefore analyte is spent less time in the column and diminishes the outcome of longitudinal diffusion.



(a) **(b)**

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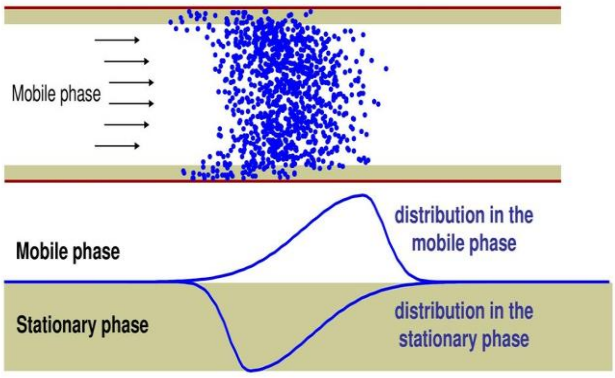
Figure 8.6: Band Broadening due to longitudinal diffusion

Resistance to mass transfer:

The analyte takes time to equilibrate between stationary phase of the column and mobile phase. If the velocity of mobile phase is high and the analyte has strong and more affinity for stationary phase, then the analyte in mobile phase will elute faster than that in stationary

phase, leading to band broadening. The band broadening is directly related to velocity of the mobile phase. Thus, the peak shape is affected by the rate of elution of analyte.



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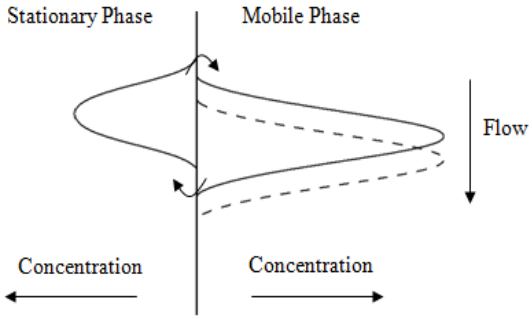

(b)
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Figure 8.7: Band Broadening due to resistance to mass transfer

8.7 EFFICIENCY OF CHROMATOGRAPHIC TECHNIQUES

The efficiency of chromatography refers to how well a chromatographic system can separate and resolve different components in a mixture. Higher efficiency means better separation, sharper peaks, and more accurate identification and quantification of individual analytes. Several factors contribute to the efficiency of chromatography:

(i) **Number of Theoretical Plates (N):** The concept of theoretical plates, introduced in the plate theory of chromatography, is fundamental to understanding efficiency. Each theoretical plate represents an idealized stage of equilibrium between the mobile and stationary phases. A higher number of theoretical plates generally indicates better separation efficiency.

(ii) **Resolution (Rs):** Resolution is a measure of the separation between two adjacent peaks in a chromatogram. It is influenced by the number of theoretical plates and the selectivity of the separation. Higher resolution leads to better-defined and more distinct peaks.

(iii) **Plate Height (H):** The plate height, also known as the height equivalent to a theoretical plate (HETP), is a measure of the efficiency of a chromatographic column. It is the length of the column required to achieve the same separation as one theoretical plate. Lower HETP values indicate better efficiency.

H = L / N, where L is the column length and N is the number of theoretical plates.

(iv) **Reducing Band Broadening:** Band broadening, or the spreading of analyte bands as they move through the column, can negatively impact efficiency. Minimizing factors such as longitudinal diffusion, eddy dispersion, and extra-column effects helps maintain peak sharpness.

(v) **Optimizing Column Parameters:** Parameters such as particle size, column length, temperature, and flow rate can be optimized to enhance column efficiency. Smaller particle sizes, longer columns, and controlled temperature can contribute to improved separation.

(vi) **Mobile Phase Composition:** The choice of mobile phase and its composition can significantly impact chromatographic efficiency. Adjusting parameters like solvent strength and pH can optimize separation.

(vii) **Selectivity:** The selectivity of the stationary phase for different analytes is crucial for achieving efficient separation. It determines how well the column can discriminate between different compounds.

8.8 MECHANISM OF SEPERATION

Chromatography is a widely used separation technique in analytical chemistry to separate and analyze complex mixtures based on the differential interaction of components with a stationary phase and a mobile phase. There are various types of chromatography, each with its own separation mechanism. Here are some common chromatographic techniques and their separation mechanisms.

A. Adsorption chromatography

Adsorption chromatography is a technique used for separating mixtures of compounds based on their interactions with a stationary phase (adsorbent) and a mobile phase (eluent). The mechanism of separation in adsorption chromatography relies on the differential adsorption of the components of the mixture onto the stationary phase. Adsorption occurs when molecules from the mobile phase are attracted to the surface of the stationary phase due to van der Waals forces, hydrogen bonding, dipole-dipole interactions, or other intermolecular forces. The extent of adsorption depends on the chemical properties of the molecules and the surface properties of the stationary phase. Components that have stronger interactions with the stationary phase will be retained longer in the column, while those with weaker

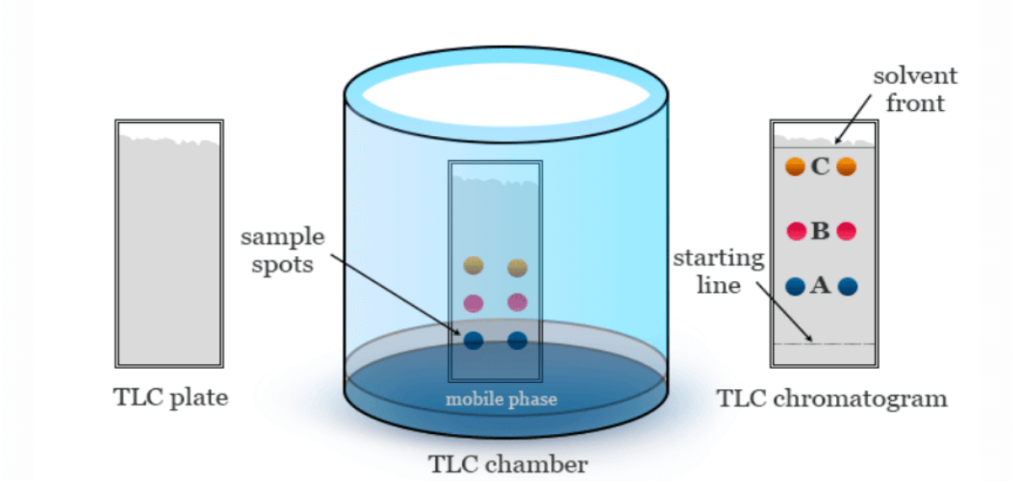
interactions will move more quickly through the column. This differential retention leads to the separation of the components as they elute from the column at different times.

For example: Thin Layer chromatography

Thin-layer chromatography (TLC) is a chromatographic technique used to separate and analyze mixtures. The separation mechanism in TLC relies on the differential affinity of the components in the mixture for the stationary phase (the thin layer of adsorbent material) and the mobile phase (the solvent). The mechanism of separation in TLC completed in the following steps:

- **Sample Application:** A small amount of the mixture to be separated is spotted near the bottom of a TLC plate. The TLC plate is usually made of glass, aluminum, or plastic, coated with a thin layer of a stationary phase material, often silica gel or alumina.
- **Development:** The TLC plate is then placed vertically in a developing chamber that contains a solvent mixture (the mobile phase). The solvent moves up the plate through capillary action, carrying the sample components with it.
- **Adsorption:** As the mobile phase moves up the plate, the different components of the sample interact with the stationary phase. Some components have a stronger affinity for the stationary phase and are more strongly adsorbed, while others have a weaker affinity and move more quickly with the mobile phase.
- **Separation:** The components of the sample separate based on their differing affinities for the stationary phase. Components that have a stronger affinity for the stationary phase will move more slowly up the TLC plate, while those with weaker affinity will move more quickly. This differential movement leads to the separation of the components along the length of the TLC plate.
- **Visualization:** Once the development is complete, the TLC plate is removed from the chamber and dried. The separated components on the plate are often not visible to the naked eye, so they need to be visualized. This can be done by exposing the plate to UV light or by treating it with a chemical reagent that reacts with the components to produce visible spots.
- **Analysis:** The separated spots on the TLC plate can then be analyzed by measuring their RF (retention factor) values, which is the ratio of the distance traveled by the compound from the original spot to the distance traveled by the solvent front. RF

values are characteristic for each compound under specific conditions and can be used to identify the components in the mixture.



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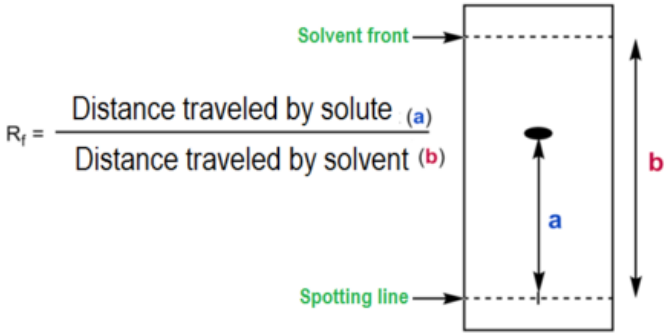
(a)



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(b)

Figure 8.8: Mechanism of separation in thin layer chromatography

B. Partition chromatography

Partition chromatography is a type of chromatography where the separation of components in a mixture is based on differences in their distribution between two immiscible phases. Typically, one phase is stationary (solid or liquid supported on a solid) while the other phase is mobile (liquid or gas). The mechanism of separation in partition chromatography involved equlibrium, partition. The seperation occures due to the differential partitioning of the components between these two phases.

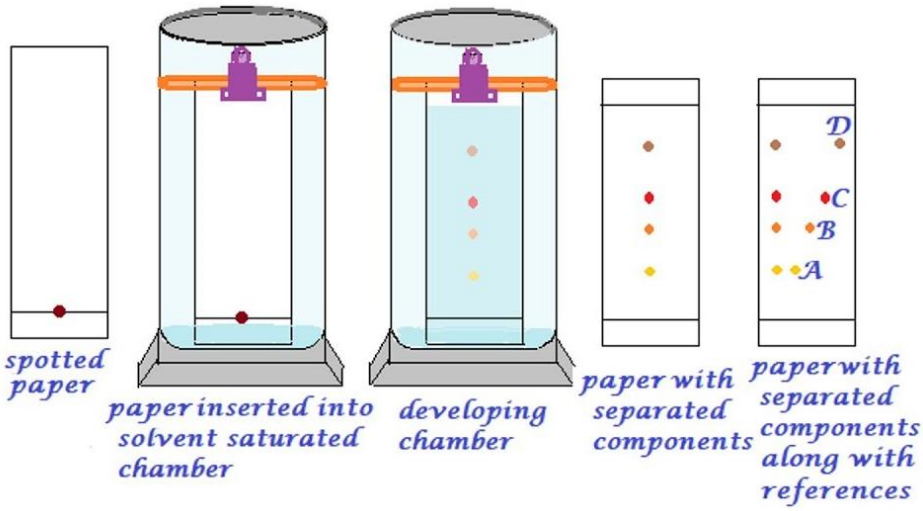
The components with higher affinity for the stationary phase spend more time interacting with it, causing them to move more slowly through the column. Conversely, components with higher affinity for the mobile phase move more quickly through the column. This differential

partitioning results in the separation of the components based on their affinity for the stationary phase.

For example: Paper Chromatography

The separation in paper chromatography is primarily based on the principles of differential partitioning and adsorption. Components that are more soluble in the mobile phase will travel further up the paper, while those that are more strongly adsorbed onto the stationary phase will move more slowly. The mechanism of separation in paper chromatography completed in the following steps:

- **Sample Application:** A small amount of the mixture to be separated is applied near the bottom edge of a sheet of special paper known as chromatography paper. This application spot should be small and concentrated to prevent overlap of the separated components.
- **Development:** The bottom edge of the paper is then immersed in a solvent or mobile phase, which travels up the paper through capillary action. The solvent carries the sample components along with it as it moves up the paper.
- **Partitioning:** As the mobile phase moves up the paper, each component of the mixture interacts differently with the stationary phase (the paper) and the mobile phase (the solvent). Components that have a stronger affinity for the mobile phase will move more rapidly up the paper, while those with a stronger affinity for the stationary phase will move more slowly. Example. Butanol: Acetic acid: Water (12:3:5) is a suitable solvent for separating amino acids
- **Separation:** As the mobile phase continues to travel up the paper, the components of the mixture gradually separate based on their differing affinities for the stationary and mobile phases. Components with similar affinities may move together, forming bands or spots on the paper.
- **Detection:** Once the development is complete and the components have separated sufficiently, the paper is removed from the solvent and allowed to dry. The separated components can then be visualized by various means depending on their properties. Common methods include UV light visualization, staining with dyes or chemical reagents, or simply observing any color changes or differences in the appearance of the spots or bands.



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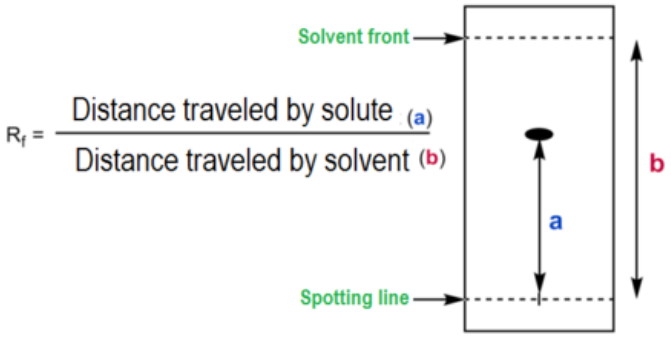
(a)



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(b)

Figure 8.9: Mechanism of separation in paper chromatography

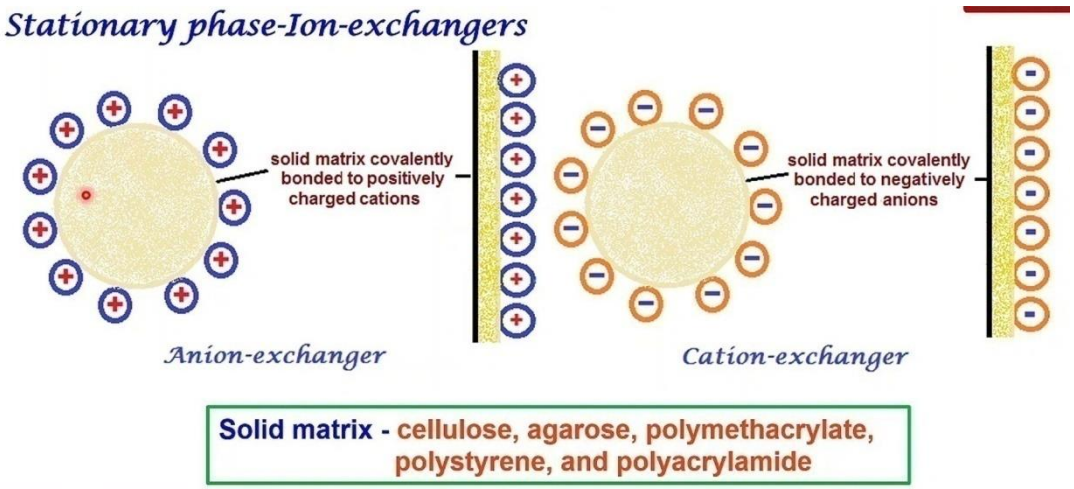
C. Ion exchange chromatography:

Ion exchange chromatography is a powerful technique used to separate charged molecules based on their interactions with charged groups immobilized on a stationary phase. The separation mechanism involves the reversible exchange of ions between the mobile phase (eluent) and the stationary phase (resin).

The stationary phase typically consists of a solid support (such as beads or a resin) with covalently bound charged groups. These charged groups can be either positively charged (cation exchange like quaternary ammonium) or negatively charged (anion exchange such as sulfonate or carboxylate groups), depending on the type of separation needed.

The charged molecules in the sample interact with the oppositely charged groups on the stationary phase. The strength of the interaction between the sample ions and the stationary phase depends on factors such as charge density, ionic strength, and pH of the mobile phase.

Ions with weaker interactions elute earlier, while ions with stronger interactions remain bound to the stationary phase for a longer time, resulting in separation. The retention time of each ion peak corresponds to its specific interaction with the stationary phase, allowing for identification and quantification of the separated ions.



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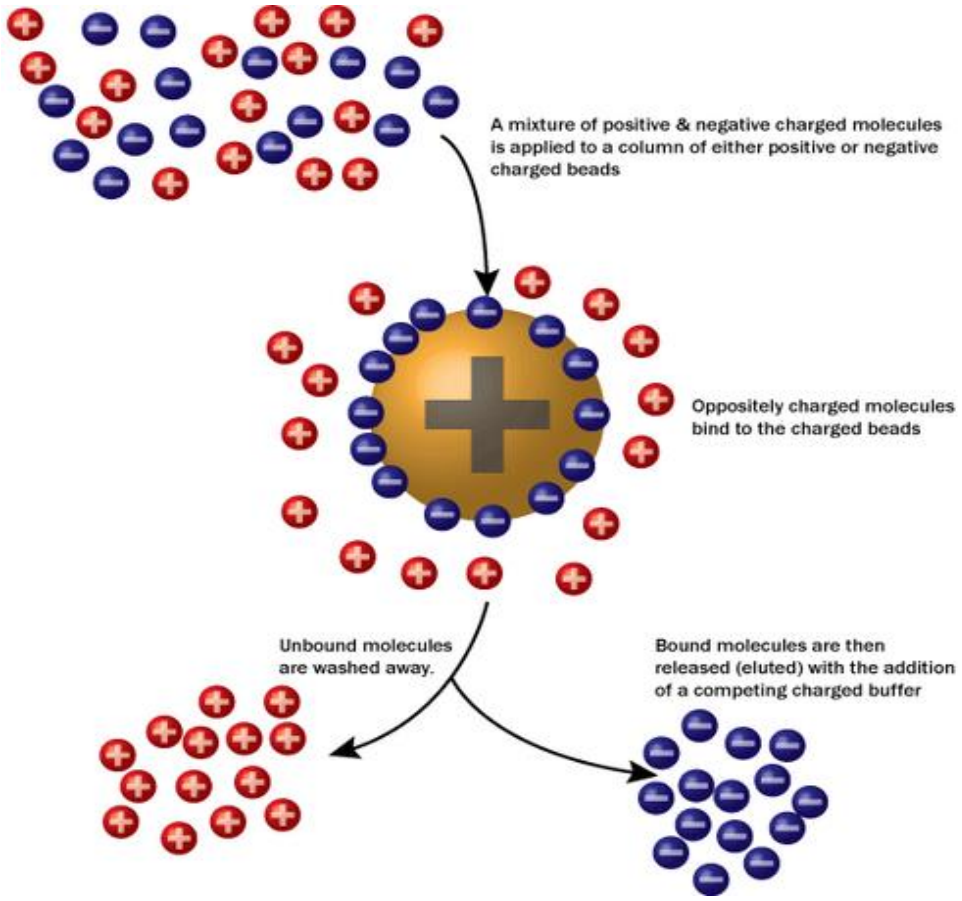

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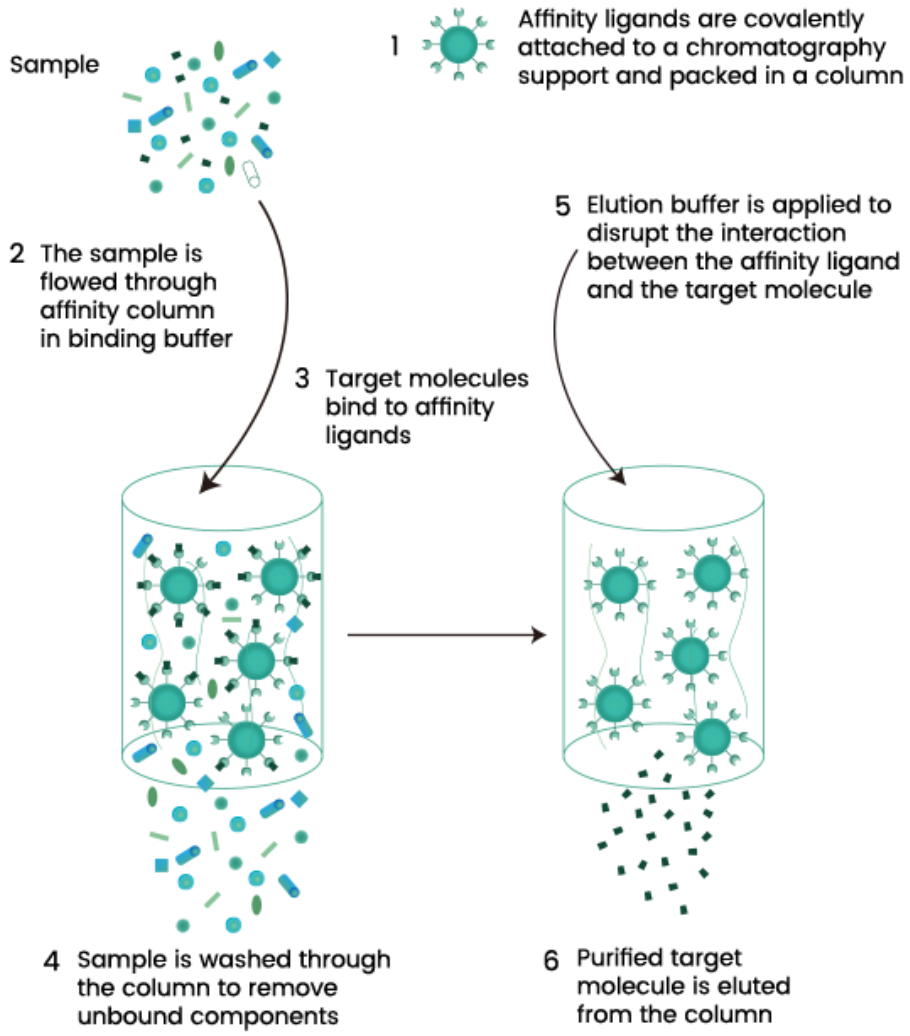
(b)

Figure 8.10: Mechanism of separation in ion-exchange chromatography

D. Affinity chromatography:

Affinity chromatography is a powerful technique used to separate molecules based on their specific interactions with immobilized ligands. The mechanism of separation in affinity chromatography relies on the selective binding of the target molecule (analyte) to a ligand that is immobilized on a solid support within the chromatography column.

The immobilization is typically achieved through covalent bonding, physical adsorption, or affinity interactions. These interactions could include various non-covalent bonds such as hydrogen bonding, van der Waals forces, electrostatic interactions, or hydrophobic interactions, depending on the nature of the ligand and target molecule. By exploiting these specific interactions, affinity chromatography allows for highly selective separation and purification of target molecules from complex mixtures with high purity and yield.

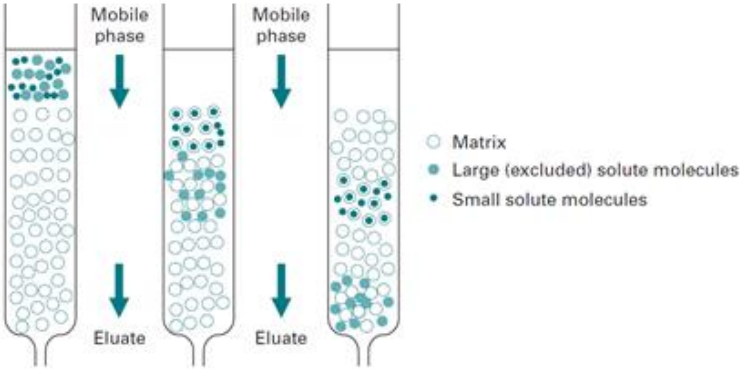


(https://cdn1.sinobiological.com/styles/default/images/pdyimg/CRO/CRO_protein_info/uu19.png)

Figure 8.11: Mechanism of separation in affinity chromatography

E. Molecular exclusion chromatography:

Molecular exclusion chromatography (also known as size exclusion chromatography or gel filtration chromatography) is a chromatographic technique used for the separation of molecules based on their size. The mechanism of separation relies on differences in molecular size and shape, which affect the ability of molecules to penetrate into the pores of the stationary phase. As the sample travels through the column, smaller molecules can enter the pores of the stationary phase and are temporarily trapped within the pores. Larger molecules, however, cannot enter the pores and, therefore, travel more quickly through the column. Thus larger molecules eluted first than smaller molecules. The retention times of the separated molecules are used to determine their molecular sizes.



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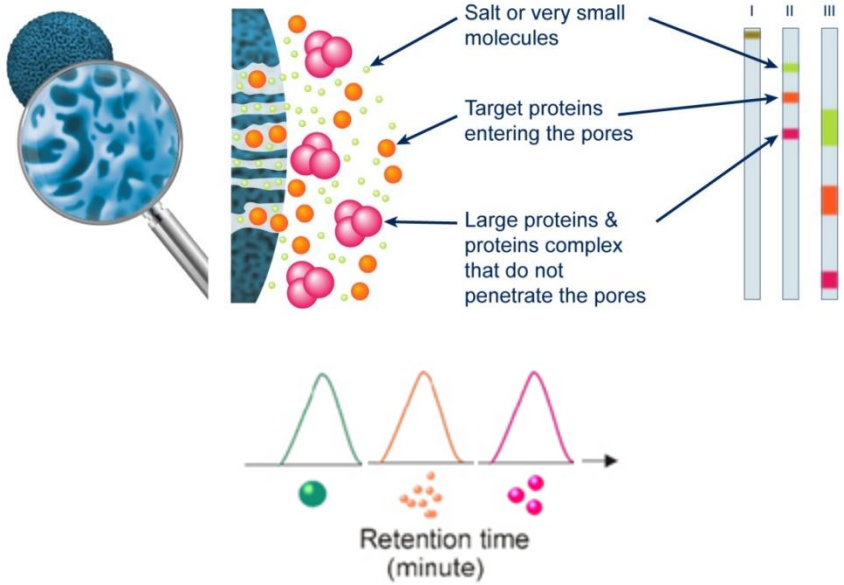

(https://blog.interchim.com/wpcontent/uploads/2020/06/SEC_pathway_Interchim_Blog_0520_948x435.jpg)

(b)

Figure 8.12: Mechanism of separation in molecular exclusion chromatography

8.9 SUMMARY

In this unit, we have learnt the following aspects of chromatography:

- The chromatographic techniques can be classified in various ways according to the shape of the stationary support, nature of the mobile phase and the mechanism of separation.
- Theory to explain the principle of different chromatographic trchniques.
- Mechanism of seperation involved in the varios types of chromatograhic methods.
- About different factors affect the efficiency of chromatographic techniques.

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8.11 TERMINAL QUESTIONS

1. Discuss the different types of chromatographic techniques based on their mechanisms of operating.
2. What is the general mechanism of separation in paper chromatography?
3. Explain the basic principle and theory of chromatography.

UNIT 9: ADSORPTION CHROMATOGRAPHY

CONTENTS:

9.1 Introduction
9.2 Objectives/ Expected outcomes
9.3 Adsorption chromatography
9.4 Theory of adsorption chromatography
9.5 Classification
9.6 Column chromatography
9.6.1 Principle of Column chromatography
9.6.2 Efficiency of techniques
9.6.3 Mechanism of Separation
9.6.4 Development of Chromatogram
9.7 Summary
9.8 Bibliography
9.9 Terminal questions

9.1 INTRODUCTION

In Unit 8, you have studied about the general aspects of chromatography including classification of chromatographic methods, theory and principle; and mechanism of separation in different chromatographic techniques like adsorption, partition, ion exchange and affinity chromatography.

In continuation to that, in this unit, you will study about one more type of chromatography, i.e. adsorption chromatography in which the separation of the components of a mixture takes place by the adsorption mechanism.

We will begin the discussion of this unit by classification, principle and efficiency of the adsorption chromatography technique. This will be followed by a brief account of the mechanism of separation operating in this technique. Finally, we will explain the development of chromatograms by frontal analyses, elution and displacement methods.

9.2 OBJECTIVES

After studying this unit you should be able to:

- Explain the classification of adsoption chromatography.
- Discuss the theory and principle of adsoption chromatography.
- Know about the column chromatography, which is a form of liquid-solid adsorption chromatography.
- Describe the efficiency of the column chromatography technique.
- Explain the mechanism of separation involved in the separation of mixture/components using adsorption chromatographic techniques.
- Describe different methods of development of chromatograms.

9.3 ADSORPTION CHROMATOGRAPHY

Adsorption chromatography is a type of chromatographic technique in which separation is achieved based on the differential adsorption of components in a mixture onto a solid stationary phase. It is commonly used in analytical chemistry and biochemistry for the separation and purification of various compounds. The some key points of the adsorption chromatography:

i) The basis of separation by adsorption chromatography is the difference between adsorption and desorption of solutes at the surface of a solid particle.

ii) Electrostatic, hydrogen-bonding, and dispersive (van der Waals) interactions are the physical forces that control this type of chromatography.

iii) In the process of adsorption chromatography, different compounds are adsorbed on the adsorbent to different degrees based on the absorptivity of the component.

iv) Adsorbent: An adsorbent is a substance that is generally porous in nature and has a large surface area that has the ability to adsorb substances on its surface through intermolecular forces. Silica gel, cellulose microcrystalline, alumina, modified silica gel, calcium carbonate, aluminium silicates, starch, sugars and other adsorbents are some of the most commonly used adsorbents.

v) Solvent: Mostly organic solvents can be used as the mobile phase. The choice of the solvents depends upon the polarity of the compounds to be resolved and upon their distribution coefficient. Commonly used sovents according to the increasing order of polarity as:

Pure water> metanol>acetone>ethyl acetate> chloroform> benzene> toluene>hexane

vi) Two different factors are exploited in separation of components by adsorption chromatography. They are:-

- Different degree of adsorption of various components on the adsorbent surface.
- Varying solubility of different components in the solvent(mobile phase) used

9.4 THEORY OF ADSORPTION CHROMATOGRAPHY

Compound are adsorbed on to the column and equilibrium set up between molecules bound to the column and those free in solution. The extent of the binding is governed by the charge, van der Waal's forces, dipole interactions, hydrogen bonding and steric factors and dependson the structure of the compounds.

The mass of solute adsorbed per unit weight of adsorbent (m) depends on the concentration of the solute (c) and Langmuir derived an equation on the basis that (a) only a monolayer is adsorbent, and (b) only a proportion of the molecules in collision will result in adsorption. This is known as the Langmuir adsorption.

$$m = \frac{K1K2c}{1 + K2c}$$

Where,

K_1 is a measure of the number of active adsorption sites per unit weight of adsorbent and depends on the nature of the adsorption.

K_2 is a measure of the affinity of solute for the adsorbent and affected by all the components of the system.

9.5 CLASSIFICATION

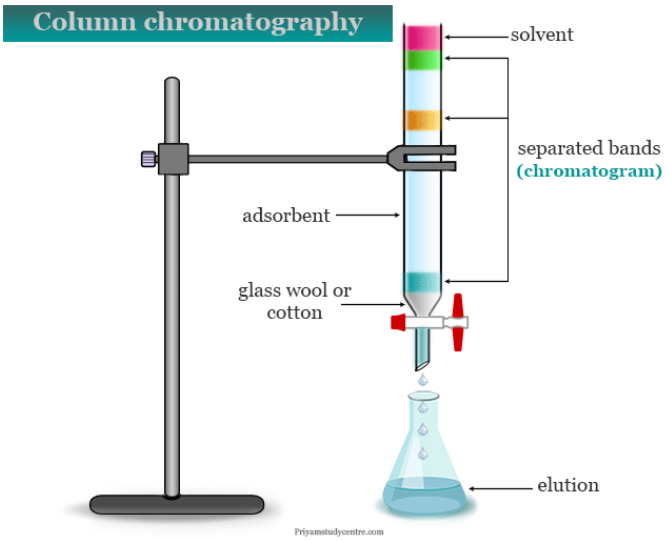
Adsorption chromatography can be classified into various types based on different criteria such as stationary and mobile phase. Here are some common classifications based on the mobile phase liquid (liquid-solid chromatography) or gas (gas-solid chromatography)

9.5.1 Liquid-solid chromatography

The mobile phase is a liquid, and the stationary phase can be a solid (e.g., silica gel). Example: Thin-layer chromatography (TLC) and coulmn chromatography. The technique of thin layer chromatography is classified as the two dimensional chromatographic technique while column chromatography which is a three-dimensional chromatographic technique.

9.6 COLUMN CHROMATOGRAPHY

The column chromatography involves the use of liquid mobile phase and a solid stationary phase; hence, it is a type of liquid-solid chromatography as mentioned above. Column chromatography is a technique used in chemistry to separate and purify individual components from a mixture. It was developed by the American petroeum chemist D.T. Day in 1900 after that M.S. Tswett the Polish botanist, in 1906 used adsorption columns for the investigations of plant pigments. Now days this method was extensively used by the chemists and other scientist, academician.



(https://www.priyamstudycentre.com/2021/11/column-chromatography.html)

Figure 9.1: Column chromatography

9.6.1 Principle of column chromatography

Column chromatography is a versatile technique widely used in analytical chemistry or laboratories for the purification of compounds. It allows for the separation of compounds based on differences in polarity, size, and other chemical properties, making it an essential tool for isolating pure substances from complex mixtures. The separation and purification of compounds based on their differential interactions with a stationary phase and a mobile phase. The principle behind column chromatography can be summarized as follows:

(i) Stationary Phase: A column is packed with a stationary phase, typically a solid support material such as silica gel or alumina. The availability of a large number of materials offer a wide range of flexibility in choosing the desired stationary phase in terms of the surface area, particle size and type of adsorbent. The stationary phase has specific

properties that enable it to interact differently with different compounds. For example, polar stationary phases like silica gel tend to interact more strongly with polar compounds, while non-polar stationary phases like alumina interact more strongly with non-polar compounds.

(ii) Mobile Phase: The mobile phase is a solvent or solvent mixture that flows through the column, carrying the sample mixture. The choice of mobile phase depends on the nature of the compounds being separated and their interactions with the stationary phase. Generally, the mobile phase should be less polar than the stationary phase to facilitate compound elution.

(iii) Adsorption and Elution: Column which is a long tube which is filled with the solid support (stationary phase). The mixture to be separated is first dissolved in a suitable solvent and its slurry is prepared which is then placed at the top of column. Different components of the mixture get adsorbed on the stationary phase to different extents. When the mobile phase is allowed to pass over stationary phase, compounds that interact more strongly (strongly adsorbed) with the stationary phase will move more slowly through the column, while those that interact less strongly (least adsorbed) will move more quickly along the mobile phase. This differential interaction causes the components to separate as they travel through the column. The various bands present in the coulmn become more define. The banded column of adsorbent is termed a *chromatogra*m, and the operation is spoken of as the *development of chromatogram*. The portion of a column which is occupied by a particularn substance (compound) is called *zone*.

(iv) Fractionation: The mobile phase is continuously added from the top of the column and allowed to move out of the bottom coloumn by opening the stop cock. The different components of the mixture keep moving downwards as bands in the column. These are then collected as different fractions in the flask placed at the bottom of the column. The different components are then obtained from the eluent by removal of the solvent.

(v) Detection: Compounds separated by column chromatography are typically detected using techniques such as UV-visible spectroscopy, refractive index detection, or fluorescence detection. This allows for the identification and quantification of separated compounds.

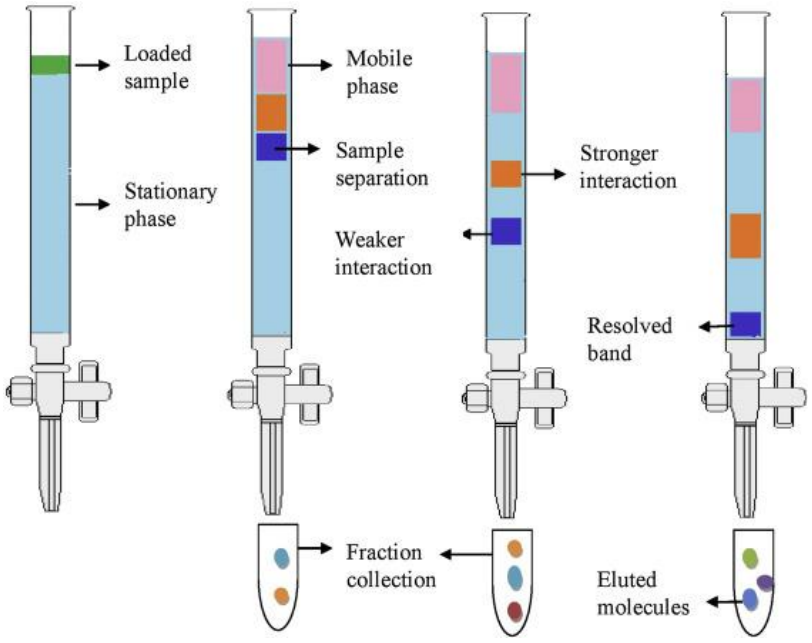


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Figure 9.2: Column chromatography with separated molecules

9.6.2 Efficiency of techniques

Column chromatography is a very useful and convenient technique, both for the effective separation of components of a mixture and for the purification of an impure compound. Virtually, any type of mixture-occurring naturally (in plants, animals or in any other source) or obtained synthetically from chemical reactions, can be separated into its components using column chromatography. Its efficiency can be evaluated based on several factors:

(i) Plate number and plate height:

(a). Number of Theoretical Plates (N):

- The efficiency of a chromatographic column is often quantified by the number of theoretical plates (N). The more theoretical plates a column has, the better its ability to separate components.
- The equation to calculate the number of theoretical plates is

$$N = \left(\frac{t_R}{\sigma}\right)^2 = 16\left(\frac{t_R}{w}\right)^2 = 5.54\left(\frac{t_R}{w_{1/2}}\right)^2$$

Where

t_R is the retention time of the peak;

σ is the standard deviation as a measure for peak width;

W is the peak width measured in time units as the distance between the intersections of the tangents to the peak inflection points with the baseline and $W_{1/2}$ is the peak width at half height.

(b). Plate Height (H):

- Plate height (H), also known as the height equivalent to a theoretical plate (HETP), is a measure of the column's efficiency.

$$H = \frac{L}{N}$$

Where

L is the column length and N is the number of theoretical plates.

- The greater the number of theoretical plates (N) or the smaller the plate height, the more efficient the analyte exchange between two phases and the greater is the efficiency of the column, which means the better the separation. That is why column efficiency is measured by N. Thus A lower plate height indicates better efficiency.

(ii) Resolution: This refers to the ability of the column to separate different compounds from each other. Higher resolution means that closely related compounds are separated effectively. Factors such as the choice of stationary phase, mobile phase, and column dimensions can affect resolution.

- The number of theoretical plates is directly related to the resolution (Rs) between two peaks in a chromatogram.
- A higher number of theoretical plates contribute to better resolution.
- Resolution can be calculated by using this formula

$$Rs = \frac{2(tR2 - tR1)}{W1 + W2}$$

Where,

Rs is peak resolution; t_{R1} and t_{R2} are the retention times, and W_1 and W_2 are the peak widths at their bases.

(iii) Nature of solvent/mobile phase: The solvent of low viscosities are generally used for the high efficiency separations. The reaseon for that this is that rate of flow is inversely proportional to viscosity and hence it becomes nesessary to select a solvent of lowest viscosity and proper elution strength.

(iv) **Dimension of column:** Longer columns generally provide better resolution but may require longer run times. The diameter of the column also influences efficiency, with smaller diameters offering higher resolution and efficiency due to reduce longitudinal diffusion. Thus the longer the column and smaller the diameter, the better will be the separation. The ideal length to width ratio for the column is 20:1 or 30:1.

(v) **Particle size of the column packing:** Smaller particle sizes and efficient packing of the stationary phase can improve efficiency by increasing surface area and reducing mass transfer limitations for interaction between the analyte and the stationary phase. Its particles should be of uniform size. The finely divided nature of stationary phase leads to better separations. Particle size from74 to149μ is suggested with the mesh size of 100 to 200 mesh.

(vi) **Sample Concentration:** Overloading the column with a high concentration of sample can reduce efficiency due to band broadening effects. Optimal sample loading should be determined empirically for each application. Ideally, the sample to the adsorbent ratio is chosen as 1:20 to 1:50. Otherwise, more concentrated samples may not lead to clear separations.

(vii) **Flow Rate**: The flow rate of the mobile phase affects the efficiency of separation. Too high a flow rate may result in poor resolution and lead to band broadening; while too low a flow rate can lead to excessively long run times. Thus the flow rate of the solvent or the mobile phase should be uniform and not very fast. This will give better separation of bands of different components of the mixture without much tailing.

(viii) **Retention Time:** Efficient column chromatography should provide reasonable retention times for compounds of interest. Too short a retention time may lead to poor separation, while too long a retention time may result in extended run times and reduced throughput.

(ix) **Detection Method:** The detection method used to monitor elution from the column can impact efficiency. High-sensitivity detection methods can improve resolution and enable the detection of low-abundance compounds.

(x) **Temperature:** Difficult solution sample are generally separated at higher temparsature while other samplea are separated at room temperature.

9.6.3 Mechanism of Separation

The separation of components of mixture using column chromatography (adsorption chromatography) involves their adsorption on the stationary support. The mobile phase then

displaces the different components selectively one by one. The separation mechanism in column chromatography relies on the principles of adsorption, partitioning, and molecular size exclusion, depending on the nature of the stationary phase used. Common stationary phases include silica gel, alumina, or polymers, which interact differently with different compounds based on factors such as polarity, size, and functional groups. For example silica gel which is polar in nature; polar solvents may have better interactions with it as compared to the non-polar ones. The polarity of the mobile phase will also affect how effectively the separations can be carried out.

The following aspects, thus, need to be considered for the separation process:

- How strongly the component is adsorbed to the stationary phase?
- How much is the surface area of the stationary phase?
- What is the binding strength of the mobile phase is there to get adsorbed on the stationary phase and how much it can displace the adsorbed components(s)?
- Which types of force of interactions involved like hydrogen bonding, van der Waals forces and dipole-dipole interactions as the process of adsorption take place?

The mechanism of separation involves several key steps:

(i) Column Packing: The first step is to prepare the column. The stationary phase is typically a solid support material such as silica gel or alumina packed into a glass column. The packing material should be chosen based on the polarity of the compounds to be separated.

(ii) Sample Loading: Once the column is prepared, the sample mixture is dissolved in a suitable solvent and loaded onto the top of the column. Care must be taken to ensure that the sample is evenly distributed on the top of the column to prevent channeling and uneven separation.

(iii) Mobile Phase Flow: A mobile phase, typically a solvent or a mixture of solvents, is continuously passed through the column. The mobile phase carries the sample mixture through the column.

(iv) Adsorption and partition: As the mobile phase travels through the column, the individual components of the sample mixture interact differently with the stationary phase. This interaction results in differential partitioning of the components between the mobile and stationary phases.

(v) **Seperation and Development of Chromatogram:** As the mobile phase flows through the column, individual components of the sample interact with the stationary phase to varying degrees. Compounds with stronger interactions with the stationary phase will move more slowly through the column, while those with weaker interactions will move more quickly. This results in separation of the components along the column.

(vi) **Elution:** Elution is the process of passing a mobile phase through the column. The choice of mobile phase (e.g., solvent or solvent mixture) depends on the nature of the sample and the stationary phase. The mobile phase carries the sample components through the column at different rates based on their interactions with the stationary phase.

(vii) **Collection of Fractions:** As the separated components elute from the column, fractions are collected at specific time intervals or based on detection of individual components. Each fraction contains a purified compound or a mixture of compounds that can be further analyzed or used for downstream applications.

(viii) **Detection:** Detection of separated components can be done using various techniques depending on the nature of the compounds and the available equipment. Common detection methods include UV-Vis spectroscopy, fluorescence detection, refractive index detection, or simply visual inspection for colored compounds.

(ix) **Analysis of Fractions:** After collection, each fraction is typically analyzed to determine the purity and identity of the separated compounds. This can be done using spectroscopic techniques, such as nuclear magnetic resonance (NMR) spectroscopy, mass spectrometry (MS), or by performing chemical tests.

9.6.4 Development of chromatogram

The most important aspect of column chromatography separations is the development of chromatograms. Three methods frontal, elution and displacement analysis have been used to develop chromatograms. Understanding the differences between them and which method will be most useful will be discussed in the details.

(i) **Frontal analysis:** Frontal analysis is a technique used in column chromatography to determine the adsorption isotherm of a solute onto the stationary phase. In this method, a fixed concentration of solute is continuously applied to the column, while the mobile phase flows through at a constant rate. As the solute passes through the column, it interacts with the stationary phase and begins to adsorb onto it.

The process begins with the solute being introduced into the column, and initially, all available adsorption sites on the stationary phase are vacant. As the solute moves through the column, it starts to occupy these sites, gradually increasing the concentration of the solute on the stationary phase until equilibrium is reached. At equilibrium, the rate of adsorption onto the stationary phase equals the rate of desorption back into the mobile phase. The least adsorbed solutes out from the column first than the strongly adsorbed solute.

The data obtained from frontal analysis can be used to calculate important parameters related to the chromatographic separation process, such as the distribution coefficient (Kd), the maximum adsorption capacity of the stationary phase (Cmax), and the affinity of the solute for the stationary phase.

Example: The eluent (solvent) contains three substances B, C and D with the strongly adsorbed ability order B < C < D, then the least adsorbed component (substance) B leaves the column first in the pure form and component C, D get adsorbed more strongly and consequently move slowly. The separation in the column and on the chromatogram can be represented schematically (Fig. 9.3).

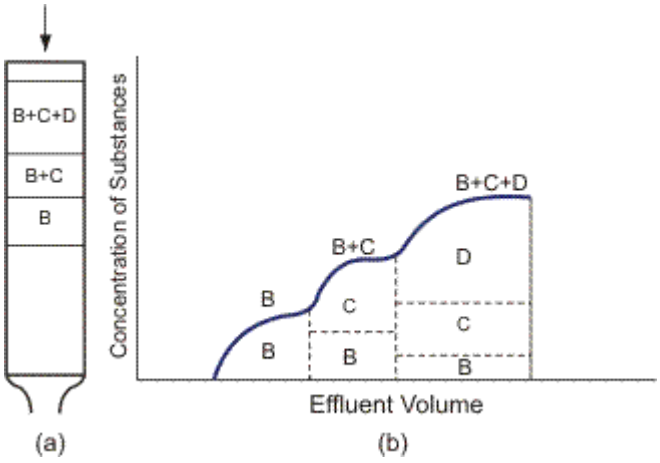

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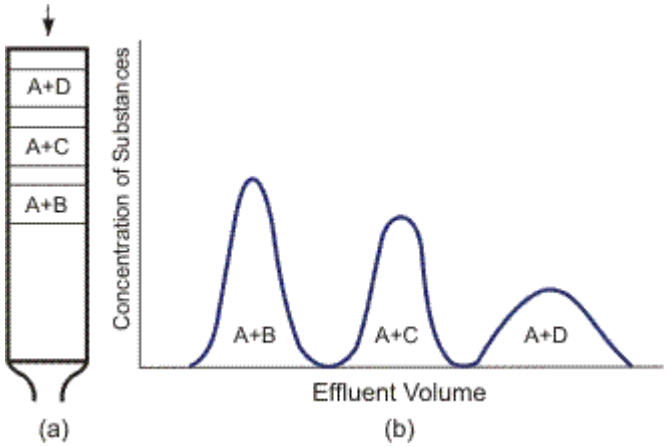
Figure 9.3: Chromatogram development in frontal analysis

(ii) Elution Analysis: This method is most widely used to develop chromatograme. In this method the chromatograph column is first washed by the eluent/ solvent (mobile phase), the eluent having lower adsorption power/afinity than any of the separated substances/components. Then the solution of analyzed mixture is added at regular intervals at the top of column into the solvent or eluent/mobile flow, the mixture in the

column being separated into components with eluent zones between them depending on its partition coefficients.

Example: A mixture contains substances B, C and D with the adsorption ability/affinity for the stationary phase in order B < C < D and the solvent A is an eluent, its adsorption ability being lower than that of B, C, D, i.e., A < B < C < D. The components get eluted in the order of their affinities with the stationary phase but their migation is determined by the mobile phase. The component can be separated completely with a zone of the mobile phase (eluent A). The separation of substances in the column and on the chromatogram is shown in Fig. 9.4



https://www.thermopedia.com/content/5056/160CFig5.gif

Figure 9.4: Chromatogram development in elution analysis

(iii) Displacement Analysis: In this method the small quantity of the sample solution added on the top of the column and the component of the mixture are separated by the continuously passed a solution of a substance (displacer) which is more strongly adsorbed than any of the components of the mixture. This results in the formation of adjoining zones of separated substances. During the process the components undergoes separation because of the differences in the partition or adsorption properties. The least adsorbed component will leave the column first followed by the others depending uopon their degree of adsorptivities.

(iv) Example: A nmixture containing B, C, D are the separated substance and E is the eluent (displacer or displacing agent) having a greater affinity for the stationary phase than the B, C, D i.e. B < C < D < E is the adsorption ability order. So that the speration order of the pure component is B > C > D. The separation of substances in the column and on the chromatogram is shown in Fig. 9.5.

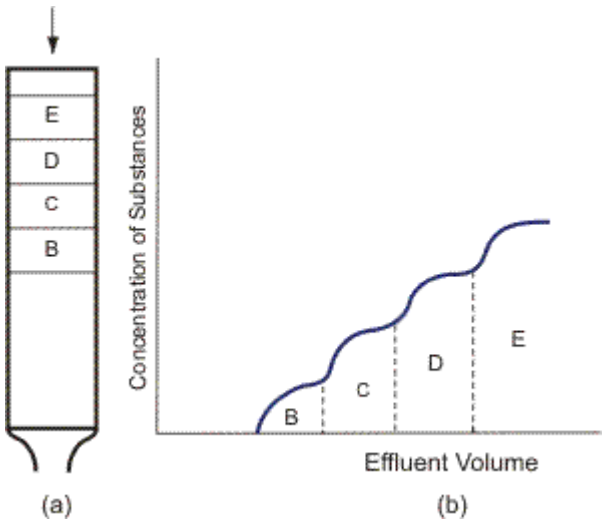


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Figure 9.5: Chromatogram development in displacement analysis

9.7 SUMMARY

In this unit, we have learnt that

- Adsorption chromatography is classified as the liqiud-solid chromatographic and gas-solid chromatographic technique.
- Adsorption chromatography is based on the phenomenon of adsorption of various components of a mixture on the stationary phase.
- The mobile phase on passing on to the stationary phase carries along with it, the least adsorbed component at a faster rate than those which are strongly adsorbed on the stationary phase.
- The technique of column chromatography (liqiud-solid chromatography) is very efficient method for the separation of a wide range of mixtures.
- A variety of adsorbents and mobile phases are used in column chromatography for separating different mixtures.
- The force of interactions involved like hydrogen bonding, van der Waals forces and dipole-dipole interactions as the process of adsorption take place.
- Three methods frontal, elution and displacement analysis have been used to develop chromatograms.
- The elution analysis is more useful than the frontal analysis and the displacement methods.

- The efficiency of the techniques depends upon the number of plat, plate height, resolution, particle size, surface area of the stationaty phase, temparature etc.

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9.9 TERMINAL QUESTIONS

1. Explain the different methods used for the development of cheomatograme in the column chromatography.
2. Disucss the principle of column chromatography.
3. Explain the different factors affecting the efficiency of the column chromatography.

UNIT10: ION EXCHANGE CHROMATOGRAPHY

CONTENTS:

10.1 Introduction
10.2 Objectives
10.3 Ion exchange chromatography
10.4 Ion exchange Materials:
10.5 Principle of ion exchange chromatography
10.6 Mechanism of Separationin
10.7 Ion-exchange Capacity
10.8 Summary
10.9 Bibliography
10.10 Terminal questions

10.1 INTRODUCTION

In Units 8 and 9 of this Block, you have studied about the charomatographic methods based on partition and adsoprtion, respectively. In this unit you will learn about ion exchange chromatography (IEC), which is another chromatographic technique based on ion exchange.

Ion exchange chromatography is widely used in biochemistry for purifying proteins and other biomolecules such as sugars, amino acids, nucleotides based on their net charge. It's also used in environmental analysis, pharmaceutical development, and many other fields where separation and purification of ions are crucial. One of the frequently employed applications of ion exchange is water softening. Ion exchange plays a significant role in the cleaning of nuclear reactor cooling water, the recovery of metals from industrial wastes, and the separation of rare earth elements.

In this unit we will discuss the different types of materials utilized in ion exchange followed by the ion exchange capacity and the discussion of principle involved in ion exchange chromatography. Lastly, we will focus on the ion exchange mechanism.

10.2 OBJECTIVES

After studying this unit, you should be able to:

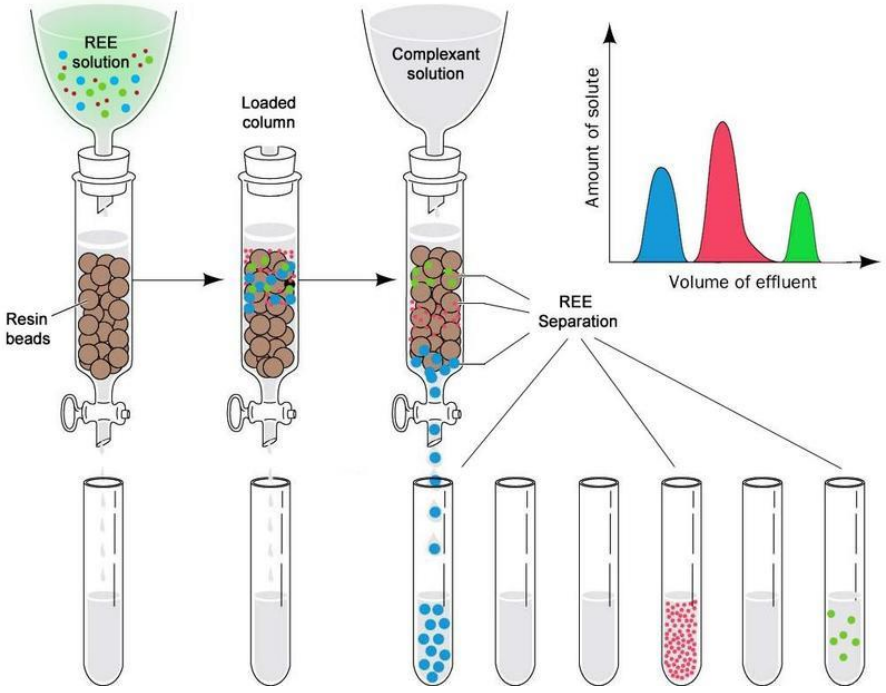
- Understand the basics of ion exchange chromatography
- Explain principle of ion exchange chromatography.

- Differentiate between natural and synthetic ion exchangers.
- Know the cationic and anionic exchangers and differentiate between a stationary phase and mobile phase.
- Explain the mechanism of ion exchange.

10.3 ION EXCHANGE CHROMATOGRAPHY

Ion exchange chromatography is a technique used for the separation and purification of ions based on their charge properties. It exploits the reversible exchange of ions between a stationary phase containing charged functional groups and a mobile phase containing ions of opposite charge.

Ion exchange chromatography (IEC) technique is a type of chromatographic technique where separation of analytes is on the basis of net surface charge of the molecules. The main advantage of using this technique is that the separation is dependent only one interaction i.e electrostatic interaction. This technique was introduced in 1960s and is still sought after for the purification of proteins, peptides, nucleic acids and other charged biomolecules. In this technique the stationary phase is usually a resin which is coated with charged moieties.



(https://www.researchgate.net/publication/317577477/figure/fig16/AS:505013674151937@1497416050333/Separation-of-rare-earths-via-ion-exchange-and-elution-chromatography-Figure-adapted.png)

Figure 10.1: Ion exchange chromatography

Ion exchange chromatography finds applications in various fields, including biochemistry (e.g., purification of proteins and nucleic acids), environmental analysis, pharmaceuticals, and water treatment. It is a versatile and widely used technique for the separation and purification of ions in both analytical and preparative contexts.

10.4 ION EXCHANGE MATERIALS

The phenomenon of ion exchange was first reported by two British agriculture chemist Thomson and Way in 1850 for the removal (exchange) of potassium or ammonium ion with calcium ion in the soil. After that Gans in 1930 introduced the natural and synthetic cation exchanger used for softening of hard water. After that in 1935 Adams and Holms explore the three dimentional polymeric chains cross linked ion exchnager.

An ion exchanger is a material that can exchange one type of ion in a solution with another ion of the same charge from the surrounding environment. Ion exchangers can be classified based on several criteria, including their charge type, structure, and mode of operation. Here's a classification based on these factors:

(i) Natural ion exchanger:

A natural ion exchanger is a material found in nature that possesses the ability to exchange ions with its surroundings. These natural materials often contain functional groups with charged sites that can attract and bind ions of opposite charge through electrostatic interactions. Examples of natural ion exchangers include certain types of clay minerals (e.g., montmorillonite, kaolinite), zeolites, and soil organic matter. These materials can play important roles in soil chemistry, water purification, and various industrial processes.

Example 1: Zeolites having cation exchange properties. These have three dimensional networks with negatively charged lattice. The alkali and alkaline earth cations which move freely, balance the negative charge. These behave as counter ions and can be exchanged with other counter ions. Their examples being the following minerals:

Analcite – $Na\,[SiAlO_6]_2.\,H_2O$

Chabazite – $(CaNa)\,[SiAlO_6]_2.\,6\,H_2O$

Naturalite – $Na_2\,[Si_2Al_2O_{10}].\,2\,H_2O$

Example 2: Montmorillonite is a type of clay mineral belonging to the smectite group. It has a layered structure composed of sheets of aluminum oxide and silicon oxide octahedra sandwiched between layers of tetrahedral silica. The layers are held together by weak van der

Waals forces, allowing them to swell and contract in response to changes in hydration and ion concentration.

In soil science, montmorillonite plays a crucial role in cation exchange processes, influencing nutrient availability and soil fertility. It can adsorb and exchange cations such as calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^{+}), and ammonium (NH_4^{+}), affecting soil structure and plant growth.

(ii) Synthetic Ion Exchanger:

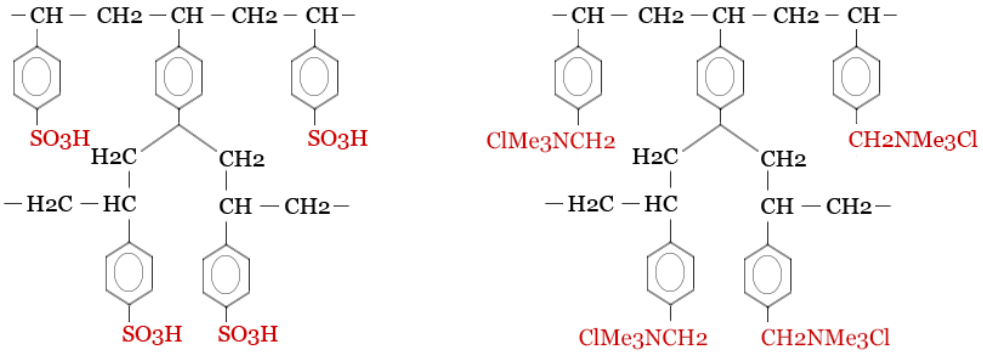
The term "synthetic ion exchanger" refers to a type of material specifically designed and synthesized to perform ion exchange processes. Thus a synthetic ion exchanger is a man-made material designed with specific chemical properties to selectively exchange ions with a surrounding solution, typically used in processes such as ion exchange chromatography, water softening, and purification in the various industries, including water treatment, pharmaceutical manufacturing, chemical processing, and nuclear power generation.

The synthetic ion exchangers are typically composed of organic or inorganic polymers with functional groups capable of interacting with ions in solution. They may have positively charged functional groups (cation exchange resins) or negatively charged functional groups (anion exchange resins), depending on the desired application.

Example 1: One example of a synthetic ion exchanger is a resin commonly known as "polystyrene-divinylbenzene copolymer" is copolymer resin consists of a three-dimensional network of polystyrene chains cross-linked with divinylbenzene. This resin is widely used in ion exchange chromatography due insoluble in water and organic solvents, excellent chemical stability, mechanical strength, and high capacity for ion exchange. It's a cross-linked polymer with functional groups attached to the polymer backbone, providing sites for ion exchange interactions.

Structure of Polystyrene-divinylbenzene:

The resin contains functional groups covalently attached to the polymer chains. These functional groups determine the type of ion exchange that occurs. For cation exchange, the functional groups are typically sulfonic acid ($-SO_3^{-}$) or carboxylic acid (-COOH) groups, while for anion exchange, they are quaternary ammonium ($-NR_4^{+}$) or tertiary amine ($-N^{+}(CH_3)_3$) groups.



Cation Exchange Resin Anion Exchange Resin

(https://www.priyamstudycentre.com/wp-content/uploads/2021/09/ion-exchage-resin-cation-anion.png)

Figure 10.2: Types of cation and anion exchange resin

(iii) Cation Exchanger:

A cation exchanger is a type of ion exchange material or resin or cross linked polymers with high molecular weight that selectively binds and exchanges positively charged ions (cations) in a solution for other ions of similar charge. In other words, it facilitates the exchange of cations between a solution and its surface. Cation exchangers typically have negatively charged functional groups, such as sulfonic acid ($-SO_3^-$) or carboxylic acid (-COOH) groups, which attract and retain cations.

Thus a cation exchanger is a material with negatively charged functional groups capable of selectively binding and exchanging positively charged ions (cations) in a solution, facilitating their separation and purification.

Example: Cation exchangers include materials like zeolites, certain clays, and synthetic resins such as polystyrene resins, carboxylic acid resins, and phosphonic acid resins. One common example of a cationic ion exchanger is a sulfonated polystyrene resin, which contains sulfonic acid groups ($-SO_3H$) attached to a polymer backbone. These sulfonic acid groups dissociate in solution to release hydrogen ions (H^+) and provide the negative charge necessary for ion exchange for example metal ions (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}). The cation exchange behaviour is represented below

$$\underset{\text{Resin}}{H_nR} + \underset{\text{Solution}}{nNa^+} \rightleftharpoons \underset{\text{Resin}}{Na_nR} + \underset{\text{Solution}}{nH^+}$$

$$2Na_nR + nCa^{+2} \rightleftharpoons Ca_nR_2 + 2nNa^+$$

(iv) Anion Exchanger:

An anion exchanger is a type of ion exchange resin or material that selectively binds and exchanges negatively charged ions (anions) from a solution with other ions of similar charge present in its structure.

They typically contain positively charged functional groups, such as quaternary ammonium groups ($-NR_4^+$) and an equivalent ampount of anions such as Cl^-, SO_4^{-2}, OH^{-1} ions etc. which attract and exchange anions from the solution. The anion exchange behaviour is represented below

$$\underset{\text{Resin}}{2RCl_n} + \underset{\text{Solution}}{nSO_4^{2-}} \rightleftharpoons \underset{\text{Resin}}{R_2(SO_4)_n} + \underset{\text{Solution}}{2nCl^-}$$

$$\underset{\text{Resin}}{RCl_n} + \underset{\text{Solution}}{nOH^-} \rightleftharpoons \underset{\text{Resin}}{R(OH)_n} + \underset{\text{Solution}}{nCl^-}$$

10.5 PRINCIPLE OF ION EXCHANGE CHROMATOGRAPHY

Ion exchange chromatography is a separation technique used in analytical chemistry and biochemistry to separate and purify ions based on their charge properties. It involves the reversible exchange of ions between a stationary phase and a mobile phase. The stationary phase typically consists of a resin or gel with charged functional groups bound to a solid support, while the mobile phase is a buffer solution containing ions of opposite charge to those on the stationary phase. When a sample containing a mixture of ions is applied to the chromatography column, the ions interact with the charged groups on the stationary phase, leading to selective retention based on their charge and affinity for the stationary phase. By passing the mobile phase through the column, the retained ions are eluted in order of decreasing affinity, allowing for the separation of the mixture into its individual components. The actual ion-wxchange mechanism is through to be composed of five distinct steps:

(i) Diffusion of the ion to be exchanger surface. This occurs very quickly in homogeneous solutions.

(ii) Diffusion of the ion through the matrix structure of the exchanger to the exchange site.

(iii)Exchange of ions at the exchange site. This is through to occur instantaneously and is an equilibrium process:

Cation exchanger:

RSO_3^- … Na^+	+	$N^+H_3R^/$	⇌	RSO_3^- … $N^+H_3R^/$	+	Na^+
Exchanger		Charged molecule to be exchange		Bound molecular ion		Exchanged ion

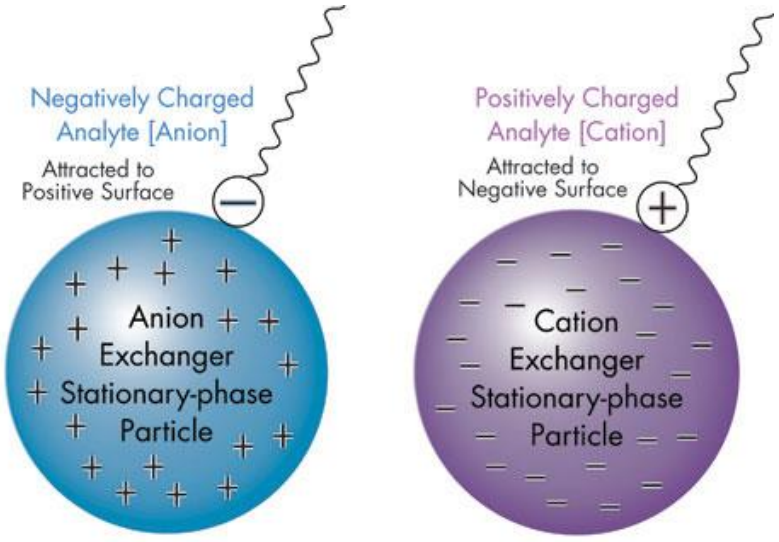
Anion exchanger:

$(R)_4N^+$ … Cl^-	+	$^-OOCR^/$	⇌	$(R)_4N^+$ … $^-OOCR^/$	+	Cl^-
Exchanger		Charged molecule to be exchange		Bound molecular ion		Exchanged ion

The more highly charged the molecule to be exchanged, the strongly it is bind to the exchanger and the slowely it is displaced by the ions.

(iv) Diffusion of the exchanged ion through the exchanger to the surface.

(v) Selective desorption by the eluant diffusion of the molecule into the external solution by adjusting the pH, oinic concentration or affinity elution.



(https://www.waters.com/content/dam/waters/en/figures/primers/hplc/primer_T_Ion_Exchange_CHromatography.jpg.82.620.resize/img.jpg)

Figure 10.3: Ion exchange chromatography

10.6 MECHANISM OF SEPARATIONIN

The mechanism of separation in ion exchange chromatography relies on the reversible exchange of ions between the stationary phase and the mobile phase. This separation process

occurs due to the interactions between the charged functional groups on the stationary phase and the ions in the sample. The mechanism can be explained in more detail as follows:

i) **Adsorption:** When a sample containing ions is introduced to the ion exchange resin (stationary phase), ions in the sample come into contact with the charged functional groups on the resin. These functional groups may be positively charged (in cation exchange) or negatively charged (in anion exchange). The ions in the sample are attracted to these charged groups via electrostatic interactions.

ii) **Ion Exchange**: As ions from the sample bind to the charged functional groups on the resin, ions of opposite charge from the mobile phase begin to replace them. This exchange process is driven by electrostatic forces. For example, in cation exchange chromatography, positively charged ions from the mobile phase replace the bound ions on the resin, while in anion exchange chromatography; negatively charged ions from the mobile phase replace the bound ions.

iii) **Equilibrium:** The ion exchange process reaches equilibrium when the rate of ions leaving the resin equals the rate of ions binding to the resin. At equilibrium, there is a dynamic exchange of ions between the stationary and mobile phases.

iv) **Elution:** Elution is the process of selectively removing the bound ions from the resin. This is achieved by passing a mobile phase through the column that contains ions with a higher affinity for the resin functional groups than the bound ions. By changing the composition of the mobile phase (e.g., adjusting pH, ionic strength), it's possible to disrupt the ion-exchange equilibrium, leading to the release of the bound ions into the mobile phase.

v) **Detection and Analysis**: As the eluted ions pass through the column, they can be detected and quantified using suitable detection techniques such as UV-Visible spectroscopy, conductivity measurement, or mass spectrometry. The elution profile provides information about the distribution of ions in the sample and allows for the separation and identification of individual components.

Example: Separation of metal ions (e.g., Na^+, K^+, Ca^{2+}, Mg^{2+}) dissolved in a solution using Cation Exchange Chromatography:

(a) Stationary Phase: Use a cation exchange resin with negatively charged functional groups.

(b) Mobile Phase: Use a buffer solution containing positively charged ions (e.g., H^+).

(c) Sample Application: Apply the mixture of metal ions to the chromatography column.

(d) Ion Exchange: Metal ions in the sample will interact with the negatively charged functional groups on the stationary phase, with different affinities based on their charge and size.

(e) Elution: By adjusting the composition of the mobile phase, selectively elute the metal ions one by one. For instance, elute Na^+ first by increasing the concentration of H^+ ions, followed by elution of K^+, Ca^{2+}, and Mg^{2+}. This process results in the separation of metal ions based on their charge properties, with each ion being eluted at a different point in time.

(f) Detection and Analysis: As each metal ion is eluted from the column, it can be detected and quantified using suitable detection methods, allowing for the identification and quantification of individual metal ions in the sample mixture.

10.7: ION-EXCHANGE CAPACITY

Ion-exchange capacity, measure of the ability of an insoluble material to undergo displacement of ions previously attached and loosely incorporated into its structure by oppositely charged ions present in the surrounding solution. Thus Ion-exchange capacity (IEC) represents the total of active sites or functional groups responsible for ion exchange resin. IEC is expressed as milliequivalent per gram of the ion exchange resin.

For example Zeolite minerals used in water softening, , have a large capacity to exchange sodium ions (Na^+) for calcium ions (Ca^{2+}) of hard water. High cation-exchange capacities are characteristic of clay minerals and numerous other natural and synthetic substances possessing ion-exchanging properties.

The IEC value (in meq/g) is determined by using the following equation:

$$\text{Capacity} = \frac{\text{V x N}}{\text{W}}$$

Where,

V= Volume of alkali (NaOH) solution used in titration

N= Strength of solution in milliequivalent per litre

W= Dry weight of resin

10.8 SUMMARY

In this Unit, you learnt that

- Ion exchange materials or ion exchanger (cation and anion exchanger) are used for separating and purification of different types of substances containing complex mixtures.
- Ion exchanger could be natural or synthetic ones. These are categorised as cation exchanger or anion exchanger materials. Further, these could be weak or strong ion exchangers.
- For cation exchange, there is a choice between strong acid groups (RSO_3H) or weak acid resins containing carboxylic acid (RCOOH) groups. The former has wider applications. Anion exchange resins contain basic functional groups attached to the polymer molecule. These are generally amines; strong base exchanges are obtained with tertiary amines and (quaternary ammonium salts) [$RN(CH_3)3^+OH^-$] and weak types with primary and secondary amines.
- The particle size of the resin plays an important role in the retention and hence, separation of materials. The other features being the temperature and the pH of the mobile phase.
- The mechanism of ion exchange involves exchange of counter ions of the resin. The selectivity coefficient determines the affinity of the ion for the resin.
- Ion-exchange capacity (IEC) represents the total of active sites or functional groups responsible for ion exchange resin. IEC is expressed as milliequivalent per gram of the ion exchange resin.

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10.10 TERMINAL QUESTIONS

1. What is ion exchanger? How they are classified?
2. Define the term ion exchange capacity.
3. Explain the mechanism of separation involved in the ion exchange chromatography.

BLOCK 3: SPECTROSCOPIC METHODS OF ANALYSIS

UNIT 11: ULTRAVIOLET–VISIBLE SPECTROSCOPY

CONTENTS:

11.1 Introduction
11.2 Objectivees
11.3 Electromagnetic radiation and spectroscopy
11.4 Absorption of electromagnetic radiations by organic molecules
11.5 Ultraviolet–visible spectroscopy
11.6 Types of electronic transitions
11.7 Selection Rule
11.8 UV-Spectrophotometer
11.9 Types of UV/Visible spectrophotometer
11.10 Sample Preparation
11.11Absorption laws
11.12 Summary
11.13 Bibliography
11.14 Terminal questions

11.1 INTRODUCTION

The most challenging task of a chemist is to determine the chemical structure of an unknown compound. There are many ways by which we can identify the unknown substance. A person can use physical methods such as boiling point, melting point, spectroscopy as well as chemical methods such as functional group testing and others to determine the structure of compounds. Spectroscopy is one of the best methods to identify a substance, which may include UV, IR, NMR, Raman and others. Here we will discuss about the various aspects of different spectroscopic techniques and more specifically about UV-spectroscopy and its uses.

11.2 OBJECTIVES

After studying this unit, you shall be able to:

- Understand what is electromagnetic radiation?
- Analyze the electromagnetic spectrum.
- Understand concept of UV-Visible spectroscopy.

- Learn about the possible electronic transitions.
- Learn about the working of UV-spectrophotometer.

11.3 ELECTROMAGNETIC RADIATION AND SPECTROSCOPY

Electromagnetic spectrum covers a wide range of electromagnetic radiations, ranging from γ rays having wavelength which are the order of a fraction of an angstrom, to radio waves having wavelength in meters or kilometers. The arrangement of all types of radiations in the order of their increasing wavelength or decreasing frequencies is known as electromagnetic (EM) spectrum. The electromagnetic spectrum includes radio and TV waves, microwaves, infrared, visible light, ultraviolet, X-rays, γ-rays, and cosmic rays, as shown in the Figure 11.1.

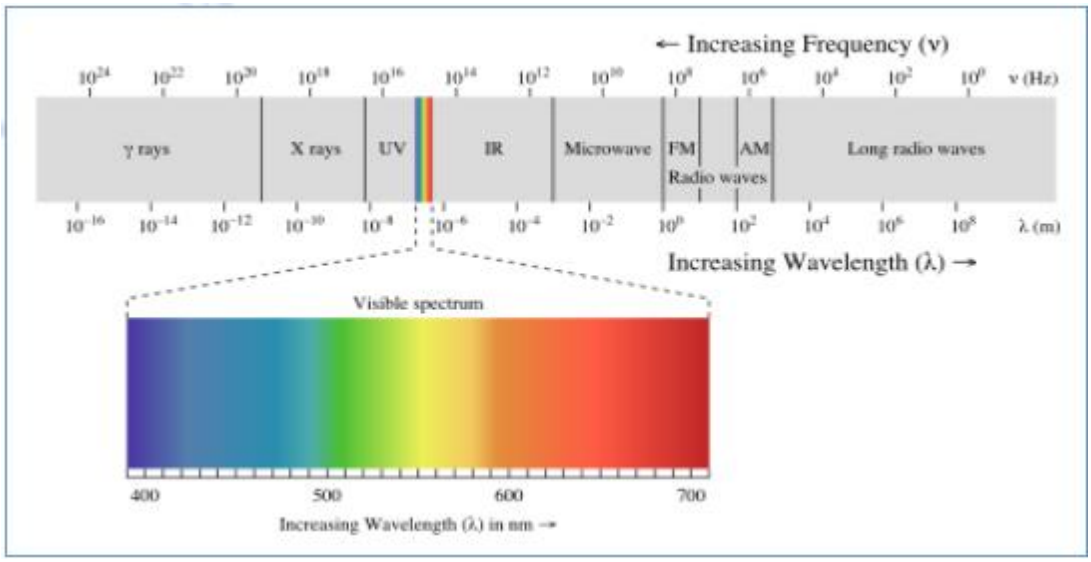


Figure 11.1: Electromagnetic spectrum

Spectroscopy: Spectroscopy is the study of interaction of electromagnetic radiations with matter. Electromagnetic radiations can interact with matter in various ways. Each interaction gives us insights about certain properties of the matter and use of electromagnetic radiations of different energies can give different information about the matter under study.

It is the motion of electrically charged particles that give rise to electromagnetic radiations. There are various forms of electromagnetic radiation e.g. radio waves, X-rays, gamma rays, infrared, visible, ultraviolet etc. All the types of radiations travel with the same velocity but differ from each other in terms of frequency and wavelength. They do not require any medium for their propagation and can travel through empty space as well as through air and other substances. Each type of electromagnetic radiation has a dual nature- wave like nature

and particle like nature. The particle nature has been established by the fact that the energy of particular radiation occurs in discrete packets or quanta known as photons. Each photon contains a certain amount of energy. The different types of radiation are defined by the amount of energy found in the photons. The energy associated with particular electromagnetic radiation is directly proportional to its frequency. The photons with the highest energy correspond to the shortest wavelengths.

11.4 ABSORPTION OF ELECTROMAGNETIC RADIATIONS BY ORGANIC MOLECULES

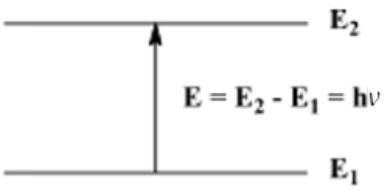
When electromagnetic radiations are passed through an organic compound, some of the part gets absorbed, while the remaining is transmitted. The absorption of energy can bring about translational, rotational or vibrational motion, electronic transition or ionization of the molecules depending upon the frequency of the electromagnetic radiation they receive (Table 11.1).

Types of Radiation	Spectral method	Energy Change involve
Gamma ray	Gamma spectroscopy	Ionisation
X-rays	X-ray Spectroscopy	Inner electrons
Ultraviolet	UV-Spectroscopy	Middle and valence shell electrons
Visible	Visible Spectroscopy	Valence shell electrons
Infrared	IR-Spectroscopy	Molecular Vibration and rotation
Microwave	ESR-Spectroscopy	Molecular rotation and spin orientation
Radio	NMR-Spectroscopy	Spin orientation of Nuclei (NMR)

Table 11.1: Energy changes depending on the type of radiation

The energy required for these transitions is quantized. Excited molecules are unstable and quickly come back to the ground state by releasing the energy they had received as electromagnetic radiation.

The wavelength and intensity of the electromagnetic radiation absorbed or emitted can be recorded with the help of spectrometer to get a spectrum. The energy required for the transition (E) from a state of lower energy (E1) to state of higher energy (E2) is exactly equivalent to the energy of electromagnetic radiation that causes transition.



$$E_1 - E_2 = E = h\nu = hc/\lambda$$

Where E is energy of electromagnetic radiation being absorbed, h is the universal Planck's constant, 6.624 x 10^{-27} J sec and ν is the frequency of incident light in cycles per second (cps or hertz, Hz), c is velocity of light 2.998 x 1010 cm s-1 and λ = wavelength (cm). Higher is the frequency, higher would be the energy and on the other side, longer is the wavelength, lower would be the energy. As we move from Gamma rays to ultraviolet region to infrared region and then radio frequencies, we are gradually moving towards regions of lower energies.

However, almost all the parts of electromagnetic spectrum are used for understanding the matter, in organic chemistry we are mainly concerned with energy absorption from only ultraviolet and visible, infrared, microwave and radiofrequency regions.

11.5 ULTRAVIOLET–VISIBLE SPECTROSCOPY

UV-Visible spectroscopy deals with the study of the electronic transitions of molecules as they absorb light in the UV (190-400 nm) and visible regions (400-800 nm) of the electromagnetic spectrum. The absorption of ultraviolet or visible radiation lead to transition among electronic energy levels, hence it is also often called electronic spectroscopy.

As a rule, the energetically favored electron promotion will be from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The resulting species is said to be in an excited state. The wavelengths at which absorption occurs, together with the degree of absorption at each wavelength is recorded by optical spectrometer. A spectrum is obtained as a result. It commonly provides the knowledge about π-electron systems, conjugated systems, aromatic compounds and conjugated non-bonding electron systems etc.

11.6 TYPES OF ELECTRONIC TRANSITIONS

The ground state of an organic molecule contains valence electrons in three principal types of molecular orbitals, namely -sigma (σ) orbitals, pi (π) orbitals and filled but nonbonding orbitals (n).

Both σ and π orbitals are formed from the overlap of two atomic or hybrid orbitals. Each of these molecular orbitals therefore has an antibonding σ* or π* orbital associated with it. An orbital containing n electron does not have an antibonding orbital because it is not formed from two orbitals. Sigma bonding orbitals have lower energy than π bonding orbitals, which in turn have lower energy than non-bonding orbitals. In the Electronic transitions, promotion of an electron from one of the three ground states (σ, π, or n) to one of the two excited states (σ∗, or π∗) takes place. As a result, there are six possible transitions- σ to σ∗, σ to π∗, π to π∗, π to σ∗, n to π∗, n to σ∗. The most commonly observed transitions and their relative energies are summarized in Figure11.2. The exact energy differences between the orbitals depend on the nature of atoms present and the nature of the bonding system.

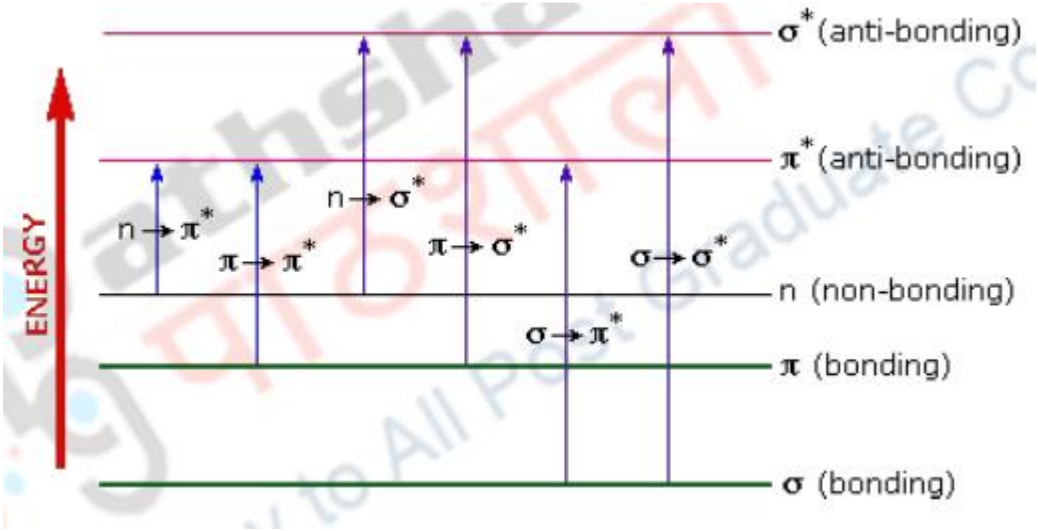


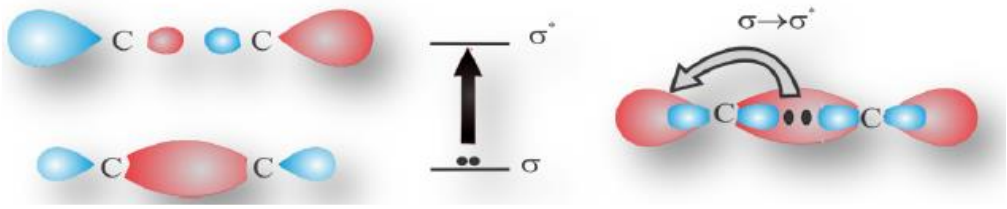
Figure 11.2: Electronic Transitions in UV/VIS spectroscopy

You can see, in each possible case, an electron is excited from a low energy, ground state orbital into a higher energy, excited state anti-bonding orbital (Figure 11.2). Each transition requires a defined amount of energy. The larger the gap between the energy levels, the greater the energy required to promote the electron to the higher energy level, resulting in electromagnetic radiation of higher frequency, and therefore shorter wavelength, being absorbed. The important modes of electronic transitions are described here.

(i) σ to σ∗

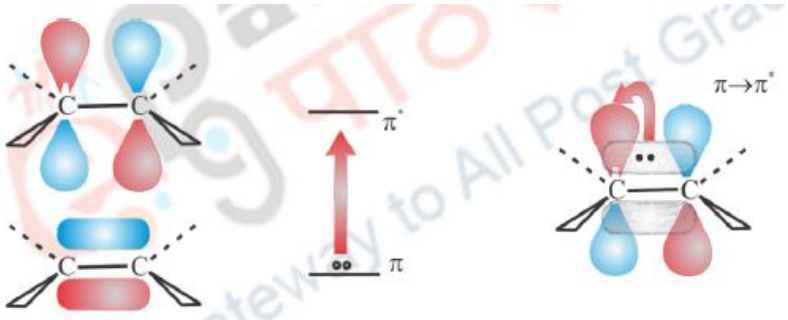
A transition of electrons from a bonding sigma orbital to the antibonding sigma orbital is designated as σ to σ∗ transition. These are high energy transitions as σ bonds are generally very strong. Thus these transitions involve very short wavelength ultraviolet light (< 150 nm) and usually fall outside the range of UV-visible spectrophotometers (200-800 nm). Alkanes

can only undergo σ to σ* transitions. Methane and ethane undergo σ → σ* transitions with an absorbance maximum at 122 and 135 nm, respectively. Study of such transitions is usually done in an evacuated spectrophotometer (< 200 nm) since oxygen present in air absorbs strongly at 200 nm and below. Similarly nitrogen absorbs at ~150 nm and below.



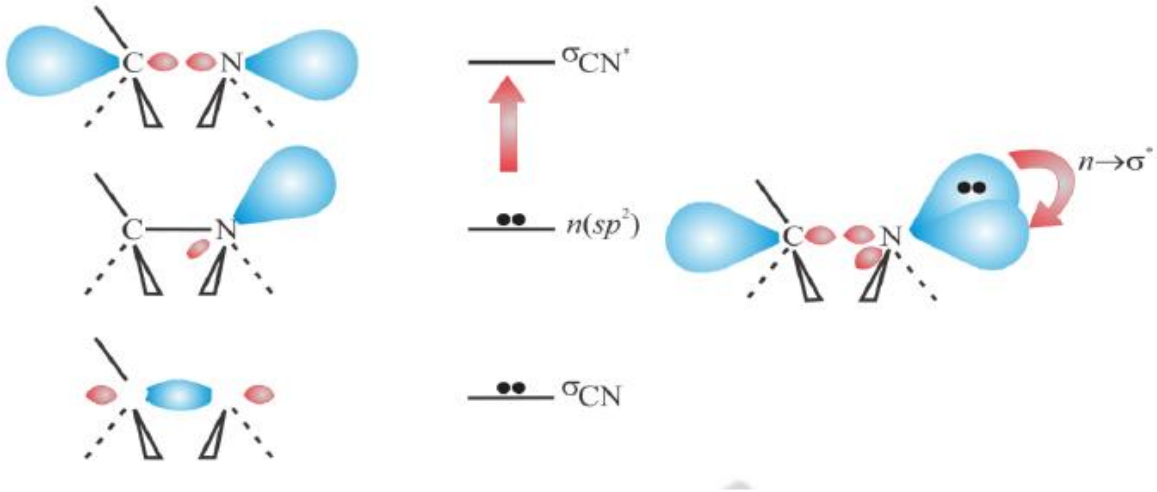
(ii) π to π∗

The transition of an electron from a π bonding orbital to a π∗ antibonding orbital is designated as π to π∗ transition. These types of transitions take place in compounds containing one or more unsaturated groups like simple alkenes, carbonyl, aromatics, nitriles, nitro etc. These transitions require lesser energy than n to σ∗ transitions. In non-conjugated alkenes, this type of transition occurs in the range 170-190 nm e.g. ethane shows absorption maxima at 171 nm. Similarly, π to π∗ transition in the range of 180-190 nm occurs in non conjugated carbonyl compounds e.g. acetone shows absorption maxima at 188 nm.



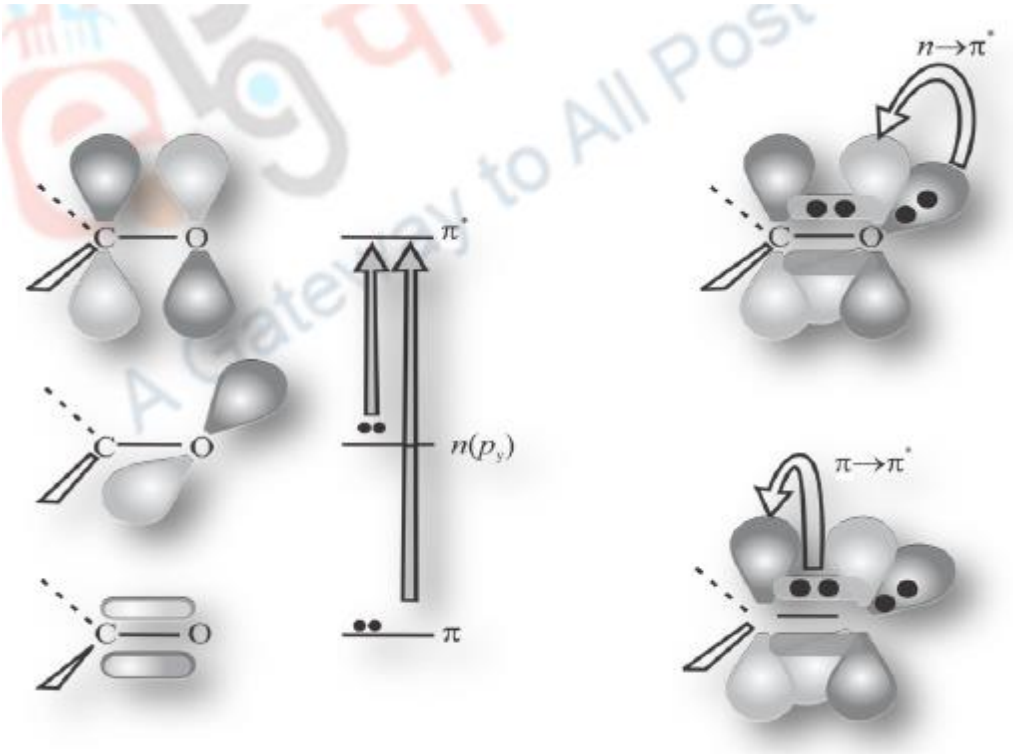
(iii) n to σ∗

The transition of an electron from a non-bonding orbital to the antibonding sigma orbital is designated as n to σ∗ transition. Saturated compounds containing atoms with lone pairs (nonbonding electrons) like saturated alcohols, amines, halides, ethers etc are capable of showing n to σ∗ transitions. Energy required for these transitions is usually less than σ to σ∗ transitions. Such compounds absorb light having wavelength in the range 150-250 nm. For example the absorption maxima for water, methyl alcohol, methyl chloride and methyl iodide are 167 nm, 174 nm, 169 nm and 258 nm, respectively.



(iv) n to π∗

The transition of an electron from a non-bonding orbital to a π∗ antibonding orbital is designated as n to π∗ transition. This transition involves the least amount of energy in comparison to all other transitions and therefore gives rise to an absorption band at longer wavelength. Saturated carbonyl compounds show two types of transitions, low energy n to π∗ (270-300 nm) and high energy π to π* (180-190 nm). The transition n to π∗ is of lowest energy but is of low intensity as it is symmetry forbidden. Thus the most intense band for these compounds is always due to π to π* transition.



11.7 SELECTION RULE

Some electronic transitions, which are otherwise theoretically possible, are generally not observed in the UV/VIS spectroscopy. Therefore there are some restrictions which govern the observable transitions.

(i) Transitions, which involve change in the spin quantum number of an electron during the transitions do not occur, i.e. singlet-triplet transitions are not allowed.

(ii) Transitions between orbitals of different symmetry do not occur. For example, transition n to $\pi*$ is forbidden because the symmetry of n and $\pi*$ do not match.

11.8 UV-SPECTROPHOTOMETER

Spectrophotometer is a kind of spectrometer, which measures the transmittance or absorbance of a sample as a function of wavelength, when light of certain intensity and frequency range is passed through the sample. Unlike a spectrometer (which is any instrument that can measure the properties of light over a range of wavelengths), a spectrophotometer measures only the intensity of light as a function of its wavelength. The key components of a spectrophotometer are:

- Light source
- Monochromator
- Sample area
- Detector and Recorder

1. Light Source

The most suitable sources of light are

(i) Deuterium lamp which emits the light in the UV-region (160-375 nm).

(ii) Tungsten lamp or tungsten-halogen lamp which emits radiation in the Visible and near infrared regions (350-2500 nm).

(iii) Xenon arc lamp which emits radiation in the range 190-800 nm.

(iv) Light emitting diodes (LED) which emits radiation in the visible range 400-800 nm. The instruments automatically swap lamps when scanning between the UV and UV-VIS regions.

2. Monochromator

The main function of the monochromator is to disperse the beam of light obtained from the primary source, into its component (Figure 11.3). The principle components of monochromator are

- An entrance slit
- A collimating lens
- A dispersing device
- A focusing lens
- An exit slit

The radiation emitted from the primary source (polychromatic radiation) enters the monochromator through the entrance slit. The beam is collimated and then strikes the dispersing element (Prism or grit) at a particular angle. Two types of dispersion devices viz. prisms and holographic gratings (Figure 11.4) are commonly used in UV-visible spectrophotometers.

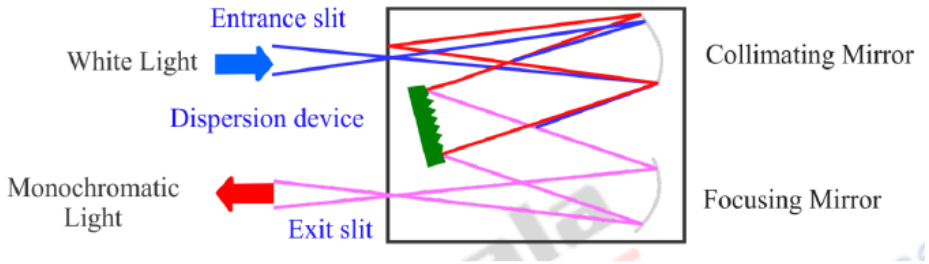


Figure 11.3: Functioning of Monochromator

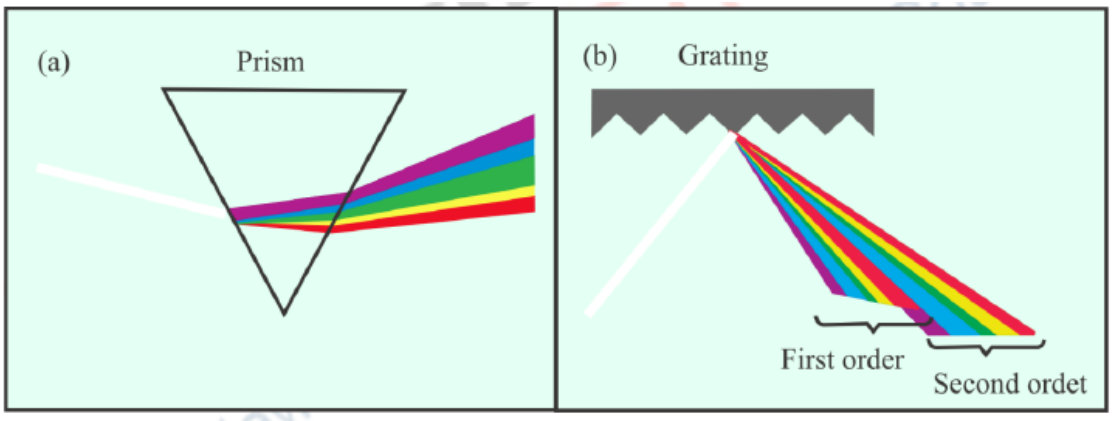


Figure 11.4: Dispersion of white light through prism and grating

Light falling on the prism is reflected at different angles, depending on the wavelength. The beam is split into its component colors. By moving the dispersing element or the exit slit, radiation of only a particular wavelength can be obtained, which leaves from the exit slit and can be used for the recording purpose (Figure 11.3). The beam selected by the slit is monochromatic and further divided into two beams with the help of another prism, which then passes through the sample and reference solutions.

3. Sample area

One of the two divided beams is passed through the sample solution and the other beam is passed through the reference solution. Although, the samples for recording spectra are most commonly liquids, but the absorbance of gases and even of solids can be measured. Both sample and reference solutions are placed in a transparent cell, known as cuvette. The cuvettes are rectangular in shape, and usually have an internal width of 1 cm (Figure 11.5).

Figure 11.5: A quartz cuvette

It is important that the material of cells must be transparent to the radiation throughout the region under study. The cells are usually made of glass, plastic as well as silica or quartz. Of these, glass cells cannot be used for the UV region as they absorb light in the UV region but can be used satisfactorily in the visible region. Quartz is transparent in all (200-700 nm) ranges and is the best choice and hence can be easily used in UV as well as visible region.

4. Detector and Recorder

A detector converts a light signal into an electrical signal. After the beams are passed through the sample under study as well as the reference cell, the intensities of the respective transmitted beams are then compared over the whole wavelength range of the instrument. Generally two photocells are used as detector in UV spectrometer to record the spectra. One of the photocell receives the beam from sample cell and second detector receives the beam

from the reference. The intensity of the radiation from the reference cell is stronger than the beam of sample cell. This results in the generation of pulsating or alternating currents in the photocells.

Spectrophotometers consist of either a photomultiplier tube detector or a photodiode detector. The commonly used detector in UV-Vis spectroscopy is photomultiplier tube (Figure 11.6). It is consists of three components:

- A cathode which emits electrons when struck by photons of radiation known as photo emissive cathode.
- Several dynodes which emit several electrons for each electron striking them.
- An anode.

In it's functioning; when a photon of radiation strikes the cathode, emission of several electrons take place. These emitted electrons are then accelerated towards the many dynodes. The first dynode is 90V more positive than the cathode. The electrons strike the first dynode, causing the emission of several electrons for each incident electron. These electrons are then accelerated towards the second dynode, to produce more electrons which are accelerated towards dynode three and so on. Finally all the electrons are collected at the anode. Several dynodes are arranged between the anode and the cathode to produce an amplification effect. Each photon usually produces 10^6-10^7 electrons, resulting in the amplified current that can be measured.

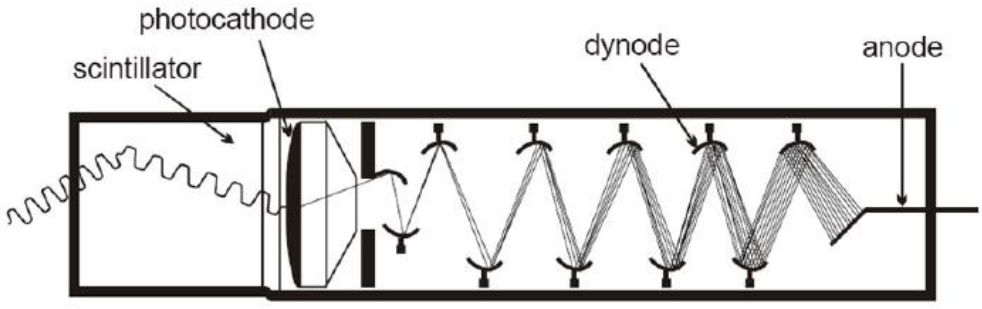


Figure 11.6: A photomultiplier tube

Photomultipliers are very sensitive to both UV and visible radiations and have fast response times. It is significant to note that Intense light may damage photomultipliers, hence they are limited to measuring low power radiation.

Photodiodes are increasingly being used as detectors in modern spectrophotometers. Photodiode detectors have a wider dynamic range and are more robust than photomultiplier

tube detectors. In a photodiode, light falling on the semiconductor material allows electrons to flow through it, thereby depleting the charge in a capacitor connected across the material. The amount of charge that is required to recharge the capacitor at regular intervals is proportional to the intensity of the light. The limits of detection are approximately 170-1100 nm for silicon-based detectors.

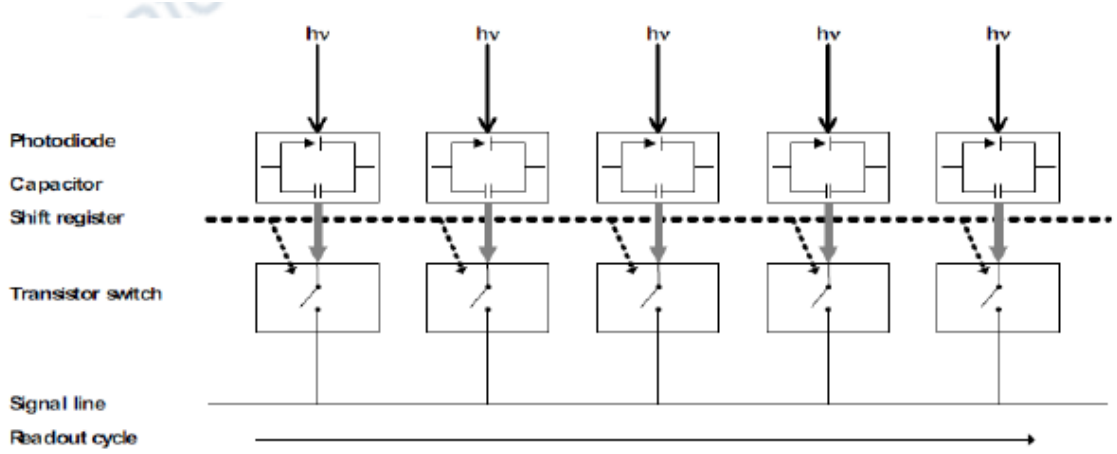


Figure 11.7: An array of photodiodes

Some modern spectrophotometers contain an array of photodiode detectors instead of a single detector (Figure 11.7). A diode array consists of a series of photodiode detectors positioned side by side on a silicon chip. Each photodiode is connected to a transistor switch via a charged capacitor When photons strike the diode, free electrical charge carriers are generated that discharge the capacitors. The capacitors are recharged at regular intervals. The amount of charge needed to recharge the capacitors is proportional to the number of photons detected by each diode, which in turn is proportional to the light intensity. The absorption spectrum is obtained by measuring the variation in light intensity over the entire wavelength range.

11.9 TYPES OF UV/VISIBLE SPECTROPHOTOMETER

There are two types of spectrophotometers, namely, single beam spectrophotometer or double beam spectrophotometer (Figure 11. 8). Each has its advantages and disadvantages.

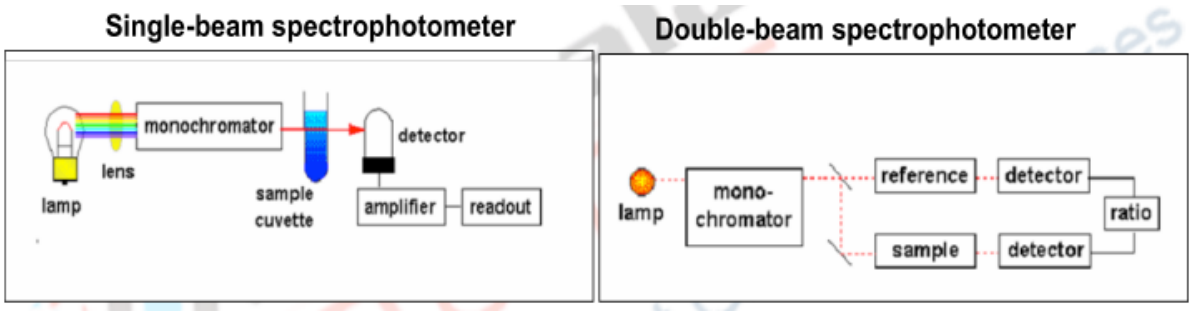


Fig.11.8: Types of Spectrophotometer

A single beam spectrophotometer has only one beam of light, which passes through the sample, therefore it requires taking reading for the reference and sampling separately.

On the other hand, in a double-beam instrument, the light is split into two beams before it reaches the sample. The two beams move simultaneously, one passing through a reference solution and the other through the sample. The reference beam intensity is taken as 100% Transmission (or 0% Absorbance), and the measurement displayed is the ratio of the two beam intensities. Of the two types of spectrophotometer, double beam spectrophotometers are faster to operate and in their performance. They provide more reproducible results because they perform an automatic correction for the loss of light intensity as the beam passes through the sample and reference solution.

11.10 SAMPLE PREPARATION

The UV-Vis spectra are usually measured in very dilute solutions. Usually 1 mg of the compound of molecular weight of 100-200 is dissolved in 100 ml of suitable solvent and only a portion is used for recording the spectra. The solvent should not absorb radiation and must be transparent over the desired range of wavelength. The solvents, which do not contain conjugated system, are most suitable for recording the UV-spectra. The solvent should also be inert to the sample. Some commonly used solvents are water, 95% ethanol, methanol and hexane.

11.11 ABSORPTION LAWS

When the radiation passes through a solution, some amount of light is absorbed. Suppose I_0 is the intensity of the incident radiation and I, the intensity of the transmitted radiation. The amount of radiation absorbed can be measured by

Transmittance $T = I/I_0$

% Transmittance = $T \times 100$

Absorbance $A = \text{Log}_{10}\ I_0/I = \text{Log}_{10}\ 1/T$

If the entire light passes through a solution without any absorption, then absorbance is zero. In this case, the percent transmittance is 100%.

If all the light is absorbed, then absorption is infinite and the percent transmittance is zero %.

Beer-Lambert Law: It gives a linear relationship between absorbance and concentration of an absorbing species. *This law states that the absorption is directly proportional to the*

concentration of absorbing substance and the length of the path of radiation through the sample. It is independent of the intensity of the incident light and each successive unit layer absorbs an equal fraction of light incident on it.

$A = \varepsilon cb$

$Log_{10} I_0/I = \varepsilon cb$

Where A is the sample's Absorbance value at specific wavelength or frequency

ε is the molar absorptivity or the molar extinction coefficient of the substance

b is the path length of the sample in cm

c is the concentration of the solute in mol L^{-1}.

The value of ε absorptivity coefficient is constant for a particular material at a particular wavelength.

Limitations of the Beer-Lambert Law

Under certain conditions Beer-Lambert law fails to maintain a linear relationship between absorbance and concentration of the solution.

(i) Deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity.

(ii) Scattering of light due to particles present in the sample.

(iii) Chemical deviations due to the specific chemical species of the sample under investigation.

(iv) Non-monochromatic radiation

(v) Fluorescence or phosphorescence of the sample

11.12 SUMMARY

In this module you have learnt that:

- Spectroscopy is the study of interaction of electromagnetic radiations with the matter and is used to identify a substance, which may include UV, IR, NMR and Raman etc.
- The arrangement of all types of radiations in order of their increasing wavelength or decreasing frequencies is known as electromagnetic spectrum.
- The absorption of energy can bring about translational, electronic, rotational or vibrational motion or ionization of the molecules depending upon the frequency of the electromagnetic radiation they receive.

- Spectrophotometer is an instrument, which measures the transmittance or absorbance of a sample as a function of wavelength, when light of certain intensity and frequency range is passed through the sample.
- Although, there are six possible transitions σ to σ∗, π to σ∗, π to π∗, π to σ∗, n to π∗ and n to σ, the most commonly observed transitions in organic molecules are π to π∗, n to σ∗ and n to π∗.

11.13 BIOBLOPGRAPHY

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11.14. TERMINAL QUESTIONS

1. Write the Beer-Lambert absorption Law.
2. Explain the electronic transitions in UV-Visible spectroscopy.
3. Explain the UV-spectrophotometer.

UNIT 12: INFRARED SPECTROSCOPY

CONTENTS:

12.1 Introduction
12.2 Objectives
12.3 Origin of Infra-red Spectroscopy
12.4 Molecular Vibrations
12.5 Selection Rule
12.6 Fundamental Vibrations
12.7 Sample preparation
12.8 IR-Spectrometer
12.9 Dispersive Infrared Spectrometer
12.10 Fourier-Transform Infrared Spectrometer
12.11 Hands-on Operation of an FTIR Spectrometer
12.12 Summary
12.13 Bibliography
12.14 Terminal questions

12.1 INTRODUCTION

The most frequent spectroscopic technique used by organic and inorganic chemists is Infrared (IR) spectroscopy. It deals with the absorption of radiation in the infrared region of the electromagnetic spectrum. IR spectrum gives sufficient information about the structure (identification of functional groups) of a compound and can also be used as analytical tool to assess the purity of a compound. The absorption of infrared radiation by a molecule causes changes in their vibrational and rotational energy levels and hence IR-spectroscopy is also known as vibrational-rotational spectroscopy. Unlike UV-spectroscopy which has very few peaks in their spectrum, IR spectroscopy provides spectrum with a large number of absorption bands and hence provide plenty of information about the structure of a compound.

12.2 OBJECTIVES

After studying this unit, you shall be able to

- To understand the concept of Infra-red spectroscopy
- To predict the number of fundamental modes of vibration of a molecule

- To know how to make samples for recording the spectra of different organiccompounds
- To understand the working of IR-spectrophotometer
- Hands-on experience of recording the IR-spectrum

12.3 ORIGIN OF INFRA-RED SPECTROSCOPY

IR-spectroscopy gives the information about molecular vibrations or more precisely on transitions between vibrational and rotational energy levels. Since the absorption of infrared radiation leads to transition between vibrational and rotational energy levels, it is also vibrational-rotational spectroscopy.

When a molecule absorb IR-radiation below 100 cm^{-1}, transitions between rotational energy levels takes place. Since these energy levels are quantized, a rotational spectrum consists of discrete lines. If a molecule absorbs radiation in the range 100-10,000 cm^{-1}, it causes transitions between vibrational energy levels. These energy levels are also quantised but vibrational spectra appear as bands rather than discrete lines. Each vibrational energy level is associated with a large number of closely spaced rotational energy levels or we can say that the energy difference between various rotational energy levels is very short than the energy difference between various vibrational energy levels. Therefore the vibrational spectra appear vibrational-rotational bands instead of discrete lines. Organic chemists are mainly concerned with these transitions especially with those occur in the range 4000-667 cm^{-1}.

12.3.1 IR regions:

Different bonds present in the spectra correspond to various functional groups and bonds present in the molecule. The infrared spectrum can be divided into three main regions: the far infrared (<400 cm^{-1}), the mid-infrared (4000–400 cm^{-1}) and the near-infrared (13000–4000 cm^{-1}). The mid IR region is of greatest practical use to the organic chemist, but the near- and far-infrared regions also provide important information about certain materials.

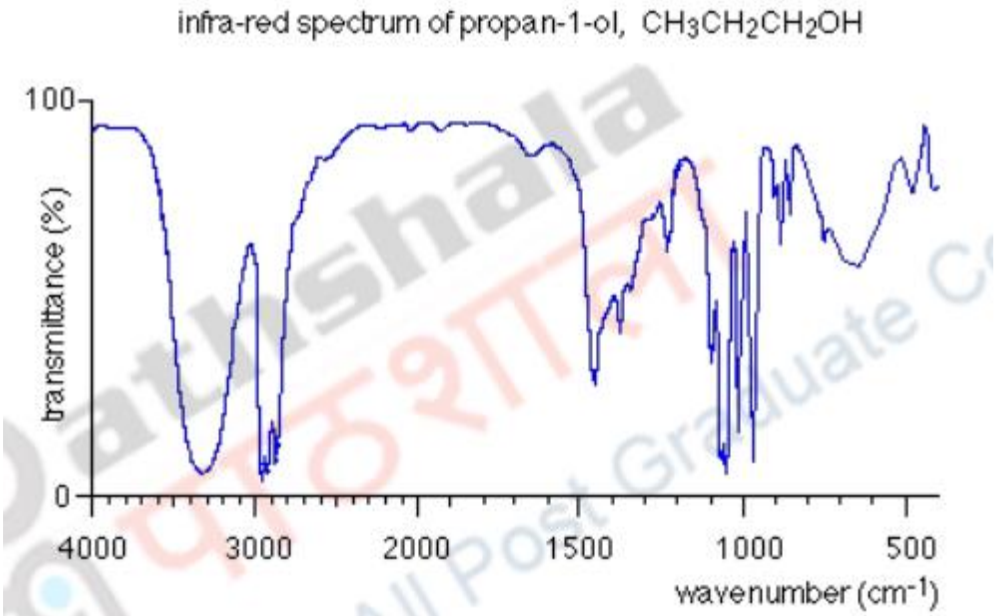
Mid IR region: The mid-infrared spectrum extends from 4000 to 400 cm^{-1} and results from vibrational and rotational transitions. This region is most useful for the organic chemist since most of the organic molecules absorb in this region. The mid-infrared can be divided into two regions viz functional group region (4000-1300) and finger print region (1300-600). **Functional group region (4000-1300):** Most of the functional groups present in organic molecules exhibits absorption bands in the region 4000-1300 cm^{-1}, hence this is known as

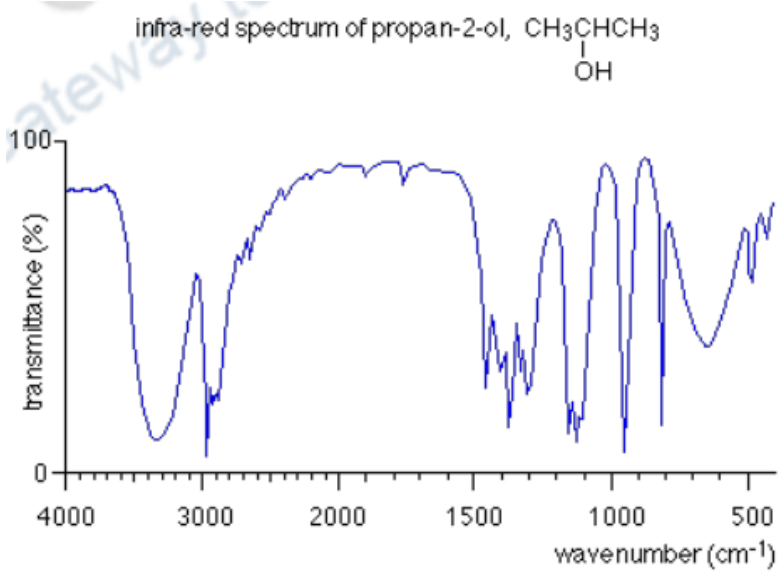
functional group region. In this region each band can be assigned to a particular deformation of the molecule, the movement of a group of atoms, or the bending or stretching of a particular bond.

Finger print region (1300-600): The region from 1300 cm-1 to 600 cm^{-1} usually contains a very complicated series of absorptions. These are mainly due to molecular vibrations, usually bending motions that are characteristic of the entire molecule or large fragments of the molecule. Except enantiomers, any two different compounds cannot have precisely the same absorption pattern in this region. Thus absorption patterns in this region are unique for any particular compound that is why this is known as finger print region.

It is very difficult to assign individual bands in this region. Two molecules having the same functional group may show similar spectra in the functional group region but their spectra differ in the finger print region. Therefore both the regions are very useful for confirming the identity of a chemical substance. This is generally accomplished by comparing the spectrum of an authentic sample. When two compounds show a good match between the IR spectra in all frequency ranges, mainly in the fingerprint region, strongly indicates that they have the same molecular structures.

Both the compounds are alcohols and contain exactly the same bonds. Now if you compare the infra-red spectra of these compounds, the functional group region is very similar for both the compounds but the fingerprint region is totally different. Therefore fingerprint region could be crucial to identify the compound. To understand the importance of finger print region to identify a compound, we can take the example of propan-1-ol and propan-2-ol.





Near-infrared region (13000–4000 cm^{-1}): The absorptions observed in the near-infrared region (13000–4000 cm^{-1}) are overtones or combinations of the fundamental stretching bands. Bands in the near infrared are usually weak in intensity. They are often overlapped and hence are less useful than the bands in mid-infrared region.

NIR shows some similarities to UV-visible spectrophotometry and some to mid-IR spectrometry.

Indeed the spectrometers used in this region are often combined UV-visible-NIR ones. Usually Hydrogen-stretching vibrations that occur in the region 3 to 6 μm, are the absorption bands due to overtones (or combination) of fundamental bands

NIR is generally used for quantitative organic functional-group analysis. The NIR region has also been used for qualitative analyses and studies of hydrogen bonding, solute-solvent interactions, organometallic compounds, and inorganic compounds

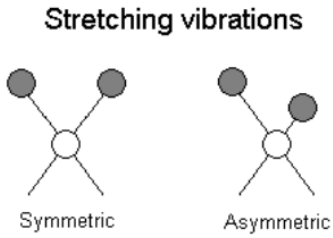
Far-infrared region (600-100 cm^{-1}): The far-infrared spectrum extends from 600 to 100 cm^{-1}. Organometallic and inorganic molecules contain heavy atoms and have weak bonds, therefore the fundamental vibrations of these molecules fall in this reigon. Lattice vibrations of crystalline materials occur in this region.

12.4 MOLECULAR VIBRATIONS

The atoms in a molecule do not remain fixed at certain positions. The two nuclei can vibrate backwards and forwards or towards and away from each other around an average position.

There are two types of fundamental molecular vibrations viz stretching (change in bond length) and bending (change in bond angle).

(i) Stretching vibrations: It involves a rhythmic movement along a bond axis with a subsequent increase and decrease in bond length. Stretching vibrations are of two types viz Symmetrical Stretching and asymmetrical stretching.



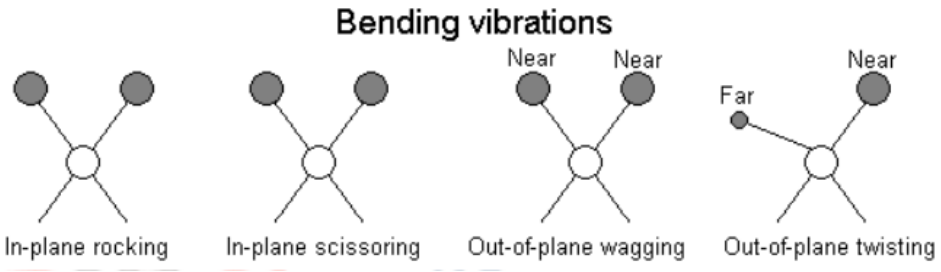
(ii) Bending vibrations: It involves a change in bond angle or movement of a group of atoms with respect to the rest of the molecule. Bending vibrations are of four types.

i) Rocking

ii) Scissoring

iii) Wagging

iv) Twisting



All the bonds in a molecule are not capable of absorbing infrared radiation but only those bonds which are accompanied by a change in the dipole moment will absorb in the infra-red region. Thus, vibrations which are associated with the change in the dipole moment of the molecule are called infra-red active transitions otherwise the vibration is said to be IR-inactive and do not show any absorption band in the IR-spectrum. Generally, larger the change in the dipole moment, the higher is the intensity of absorption. Hence the vibrational absorption bands in simple hydrocarbons are weak while bands associated with bonds connecting atoms with considerable electronegativity difference give strong bands.

12.5 SELECTION RULE

IR-radiation is absorbed only when a change in dipole moment of the molecule takes place. Complete symmetry about a bond may eliminate certain absorption bands. Therefore number

of absorption bands observed is not exactly equal to the fundamental vibrations, some of the fundamental vibrations are IR-active while others are not. This is governed by selection rule described below.

(i) In a molecule with a centre of symmetry, the vibrations symmetrical about the centre of symmetry are IR-inactive.
(ii) The vibrations which are not symmetrical about the centre of symmetry are IR-active.

Here are some examples which could explain the selection rule.

(i) All the symmetrical diatomic molecules such as H_2, N_2 and Cl_2 etc. are IR-inactive.
(ii) The symmetrical stretching of the C=C bond in ethylene (centre of symmetry) is IR-inactive.
(iii) The symmetrical stretching in CO_2 is IR-inactive, whereas asymmetric stretching is IR-active.
(iv) Cis-dichloro-ethylene molecule shows C=C stretching bands whereas trans molecule does not show this band.

12.6 FUNDAMENTAL VIBRATIONS

The IR spectrum of a compound may show more than one vibrational absorption bands. The number of these bands corresponds to the number of fundamental vibrations in the molecule which can be calculated from the degree of freedom (DOF) of the molecule. A molecule comprising of n atoms has a total of 3n DOF. In a nonlinear molecule, three of these degrees of freedom are rotational and three are translational and the remaining (3n-6) correspond to vibrational degree of freedom or fundamental vibrations. Whereas in a linear molecule, only two degrees of freedom are rotational (because rotation about its axis of linearity does not change the positions of the atoms) and three are translational. The remaining (3n-5) degrees of freedom are vibrational degree of freedom or fundamental vibrations.

Simple diatomic molecules have only 1 bond and only 1 vibrational band. If the molecule is symmetrical such as hydrogen, nitrogen, and chlorine, the band is not observed in the IR spectrum. Asymmetrical diatomic molecules, e.g. CO and iodine chloride absorb in the IR spectrum.

It has been observed that in actual IR spectrum, the theoretical number of fundamental bands is seldom observed because there are certain factors which may increase or decrease the number of bands. Some fundamental vibrations lie outside the IR region (4000-400 cm^{-1}),

whereas some are too weak to be observed. Few fundamental vibrations are too close that they merge into one another. The occurrence of degenerate bands (bands of same frequency) also cause decrease in the fundamental vibrational bands.

For example: Carbon dioxide, CO_2 is linear and has four fundamental vibrations but actually it shows only two bands (666 cm^{-1} and 2350 cm^{-1}). The symmetrical stretching vibration of CO2 is inactive in the IR because this vibration produces no change in the dipole moment of the molecule. The two scissoring or bending vibrations are equivalent and therefore have the same frequency (degenerate) at 666 cm^{-1}. The asymmetrical stretch of CO_2 gives a strong band in the IR at 2350 cm^{-1}.

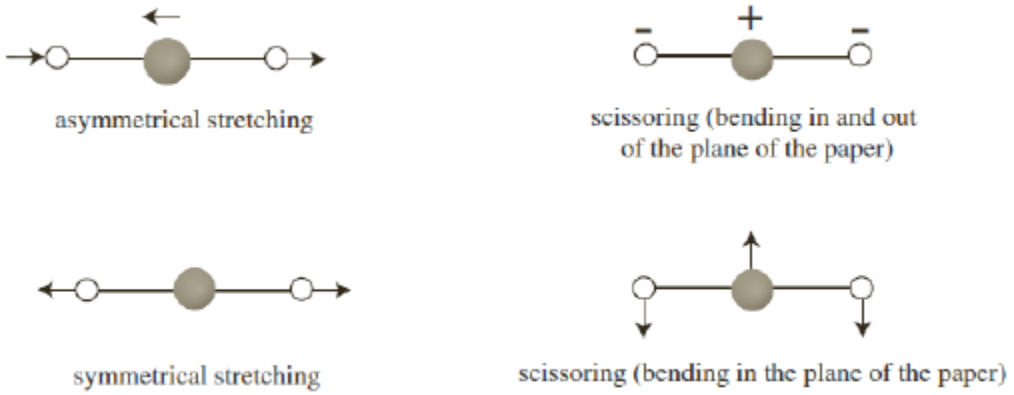


Figure 12.1: Fundamental vibrations in CO_2 molecule

The appearance of certain types of non-fundamental (overtones, combinations of fundamental vibrations or difference of fundamental vibrations) bands increases the number of bands as compared to that expected from the theoretical number of fundamental bands. All these bands have very weak intensity than the fundamental vibration bands.

Overtones bands: In addition to the fundamental vibrations, other frequencies can be generated by modulations of the fundamental bands. An overtone band occurs when the molecule makes a transition from the ground state (v=0) to the second excited state (v=2), where v is the vibrational quantum number. The intensity of the overtone band is very low as compared to the fundamental band and they are usually found in the near infrared region. Based on the harmonic oscillator approximation it has been found that the energy of the overtone transition is about n times of the fundamental vibration associated with that particular transition. Suppose a compound shows strong absorptions at x and y cm^{-1} then it may also give rise to weaker absorptions at 2x, 2y, 3x and 3y cm-1, respectively. The intensity of overtones bands decreases as the order of the overtone increases, i.e. the intensity

of 3x or 3y overtones will be less than the 2x and 2y. Therefore second and third overtones are rarely observed.

Combination Bands: Combination bands are observed when two or more than two fundamental vibrations are excited simultaneously. If there are two fundamental vibrations at x and y cm^{-1} then it may also give rise to absorption bands at (x+y), (x+2y), (2x+y) cm^{-1}.
Difference bands: It is also possible to have a difference band where the frequencies of two fundamental bands are subtracted, i.e. (x-y), (x-2y), (2x-y) cm^{-1}.

Fermi bands/resonance: When a fundamental vibration couples with an overtone or combination band, the coupled vibration is called Fermi resonance. As a result, two strong bands are observed in the spectrum, instead of the expected strong and weak bands. Fermi resonance is often observed in carbonyl compounds.

A practical use for understanding overtones and combination bands is applied to organic solvents used in spectroscopy. Most organic liquids have strong overtone and combination bands in the mid-infrared region, therefore, acetone, DMSO, or acetonitrile should only be used in very narrow spectral regions. Solvents such at CCl_4, CS_2 and $CDCl_3$ can be used above 1200 cm^{-1}.

12.7 SAMPLE PREPARATION

IR spectrum of a compound can be recorded in many different forms, such as liquid, solid, gas and solution. Some of the materials are opaque to infrared radiation, so in order to obtain spectra they must be dissolved or diluted in a transparent matrix. For recording IR spectra, the sample should be properly dry as water absorb near 3710 and 1630 cm^{-1}. The samples should be perfectly dried, since cell materials (NaCl, KBr) are usually spoiled by the moisture.

(i) Solid samples: There are several methods by which an IR spectrum of a solid sample can be recorded.

(a). As a pressed disc: The first common method involves the mixing of finely ground solid sample with powdered potassium chloride. A translucent pellet of this powder mixture is formed by pressing it in a mechanical pressure. The main advantage of using KBr is that it does not interfere with the bands due to compound since KBr is transparent to IR radiation 4000-650 cm^{-1} and thus gives better spectra. The disadvantage of this method is that KBr absorbs water quickly which may interfere with the spectra that is obtained.

(b). As a mull or paste: Finely ground compound is mixed with an oily mulling agent (usually Nujol) using a pestle and mortar. A thin film of the mull is placed between two flat plates of NaCl and the spectrum is measured. The main disadvantages of this method is that nujol has absorption bands at 2924-2860, 1462, 1380 cm^{-1}, therefore no information about the observed compound can be obtained in this region.

(c). As a film: The third method is to dissolve the soild sample in a suitable, non-hygroscopic solvent usually methylene chloride or carbon tetra chloride. A drop of this solution is deposited on surface of Potassium bromide or Sodium chloride plate. The solution is then evaporated to dryness and the film thus formed on the KBr disc is analysed directly to obtain the IR spectrum. The most important thing is that the film should not be too thick otherwise light cannot pass through it. This method gives good results with dilute solution of the compound in a non-polar solvent.

(ii) Liquid samples: Liquids are studied neat or in solution. A drop of neat liquid sample or a solution of the sample in an appropriate solvent is placed between two plates of a salt (sodium chloride or potassium bromide) to give a thin film and analysed to obtain the spectrum. The plates are transparent to the infrared light and do not introduce any lines onto the spectra. Salt plates break easily and are water soluble therefore compounds analysed by this method should be free from water. Spectrum obtained by this method is known as neat spectrum since no solvent is used in recording the spectrum.

(iii) Gaseous samples: The gas is introduced into a special cell with a long path length and the walls of its both the ends are normally made up of NaCl. Gases have very less densities compared to liquids, and hence path lengths should be correspondingly greater, usually 10 cm or longer. The vapor phase technique is limited because most of the organic compounds have too low vapor pressure to produce a useful absorption spectrum.

It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to differences in the samples' physical states.

12.8 IR-SPECTROMETER

Traditionally, dispersive infrared spectrophotometers, developed in 1940s, were used to obtain infrared spectra. In 1960s, a new method was developed known as Fourier-transform infrared (FT-IR) spectrometers. But due to high cost of the instrument, this was tended to be

used for advanced research only at that time. Gradually, technology advancements in computers and instruments have reduced the cost and enhanced the capabilities of an FT-IR spectrophotometer. Today they are predominantly used and have improved the acquisition of infrared spectra dramatically.

12.9 DISPERSIVE INFRARED SPECTROMETER

The basic components of a dispersive IR spectrometer include a radiation source, Sample and reference cells, monochromator, detector, amplifier and recorder. A schematic diagram of a typical dispersive spectrometer is shown in Figure 12.2.

Radiation source: The common IR radiation source are inert solids that are heated electrically to 1000 to 1800 °C to promote thermal emission of radiation in the infrared region of the EM spectrum. The most common sources are Nernst filament (composed of rare-earth oxides such as zirconium, cerium and thorium), Globar (composed of silicon carbide), and Nichrome coil. They all produce continuous radiations, but with different radiation energy profiles. The beam from the source is divided into two equivalent beams, one passing through the sample and the other as reference beam.

Sample and reference cells: Like UV sample tubes (cuvettes) glass or quartz cannot be used to make the sample cells for IR-spectroscopy, because they absorb strongly in most of the IR region. Alkali metal halides such as KCl, NaCl are commonly used as they are transparent to the IRregion.

Monochromator: The monochromator is a device used to disperse or separate a broad spectrum of IR radiation into a continuous spectrum of frequencies of Infrared light. The monochromator consists of rapidly rotating chopper that passes the two beams alternately to a diffraction grating. The slowly rotating diffraction grating varies the frequency or wavelength of radiation and sends it the individual frequency to the thermocouple detector which generates an electrical signal as a response.

Detectors and Amplifier: Detectors are devices that convert the radiant energy into an electrical signal. The detector determines the ratio between the intensities of the reference and sample beams. Due to the difference in the intensities of the two beams falling on the detector, an alternating current starts flowing from the detector to the amplifier, where it is amplified and relayed to the recorder. The detectors used in IR spectrometers can be categorized into two classes: thermal detectors and photon detectors. Thermal detectors consists of several

thermocouples connected together to produce greater sensitivity. They measure the heating effect produced by infrared radiation that causes the flow of current. The current produced is proportional to the intensity of radiation falling on the thermal detector. Photon detectors rely on the interaction of IR radiation and a semiconductor material. Non-conducting electrons are excited to a conducting state and therefore producing a small current or voltage.

Recorder: It records IR-spectrum as a plot of frequency of absorbed radiation and intensity of absorption in terms of transmittance. Unlike UV-spectroscopy, here we use the wavenumber unit. As the detector records the ratio of the intensities of the two beams therefore percent transmittance is recorded.

Transmittance (T) = I/I_0

Percent transmittance (%T) = I/I_0 X 100

Where I_0 is the intensity of the incident radiation and I is the intensity of the radiation emerging from the sample.

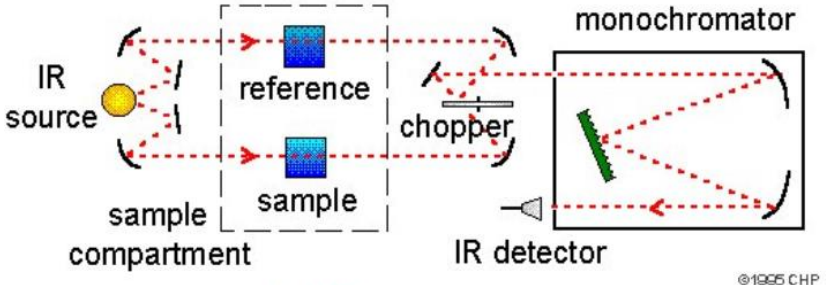


Figure 12.2: Schematic diagram of a dispersive IR spectrometer

12.10 FOURIER-TRANSFORM INFRARED SPECTROMETER

Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. They have greatly extended the capabilities of infrared spectroscopy and have been applied to many areas that are very difficult or nearly impossible to analyze by dispersive instruments. Instead of viewing each component frequency sequentially, as in a dispersive IR spectrometer, all frequencies are examined simultaneously in Fourier transform infrared (FTIR) spectroscopy.

The basic components of an FTIR spectrometer are shown schematically in Figure 12.3. The radiation emerging from the source is passed through an interferometer to the sample before reaching a detector. Then the signal is amplified and converted to digital form by an analog todigital converter and transferred to the computer in which Fourier transform is carried out.

Interferometer divides radiant beams, generates an optical path difference between the beams and then recombines them in order to produce repetitive interference signals measured as a function of optical path difference by a detector. Thus interferometer produces interference signals, which contain infrared spectral information generated after passing through a sample.

The most commonly used interferometer is a Michelson interferometer. It consists of three active components: a moving mirror, a fixed mirror, and a beam splitter (Fig. 12.3). The two mirrors are perpendicular to each other. The beam splitter is a semi-reflecting device and bisects the plane ofthese two mirrors. The beam splitter is often made by coating a thin film of germanium or iron oxide onto an 'infrared-transparent' substrate such as potassium bromide or cesium iodide.

The energy goes from the source to the beam splitter which splits the beam into two parts. One part is transmitted to a moving mirror; one part is reflected to a fixed mirror. The moving mirror moves back and forth at a constant velocity. The two beams are reflected from the mirrors and recombined at the beam splitter. The beam from the moving mirror has traveled a different distance than the beam from the fixed mirror. When the beams are combined an interference pattern is created. Since some of the wavelengths recombine constructively and some destructively. This interference pattern is called an interferogram. This interferogram then goes from the beam splitter to the sample, where some energy is absorbed and some is transmitted. The transmitted portion reaches the detector. The detector reads information about every wavelength in the infrared range simultaneously.

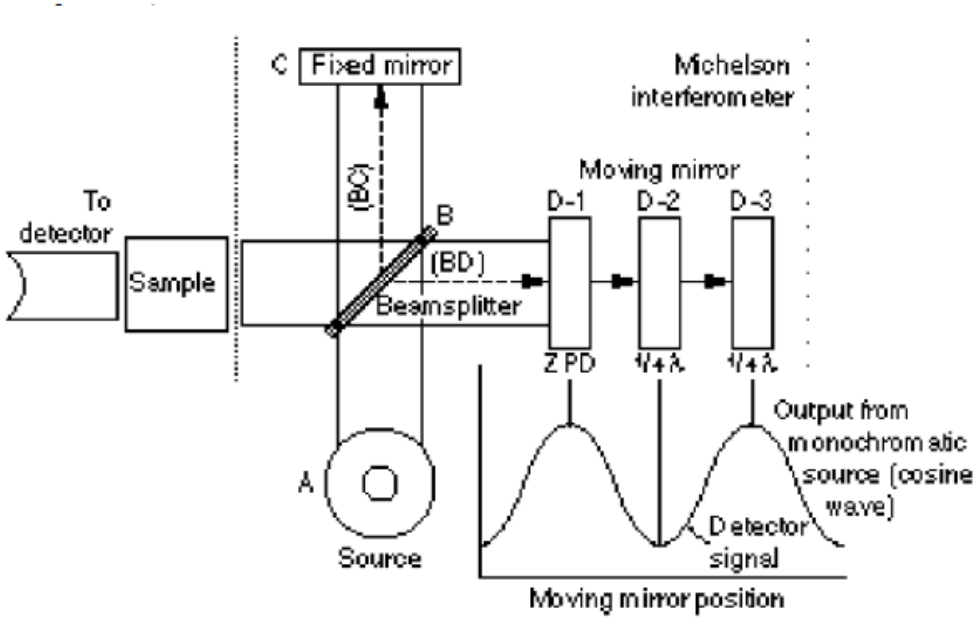


Figure 12.3: Schematic presentation of typical FTIR spectrometer

The moving mirror produces an optical path difference between the two arms of the interferometer (the relative position of moving mirror to the fixed mirror). If the two mirrors are at equal distance from the beam splitter, the two beams travel the same path length. Therefore two beams are totally in phase with each other and hence they interfere constructively and lead to a maximum intensity reaching to the detector. When the moving mirror travels in either direction by the distance λ/4, the optical path is changed by 2 (λ/4), or λ/2. The two beams are 180° out of phase with each other, and thus interferes destructively resulting minimum intensity reaching the detector. If the moving mirror further travels by λ/4, then the optical path difference will be 2 (λ/2), or λ. The two beams are again in phase with each other and result in another constructive interference again giving a maximum response in the detector. Such a maximum will be observed whenever the path difference is an integral multiple of λ.

Thus moving mirror is the key component of interferometer, because alternate light and dark images will reach the detector if the mirror is slowly moved either away from or towards the beam splitter. When the mirror is moved at a constant velocity, the intensity of radiation reaching the detector varies in a sinusoidal manner to produce the interferogram output shown in Fig. 12.3. The interferogram is a complex signal but its wave like pattern contains all the frequencies that make up the infrared spectrum. It is actually a time domain spectrum and records the detector response changes versus time. If the sample happens to absorb at this frequency, the amplitude of the sinusoidal wave is reduced by an amount proportional to the amount of sample in the beam.

Now to obtain the infrared spectrum, the detector signal is sent to the computer, where mathematical operation known as Fourier transformation converts the interferogram (a time domain spectrum displaying intensity versus time) to the final IR spectrum, a frequency domain spectrum showing plot between intensity of signal versus frequency.

12.11 HANDS-ON OPERATION OF AN FT-IR SPECTROMETER

Step 1: First step is the sample preparation. Sample preparation has already been discussed in the above section.

Step 2: The second step is to obtain an interferogram of the background which consists of the Iractive atmospheric gases carbon dioxide (doublet at 2360 cm^{-1} and sharp spike at 667 cm^{-1} in Fig. 12.4) and water vapors (two irregular groups of lines at about 3600 cm^{-1} and about 1600 cm^{-1} in Fig. 12.4). Nitrogen and oxygen are not IR-active hence do not absorb in IR-

region. This interferogram is subjected to Fourier transform which gives the spectrum of background. Figure 12.4 shows an example of an FTIR background spectrum.

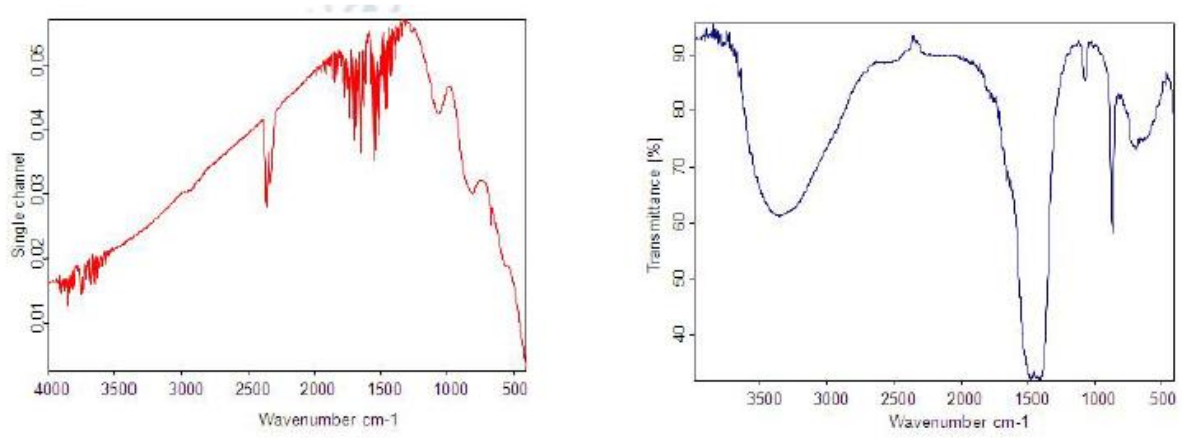


Figure 12.4: FTIR background spectrum

Step 3: In the third step, spectrum of the sample under investigation is obtained by the same procedure. This spectrum contains absorption bands from the sample as well as the background (gaseous or solvent).

Step 4: The ratio between the single-beam sample spectrum and the single beam background spectrum gives the spectrum of the sample (Figure 12.4). Computer software automatically subtracts the spectrum of the background from the sample spectrum.

Step 5: Finally the data obtained is analyzed by assigning the observed absorption frequency bands in the sample spectrum to appropriate normal modes of vibrations in the molecules.

12.12 SUMMARY

- Absorption of electromagnetic radiation in infrared region can cause changes in the vibrational and rotational energy states.
- A molecule consisting of n atoms has a total of 3n degrees of freedom.
- The number of fundamental vibrational bands in a molecule is equal to the degree of freedom of a molecule however these numbers of bands is seldom obtained because of the occurrence of certain non-fundamental bands such as overtones, combinations of fundamental vibrations or difference of fundamental vibration bands.
- The IR-spectrum can be obtained in all the three states, solid, liquid and gas.
- Fourier-transform infrared spectrometers are superior than the traditional dispersive spectrometers and gives high resolution spectrum in less time.

12.13 BIBLIOGRAPHY

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12.14 TERMINAL QUESTIONS

1. Discuss the various molecular vibrations in IR spectroscopy.
2. Explain the IR spectrometre.
3. Write short note on finger print region.

BLOCK 4: LABORATORY WORK

UNIT 13: LABORATORY HAZARDS AND SAFETY PRECAUTIONS

CONTENTS:

13.1 Introduction
13.2 Objective
13.3 Purpose of laboratory & chemical safety
13.4 Types of hazards in the laboratory and their prevention
13.5 Laboratory safety
13.6 Assess and minimize the risk of the hazards
13.7 Summary
13.8 Bibliography

13.1 INTRODUCTION

In the laboratory it is require great care and attention in order to avoid safety hazards occures due to delicate lab instrument, open flames, hazardus chemicals etc. Negligent handling of dangerous/harmful chemicals can result in both short-term (acute) and long-term (Chronic) health issues. Burns, eye injuries, lung diseases, asphyxiation, and suffocation are some of these potential issues. Chemicals cause adverse reactions in the body through ingestion, inhalation, skin contact, and percutaneous exposure. No matter how much is being used or how it is used, a substance, operation, or activity has intrinsic hazardous characteristics or properties. Various risks to human health and physical injury can be posed by chemicals given below:

Health Hazards	Physical Hazards
Toxic	Combustible
Carcinogenic	Flammable
Mutagenic	Explosive
Reproductive toxins	Reactive or pyrophoric
Sensitizers	Oxidizers
Irritants and Corrosives	Corrosive
Asphyxiants	Compressed Gas and Liquid

The chemistry practical could involve a minor incident. Inform your teacher or the lab attendant right away, remain calm, do not panic, and use the first aid provided in the laboratory.

However, if any of these symptoms occur, you should immediately stop working, take off your personal protective equipment, wash your hands, and contact your healthcare provider.

- Unusual taste or odor,
- Respiratory irritation, coughing, choking, or shortness of breath,
- Sudden headache, dizziness, blurred vision, or loss of consciousness,
- Burning or painful sensation,
- Swelling, reddening, or itching skin.

13.2 OBJECTIVE

After completing this unit learners will be able

- To known 'What is a laboratory hazard'? The physical hazards and the chemical hazards in the laboratory.
- How to prevent chemical hazards in the laboratory.
- To know the effect of laboratory incidents on learner's health, such as heat burns, glass cuts, and the inhalation of gas.
- To assess and reduce the risks associated with chemical hazards in the laboratory.

13.3 PURPOSE OF LABORATORY & CHEMICAL SAFETY

- To promote safety awareness and encourage safe working practices in the laboratory.
- Safety guidelines should serve as a reminder of things you can do to work more safely and are applicable to all users of the laboratory.
- All learners are expected to adhere to safety guidelines and maintain safety standard strictly.

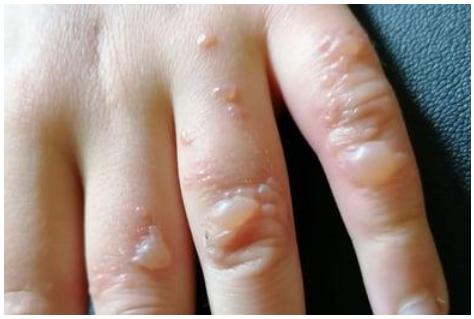
13.4 TYPES OF HAZARDS IN THE LABORATORY AND THEIR PREVENTION

Chemical and physical hazards in the laboratory fall into five major categories. Now discuss each category in details with their prevention in the laboratory.

- Chemical burns
- Heat burns
- Eyes injuries
- Injury from glassware
- Inhaling dangerous gases

13.4.1 Chemical burns

Acids, bases, etching solutions and solvents are commonly used in chemistry lab and classified as corrosive substance, and also present a serious health hazards such as chemical burns, tissue damage, organ damage, asphyxiation, corneal damage, which can lead to blindness and genetic damage if used improperly.



(Burns are a common type of hazard when dealing with harmful substances).

- Wear the gloves when working in lab.
- If the skin burn with acid , wash it with ammonium hydroxide, while in case of concentrated H_2SO_4 wash affected part with Barium chloride solution and then with cold water and apply burnol.
- If the skin burn due to the concentrated/ stong alkali (base), washed it with acetic acidand finally with cold water and apply burnol. If the injury is deep then immediately contact with the health consultant/doctor.

13.4.2 Heat burns

Burners and other heating devices are frequently used in laboratories to expedite chemical reactions and processes. As with any activity that involves fire, it is important to be aware of the potential risks associated with heat-related injuries. If exposed to temperatures higher than 70°C, it is likely that a burn will occur, even if the skin is only exposed for a split second.

It is essential to maintain a safe distance away from open flames and heating devices in order to reduce the likelihood of heat-related burn injuries in the laboratory.

- Skin clothing and protective equipment should be kept away from any other combustible materials in the vicinity. Furthermore, it is imperative to ensure that burners are not left on after use.
- If a heat-related burn occurs while in the laboratory, it is recommended to immediately put the affected area in cold running water and hold it for a few minutes before allowing the burning sensation to subside. After that apply coconut oil or burnol on the burnt part.

(The heat generated by Bunsen burners can create a range of serious physical hazards for laboratory learner who are using the equipment)

13.4.3 Eye injuries

In the laboratory at the time of working, you need to be aware of the chemicals that can be harmful to your eyes. You can be exposed to chemicals if you accidentally release liquids or gases that can damage your eyes. The severity of your injury depends on hazardus properties of chemical are and how much you have been exposed to it. For instance, if you get a mild eye injury from exposure to a chemical, it could just cause redness and irritation. But if you get a really bad eye injury, it could lead to permanent blindness. To prevent eye injuries in the lab, you need to wear the right protective eyewear.

- If the eyes injuries occur due to the some pungent vapours in the eye first go away from the working place (lab) in the open place and wash your eye with cold water. If still eatvhing persists consult an eye doctor immediately.

- If chemical solution or dust particle enter into eye thenwash your eye with cold water untill you feel relief.
- If acid has been entered into eye then eye must be washed with a dilute solution of alkali sodium bicarbonate solution few timesand after that with cold water till you feel relief. an eye doctor
- If base/alkali has been entered into eye then eye must be washed with dilute boric acid solution and finally washed with cold water till irritation persists. If still problem exist immediately consult an eye doctor.

13.4.4 Injury from glassware

The use of laboratory glassware for the storage and mixing of hazardous chemicals is a common practice; however, there is a risk of laboratory glassware breaking. If the glass is broken, it can expose sharp edges, particularly if it is very thin, which can cause severe eye and skin damage. Therefore, it is important to take steps to reduce the risk of glass breaking in laboratories.

- In order to prevent cuts from glassware, it is important to handle the glassware with caution. It is recommended to hold the glassware in a secure grip and to avoid handling the glassware with wet or wet hands.
- It is important to ensure that when glassware is not in use, it is stored in a safe and secure place where there is no potential for it to fall and shatter. If glassware is not stored in an accessible cupboard with a well-maintained and even surface, it is likely to fall and break, potentially exposing to physical injury.
- If the is due to the breakage of some glassware, glass apparatus, wound washed with sprit and then aqueous alum solution because alum is antiseptic in nature and can also help in stop bleeding by coagulation.
- It is essential to take prompt action in the case of a glass cut in order to avoid the development of an infection. If a cut is sustained from glassware, the first aid officer/doctor should be contacted so that they will dress the wound.

13.4.5 Inhaling dangerous gases

A wide variety of hazardous chemicals emit toxic vapors and gases that pose a risk to human life. The health consequences associated with exposure to these hazardous vapors can be

classified as acute, chronic, or both. Acute consequences are those that occur immediately after exposure to the vapors. Chronic consequences are those that do not occur immediately but occur months and even years after exposure. Heath effects of gas inhalation can include symptoms such as:

Irritation to mucous membranes in the nose, throat, respiratory tract; Headache; Vomiting; Coughing; Burning; Difficulty in breathing etc.

- If you feel any symptoms occurs due to the inhalation of gaes first go away from the working place (lab) in the open place. If still feel some problems consult with doctor immediately.

13.5 LABORATORY SAFETY

In the laboratory following safety will be taken while working in the lab.

(i) Laboratory hygiene
(ii) Fire safety
(iii) Chemical safety
(iv) Personal safety

(i) Laboratory hygiene

- Scrub hands thoroughly when finished.
- Avoid cross contamination
- Do not touch self, faucets, doorknobs, notebooks, pens etc. with gloves on.
- Keep a pen or two in your drawer for lab use only.
- Clean and disinfect your workspace

(ii) Fire safety

- Never leave flames unattended.
- Do not use flammables near ignition sources.
- Fire Extinguishers
- Fire Blanket
- Fire alarm pulls

(iii) Chemical Safety

- Wear gloves and glasses where appropriate.
- Follow instructor's directions.
- Dispose of waste properly-Do Not pour down the drain.

(iv) Personal Safety

- Lab coat to be worn all the time.
- Safety goggles must be worn all the time while working in the lab.
- Wear sensible clothing and Wear shoes.
- Appropriate gloves while handling chemicals.
- Working of alone student is not allowed

13.6 ASSESS AND MINIMIZE THE RISK OF THE HAZARDS

When you are working in a chemical lab, there is a risk associated with every chemical and glassware you use. Once you have evaluated the risks, your next step is to consider how you can reduce exposures. There are following step to assess and minimize the risk of hazards in the laboratory.

13.6.1 Before an experiment

This is likely the most significant steps you can take to reduce the risk in any laboratory environment. While incidents can occur even in the well-prepared environment, meticulous attention to detail can reduce the risk.

I. Know what you are working with. It is important to always recognize the substance that is being used and to consider how to reduce the exposure to that substance during the experiment. For example, sodium hydroxide is commonly known as lye or caustic soda. If you are unsure, look for the Chemical.

II. Ensure that the proper concentrations are prepared. In laboratory should not routinely work with basic (NaOH) or acidic (HCl) solutions at concentrations greater than 1 M.

III. Ensure that all chemical bottles are properly labeled. For example sodium hydroxide, the bottle should have the chemical name (“sodium hydroxide”) spelled out, not just the formula (“NaOH”), and the concentration of the solution should also be listed.

- The signal words “Danger”, “Warning”, and “Caution” are used to describe the level of the hazard.
- Words such as “Caustic”, “Corrosive”, and “Flammable” are used to describe specific hazards.

IV. Write down all the chemicals you are going to use and how much you will need for the experiment.

V. Consider the physical arrangement and the facilities available in your laboratory.

13.6.2 During an experiment

It is essential that learners are monitored consistently in the laboratory. The teacher must be physically present in the duration of the experiment, focusing on the students throughout.

I. Use the lowest concentrations and smallest volumes possible for all chemicals. Do not allow learners to handle solids that are classified as fatal or toxic if swallowed.

II. Wear appropriate eye protection that offers both impact and splash protection. This is not only for your safety but also as a precaution in the event that an accident is caused by someone else in the laboratory.

III. Wear appropriate protective clothing (laboratory apron, coat, and gloves).

IV. Long hair must be pulled back, and clothing must be tucked in.

V. After transferring a chemical (solid or liquid) from a reagent bottle into a secondary container, be certain that the reagent bottle and the container are properly closed.

VI. Students should take only the amount required of each reagent. If there is excess, it must be disposed of properly and not returned to the reagent container.

VII. No mixing of chemicals should be allowed, other than that specified in an experimental procedure.

13.6.3 What if an emergency occurs?

I. If the chemical is in the eye: Flush water using an eyewash station for at least 15 minutes. Medical attention must be summoned as soon as possible.

II. If the chemical is swallowed or ingested: Do not induce vomiting unless the SDS recommends vomiting. Medical attention must be summoned as soon as possible.

III. If the chemical comes into contact with skin: Rinse the affected area for 15 minutes with tap water. It may be necessary to use a safety shower. If the safety shower is used, all contaminated clothing should be removed while the person is under the safety shower, and medical attention must be summoned as soon as possible.

13.6.4 After an experiment

I. Return any chemicals (excess reagent, product, or waste) to the appropriate location, or dispose of them as instructed.

II. Clean any used glassware and return the items to the appropriate location.

III. Ensure that all chemicals are properly stored. Make sure that the caps on the reagent bottles are tightly secured.

IV. Ensure that benches are clean before the next class comes in. One of the major causes of accidents is carelessness on the part of someone else.

V. All gas outlets are closed; especially burners were used during the experiment.

13.7 SUMMARY

- Keep tabletops clean. Return all equipment to its original location before leaving the lab.
- Report all accidents, no matter how minor, to the instructor. If you break something made of glass, be sure to use dustpan and hand broom to sweep it up and dispose of it in the glass waste receptacle.
- In case of an emergency where we have to evacuate, proceed out the nearest exit.
- Both the door should remain open all the time while working in the lab.
- Never put anything in your mouth while in the lab (including chemicals, solutions, food and drink)
- All food and drinks should be restricted to sitting area only.

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UNIT 14: CRITERIA OF PURITY

CONTENTS:

14.1 Introduction
14.2 Objectives
14.3 Purification of organic compounds by crystallization and distillation
14.3.1 Crystallization
14.3.2 Distillation
14.4 Melting point
14.5 Boiling point
14.6 Experiment
14.6.1 Experiment 1: Determination of melting point
14.6.2 Experiment 2: Determination of boiling point
14.7 Summary
14.8 Bibliography

14.1 INTRODUCTION

In this unit we study the techniques used to purify and separate compounds. Organic compounds must be purified, even though it is a difficult process, either after they are extracted from their natural source or synthesized in a lab. The type of the organic substance and the contaminants it contains determine the purification process. Since organic compounds typically have distinct melting and boiling temperatures, melting or boiling them is a simple way to determine their purity.An organic compound is purified when undesirable contaminants are eliminated. The following is a list of common purifying techniques:

- Sublimation
- Crystallisation
- Distillation
- Differential Extraction
- Chromatography

You performed experiments to purify a solid and a liquid product by crystallization and distillation. In these tests you will learn about very important purity criteria. They are useful for checking whether a compound is pure or not. Two criteria are the melting point and boiling point of solid and liquid products. You must have learned in theoretical

courses that these physical properties are characteristic of a compound and help to identify them. You will learn the theoretical concepts related to these criteria and then learn the melting point of a solid and the boiling point of a liquid.

14.2 OBJECTIVES

Under this unit you will be able to:

- Purification of organic compound by crystallization and distillation method.
- Learn to determine the melting and boiling point procedure of various organic compounds.
- Define boiling point and describe the method of its determination; Explain the effect of impurity on the boiling point of a liquid; and Determination of the boiling points of the given liquids.

14.3 PURIFICATION OF ORGANIC COMPOUNDS BY CRYSTALLIZATION AND DISTILLATION

14.3.1 Crystallization

An approach for purifying chemicals is crystallization. Method for separating particulates from a solution by separation.

As a result of arranging themselves in a well-defined three-dimensional lattice, atoms or molecules of a substance reduce the total energy of the system through a process known as crystallization. The bonds between atoms or molecules of a substance become more defined when it undergoes crystallization.

Figure 14.1: Structure of the crystals

A solid material dissolves in a liquid when it is added and stirred. On the other hand, there comes a point at which adding more and more trustworthy to the liquid causes it to dissolve completely. A saturation solution is the fluid at this point, which is also referred to as a saturation point.

The idea behind this is that various contaminants and compounds dissolve in different solvents. A solvent is selected in which the product to be purified exhibits sparing solubility, meaning it is soluble at higher temperatures but sparingly soluble at lower ones. Once the solution is saturated, it is heated and cooled, at which point the compound crystals are filtered out.

For instance, water can crystallize benzoic acid crystals. Hot water makes benzoic acid soluble, but it is only weakly soluble in cold water.Repetition of crystallization is carried out if the mixture contains impurities with solubility similar to that of the substance to be purified.

A. Crystallization Process

1. The mixture is warmed within a visible container.
2. The molecules of the solvent begin to evaporate, leaving the solvents behind.
3. Solute crystals begin to accumulate on the solution's surface as it cools.
4. Crystals are gathered and dried in accordance with the needs of the product.
5. The filtration procedure separates the liquid's undissolved solids.
6. The rate of cooling determines the size of the crystals that are created during this process.
7. If the solution cools down quickly, a lot of small crystals form.
8. Slow cooling rates lead to the formation of large crystals.

B. Crystallization Examples

Water of crystallization is the term used to describe the constant number of water molecules that make up one unit of a salt compound. Alternatively stated, stoichiometric ally-bound water crystallizes. For instance, hydrated copper sulphate has the chemical formula $CuSO_4$ $5H_2O$. Five water molecules help copper sulphate consolidate. The most useful application of crystallization is in the production of salt, which may be done most affordably via salt crystallization. The method can also be used for crystal production and compound purification. The water molecules that comprise a crystal's structure can sometimes be referred to as the "water of crystallization." They help the crystals develop and crystallize. An

antibacterial and anti-fungal substance that can be used topically is copper sulphate or $CuSO_4.5H_2O$.

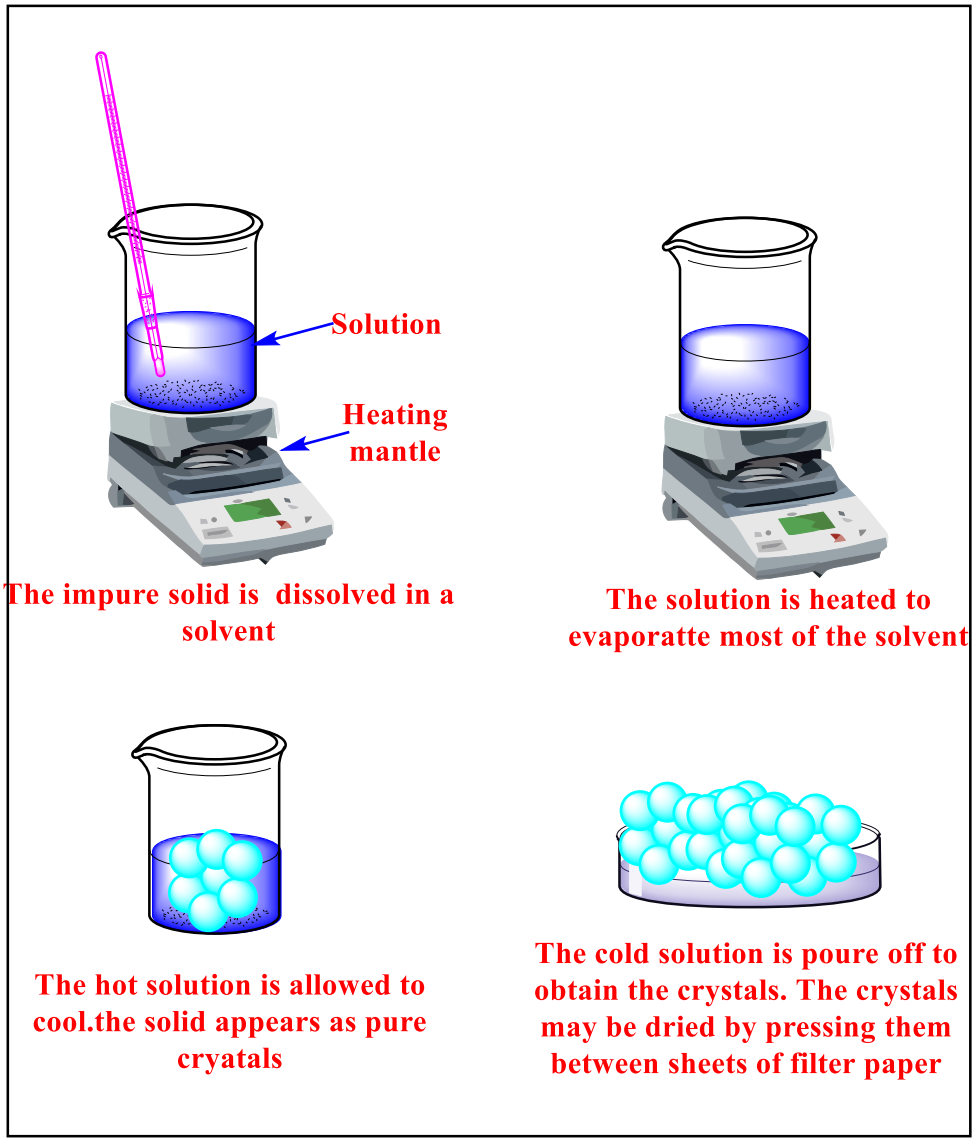


Figure 14.2: Crystallization Process

14.3.2 Distillation

The process of a component in a liquid mixture being selectively boiled and then condensed is called distillation. Using this separation process, one can use the combination to extract (almost) pure components or to raise the concentration of a specific element in the mixture. Distillation works by pushing one of the liquid mixture's components into a gaseous form, taking advantage of the differences in their boiling temperatures. The fundamental idea of distillation is that liquid mixtures can be divided based on the variations in their boiling points. The temperature at which a liquid's vapour pressure equals atmospheric pressure is known as the boiling point. Volatile liquids and those that are not are separated using this procedure. Below is the setup.

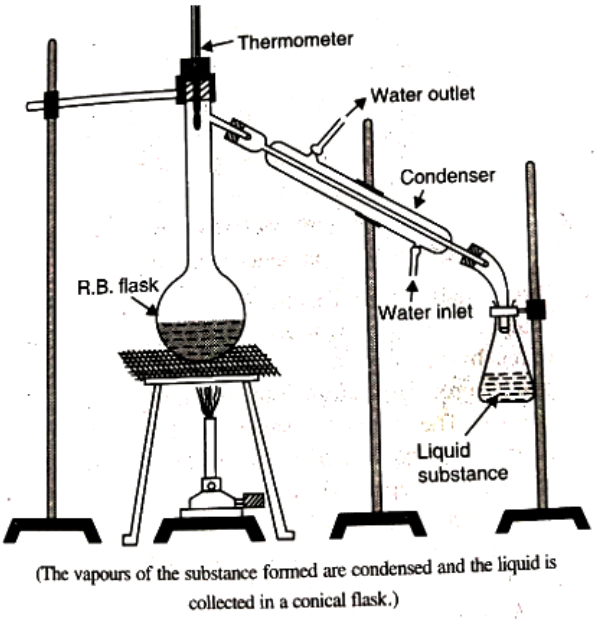


Figure 14.3: Distillation Process

After being taken in the RB flask, the mixture is boiled. The component that is more volatile or has a lower boiling point evaporates more quickly and gathers in a different container. Condensation occurs more quickly when a condenser is utilized.

Distillation, for instance, can be used to separate a mixture of aniline and chloroform. Aniline boils at 189°C, while chloroform reaches a boiling point of 60°C. The separation of a mixture of aniline and chloroform can, therefore, be accomplished via distillation.

A. Fractional Distillation

When there is little variation in the boiling points of the liquids, this approach is used. A fractionating column is attached to the RB's mouth since the vapour from these liquids may condense together. The purification of a liquid that contains contaminants from other volatile liquids or the separation of two or more liquids with differing boiling points from a mixture are two applications of this technique. Because of this, fractional distillation is predicated on the variation in the liquids' boiling points within the sample.

The fractional distillation method involves gradually heating combinations of volatile liquids in a specialized distillation apparatus. The resulting liquid fractions, which are acquired as distillates within appropriate temperature ranges, are then collected in individual receiver flasks.

This has an impact on the mixture's parts' partial separation. More low boiling point liquid is present in the first fractions that were collected, and more high boiling point liquid is present

in the final fractions. To achieve purer fractions than those acquired previously, the resulting fractions are distilled once more. To get the pure liquids, this process is performed numerous times. The flask is fastened to a fractionating column in the factional distillation equipment by means of a water condenser at its top end, which is attached to the receiver flask. It is not necessary to continuously distil the fractions because the process of vaporization and condensation of the fractions in the fractionating column happens automatically, separating the elements. The fractionating column is a long glass tube which has many obstructions.

These impediments expand the region on which vapours can cool. The liquids vaporize and enter the fractionating column when the mixture is heated gradually. Less volatile or liquid components with a high boiling point condense (liquefies) when the vapour rises in the column and descends. This liquid further condenses the less volatile liquid component as it contracts with upward-moving vapours, lowering it to the distillation point. As they ascend via the condenser pipe and depart, the vapours of the more volatile or low boiling point liquid components condense (liquefy). The procedure is carried out multiple times, using the liquid that is collected in the receiver and the liquid that is still in the distillation flack. This facilitates the efficient separation of a liquid mixture's constituent parts.

This technique is used to cleanse the liquids as well as separate the constituent parts of a liquid mixture with closer boiling points, such as toluene (b.p. 110^0C) and benzene (b.p. 800C).

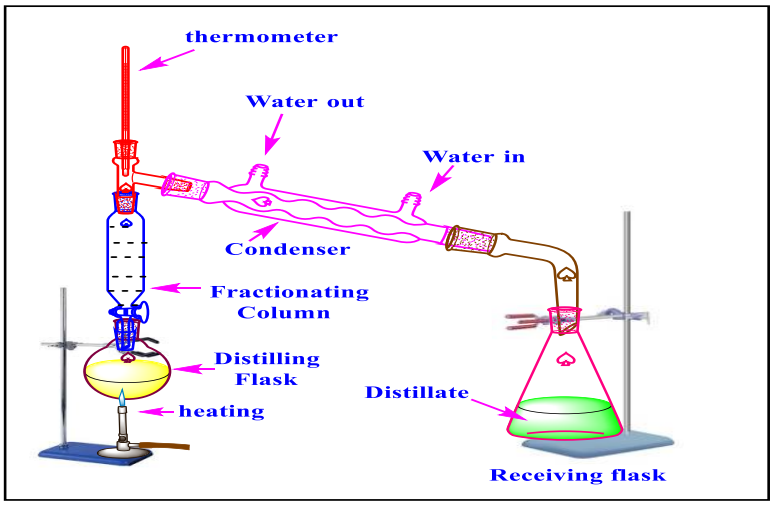


Figure 14.4: Fractional Distillation

B. Vacuum Distillation

The liquids will boil at a lower temperature than their boiling points if they were distilled in an atmosphere with lower pressure because the boiling point is dependent on the atmospheric

pressure. To do this, a vacuum pump is used. The reduction in atmospheric pressure causes the liquids to boil more quickly, which speeds up the distillation process as a whole.

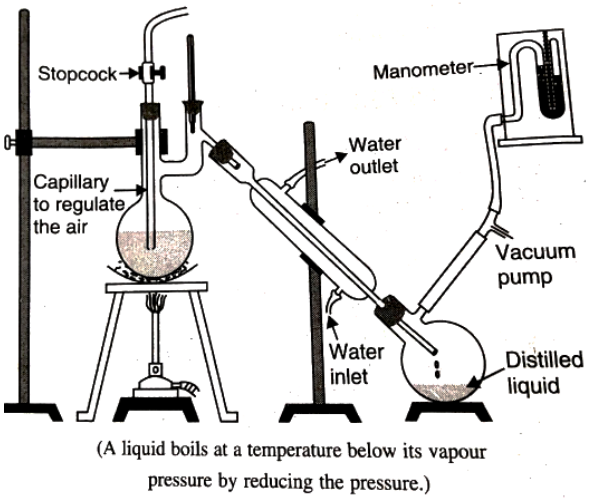


Figure 14.5: Vacuum Distillation

C. Steam Distillation

Using the steam distillation process, organic liquids and solids that are immiscible in water and volatile in steam are refined. Examples of such substances include aniline, nitrobenzene, chlorobenzene, benzaldehyde, and o-nitrophenol. Using this technique, essential oils are also collected from flowers and plants.

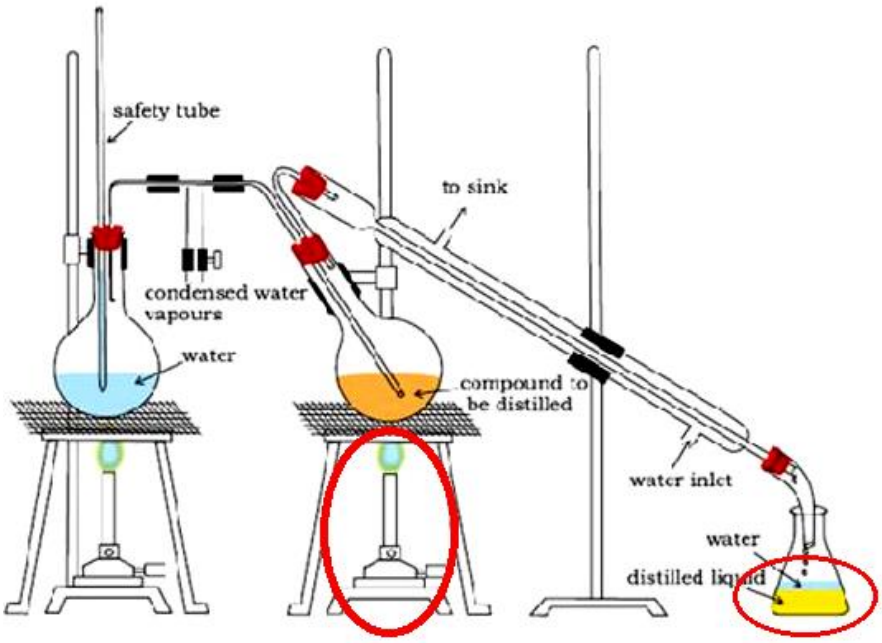


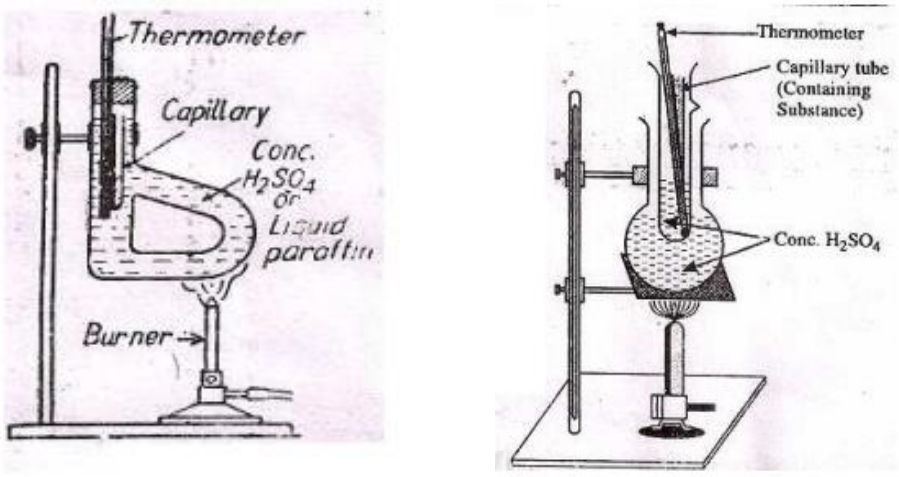
Figure 14.6: Steam Distillation

In the distillation flask, impure organic liquid is heated after being combined with a small amount of water. Steam is transferred from the steam generator into this heated mixture. Both the water and the organic liquid vapourize at the mixture's boiling point, and the vapours condense after going through the water condenser. Two layers of the distillate are gathered in the receiver. The separating funnel keeps the organic liquid and water apart. Boiling would have continued until the air pressure was equal in the absence of aqueous tension. Now that steam has been added, this process moves more quickly.

14.4 MELTING POINT

"Melting point is the temperature at which a solid and liquid exist in equilibrium with each other at a given pressure, or it is the temperature at which a solid begins to change to a liquid under a pressure of one atmosphere".

This is the most important and significant step in the identification of a solid organic compound or to test the purity of a given solid organic compound. The experiment is usually carried out by capillary tube method using Thiele's tube Figure 14.6 (a) or most conveniently using the flask and test tube Figure 14.6 (b) available in every chemistry lab.



(a) Determination of Melting point by melting point by Thiele's method

(b) Determination of flask and test tube method

Figure 14.6: Different methods for melting point determination

In actual practice, a small quantity of the organic substance whose melting point is to be determined is finely powdered between the pieces of filter paper or on a porous plate with the help of a spatula and introduced in a glass capillary tube closed at one end by heating in a Bunsen flame. The material is picked by gentle tapping the capillary on the table, the capillary is then attached to the lower end of the thermometer with its sealed end down.

The thermometer is then placed in a thiele's tube or test tube containing conc. H_2SO_4 or paraffin oil in such a way that the liquid covers the filled length of the capillary and the open end of the capillary remains above the surface of the liquid (to avoid the entry of the liquid into the capillary). The test tube (in the flask and test tube method) in turn, is placed in a flask containing the same bath liquid as in the test tube as shown in Figure 14.6 (b) The flask is gently heated and the burner is removed from time to time so that the slow steady rise in temperature is maintained and this rise in the temperature is observed carefully. The temperature at which the solid substance melts completely and becomes almost transparent is recorded. This is the melting point of the organic solid substance used. Traces of impurities or moisture considerably lower the melting point. Hence the solid organic compound taken for the determination of melting point should be pure and dry.

Mixed Melting Point: The mixed melting point is determined to establish the purity of known organic compounds. A small amount of the compound under investigation is mixed with a little of pure compound from the laboratory and the melting point of such a mixture is determined in the usual manner. If the value of the melting point of the mixture is the same as that of the pure compound then the compound under investigation is pure but if the value of its melting point is lower than that of the pure compound, the compound taken is impure. Thus this technique not only helps in the identification of an organic compound but also in establishing the purity of known organic compound.

14.5 BOILING POINT

You know that the boiling point is another very important test to check the purity of liquids. In fact, like melting point, this property can be used to identify the compounds. In very simple way, boiling point, abbreviated b.p. is the temperature at which a liquid changes to a gas. Unlike the melting point, it is difficult to achieve a uniform and sharp temperature b.p. It is usually observed between 2-3^{o}C.

A. Siwoloboff's method for determination of boiling points

Boiling point of liquid can be determined by Siwoloboff's method, which will be described in detail in the experiment on determination of boiling point of the liquids given in below.

Siwoloboff's method:

This method requires two tubes, standard melting point capillary tube, 90-110 mm long and wider, 3-5 mm diameter and 80-100 mm long. The capillary tube is closed at one end and the seal is made by holding it in the flame. The wider tube is also sealed at one end. The capillary tube is placed inside the wider tube with the open end facing down as shown in Figure 14.7.

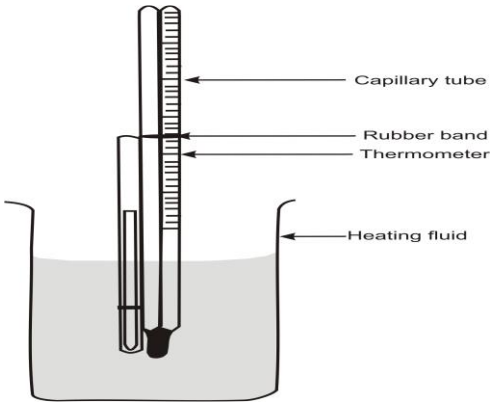


Figure 14.7: Assembly of boiling point apparatus

Then using a pipette, the liquid for which the boiling point has to be determined is put into the wider tube such that its level is about 2 mm above the seal in the capillary tube. The tube is attached to the thermometer keeping the liquid at level with the mercury bulb of the thermometer. A rubber band may have to be used for the purpose. The thermometer with attached tubes is inserted into a heating bath.

B. Factors affecting the boiling point

Boiling point is a property of a liquid it depends on the structural properties of liquid compound. The following factors affect the boiling point:

1. Polarity

Interactions are due to polar covalent bonds or formal charges and non-covalent interactions include dipole-dipole interactions, H-bonding and van der Waals forces. Liquid molecules are held together by tight non-covalent interactions. When the liquid is heated, these interactions are broken and the liquid begins to change to a gaseous state. Thus, increased H-bonds, polar covalent bonds, or formal charges in the molecule tend to raise the boiling point.

2. Molecular mass

A compound with a higher molecular weight has more atoms that can participate in non-covalent interactions. The greater the number of non-covalent interactions, the more energy is

required to break the non-covalent interactions to change the composition from the liquid phase to the gas phase. Thus, a higher molar mass has a higher boiling point.

3. Shape of the molecule

Molecules with similar molecular formula and functional groups differ in boiling point depending on whether they are straight chain or branched. Straight chain compounds were observed to have higher boiling points than branched chain compounds. Branching prevents the molecules from packing too tightly together and leads to weak non-covalent interactions. Therefore, molecules require less energy to change phase, i.e., from liquid phase to gas phase.

14.6 EXPERIMENT

EXPERIMENT 1: DETERMINATION OF MELTING POINT

Let us learn to determine the melting point of organic compounds like naphthalene/ benzoic acid.

1. Aim

To determine the melting point of organic compounds like naphthalene and benzoic acid.

2. Materials Required

Naphthalene, benzoic acid, the aluminium block, stand with clamp, capillary tube, tripod, thermometer, and kerosene burner.

3. Procedure to determine the melting point of Naphthalene

(i) Take a capillary tube and close its one end by heating the end in the flame for 2-3 minutes.

(ii) Take naphthalene fine powder on a tile.

(iii) Firmly hold the closed end of the capillary tube between your fingers and thumb.

(iv) Open end of the capillary tube touch on powdered naphthalene.

(v) Gently tap the capillary tube on the table to fill the compound in the capillary tube to about a length of 1–2 cm.

(vi) With the help of a thread, attach the capillary tube to a thermometer as shown in the figure 14.8.

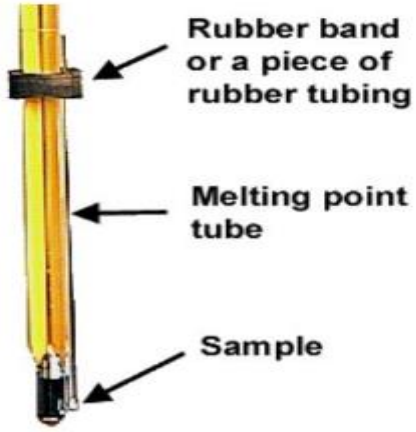


Figure 14.8: Attach the melting point tube to the thermometer

(vii) Place the capillary tube (with naphthalene powder) in the middle groove of the aluminum block.

(viii) Place the Aluminum block on a tripod stand above the kerosene burner and start heating the block with the burner.

(ix) Keep continuous watch of the temperature and note the temperature (t_1) as soon as the substance begins to start melt.

(x) The compound is melted completely note this temperature (t_2) fastly,and average of the two readings gives the correct melting point of the substance.

4. Result:

Melting point of compound was found to be =…… ^{o} C

EXPERIMENT 2: DETERMINATION OF BOILING POINT

You are given liquid to determine their boiling points. Follow the procedure and report the result.

1. Aim

To determine the boiling point of given liquid compound.

2. Requirements

Boiling point apparatus, Bunsen burner, Iron stand with clamp, Capillary tubes, Thermometer, liquid compounds

3. Procedure

Follow the steps given below for this experiment.

(i) Take a small volume (≈ 5 ml) of the liquid in a small test tube as provided by lab bearer.

(ii) Place a capillary tube, sealed at one end, with open-end down into the liquid contained in the test tube. Attach a thermometer to the tube with a rubber band, and clamp the apparatus to an iron stand.

(iii) Immerse the assembly in a water bath (or an oil bath for samples with boiling point higher than 100^{o}C). Observe the temperature carefully.

(iv) With increase in temperature you will see a rapid evolution of bubbles from the end of the tube. Continue heating for about 5-10 seconds.

(v) Remove the burner or the hot plate, but do not take the assembly out of water bath (or oil bath), and carefully watch the capillary.

(vi) You might see the bubbles continuously coming out until the pressure exerted by the vapor of the liquid becomes equal to the atmospheric pressure.

(vii) Again observe the status of bubbles. The bubbles will slow down with lowering of temperature and at some point; the liquid will rise into the capillary.

(viii) Read the thermometer value and record the temperature when the bubbles stop.

(ix) The temperature observed when this happens should be the observed boiling point of the liquid.

(x) Compare the temperature noted by you with the literature value of the boiling point for the liquid used. The difference should not be more than 2-3^{o}C.

(xi) Report the result in your note-book.

4. Result:

Boiling point of given liquid compound was found to be = ……^{o}C

14.7 SUMMARY

The summery of the present unit is :

- Purification methods include crystallization and distillation.
- Crystallization is a technique used for the purification of substances.
- The Melting point of a solid is the temperature at which it changes state from solid to liquid at atmospheric pressure. At the melting point the solid and liquid phase exists in equilibrium. The melting point of a substance depends on pressure and is usually specified at standard pressure.
- Learnt how to determine boiling point of unknown compounds and also discussed methods of determination of boiling point.

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UNIT 15: TITRATIONN AND CHROMATOGRAPHY

CONTENTS:

15.1 Introduction
15.2 Objectives
15.3 Titration
15.4 Chromatography
15.5 Experiment 1: Determination of strength of a given sodium hydroxide (NaOH) solution
15.6 Experiment 2: Separate and identify the sugars present in the given mixture by chromatography
15.7 Summary
15.8 Bibliography

15.1 INTRODUCTION

In this unit you will be learn about the titration and the chromatography techniques used in the analytical chemistry. A titration is a technique used to determine the concentration/strength of an unknown solution. Chromatography techniques used for the separation and purification of mixture/compounds.

15.2 OBJECTIVES

After completing this unit you should be able to

- Know the titration and its types.
- Know the strong and weak acid-base titration.
- Determine the strength of solution by using acid/base titrations.
- Learn the separation technique basically chromatyography.
- Separate and identify the sugars by using thin layer chromatography (TLC) and calculate R_f values.

15.3 TITRATION

Titration is a process of mixing of two solutions in order to react in a conical flask. One solution is with known strength or standard while the other solution is unknown solution or solution whose strength is not known. The solution which is to be titrated is taken in a conical flask with the help of a pipette and other solution is taken in a burette. Indicator is added to

the conical flask in order to detect the end point or equivalence point. Two solutions are mixed dropwise by opening the tap of the burette. A sharp change in color indicates the end point. At this point, the reaction between two solutions is just completed.

A. Types of titration:

There are generally four types of titration depending on the reaction taking place between the two solutions. These are as follows:

1. **Neutralization titration:** These titrations are also known as acid- base titration as it involves two solution, one is of acid while the other is of base. For example, mixing of sodium hydroxide (base) with oxalic acid. This titration is further classified into acidimetry and alkalimetry. In acidimetry, the strength of an acid is determined by titrating it with standard alkali solution. In alkalimetry, the strength of an alkali is determined by titrating it against standard solution of an acid.
2. **Redox titration:** As the name indicates, redox titration are those titration in which on mixing two solutions, one solution undergoes oxidation while the other solution undergoes reduction or in simple words we can say that redox reaction occurs on mixing. These are also known as reducation- oxidation titration. The substance which undergoes oxidation is known as reducing agent while the substance that undergoes reduction is known as oxidizing agent. In redox reaction, both oxidation and reduction takes place simultaneously. For example, mixing of ferrous ammonium sulphate (FAS) and acidified KMnO4, in which FAS undergoes oxidation and and KMnO4undergoes reduction. Redox titration includes iodine titration where iodine is used as an oxidizing agent. There are two types of iodine titration, one is iodimetric and another is iodometric titration. In iodimetric titration, standard iodine solution is directly titrated against some reducing agent. The reducing agent used is generally hypo solution, $Na_2S_2O_3$. In iodometric titration, iodine is liberated from iodine solution by using some oxidizing agent and then the liberated iodine is titrated with a standard solution of a reducing agent.
3. **Precipitation titration:** As the name indicates, on mixing two solutions there is a formation of precipitate. Precipitate is a solid mass which get accumulate at the bottom of the solution. For example, on mixing of sodium chloride (NaCl) with silver nitrate solution (AgNO3), there is a formation of precipitate of silver chloride (AgCl). Precipitation titration is also known as Argentometric titration viz; AgNO3 is used as

one of the solution during titration for the estimation of chloride content in water using K_2CrO_4.

4. **Complexometric titration:** As the name indicates, on mixing two solutions there is a formation of a complex. Complexes are formed by metals and ligands; in which ligand donate lone pair of electrons to metal mainly transition elements. For example, in the determination of hardness present in given water sample, there is a formation of a complex between Ca2+/ Mg2+ with EDTA. EDTA is a hexadentate ligand.One of the solution is of ligand and the other is of a metal containing compound.

B. Indicators:

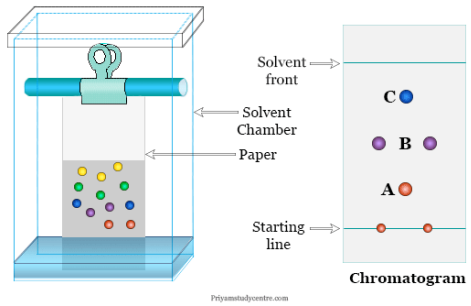
Indicators are those chemical substances that indicate the end point during titration by color change. There are three types of indicators:

1. **Internal indicators:** Indicators which are added in the conical flask containing on of the solutions are known as internal indicators. For example, phenolphthalein, methyl orange etc.
2. **External indicators:** Indicators which are used outside the conical flask (in a white tile) are known as external indicators. For example, potassium ferricyanide, $K_3[Fe(CN)_6]$.
3. **Self-indicators:** In titration, two solutions are used. When one of the solutions itself acts as an indicator, it is known as self-indicator viz;, potassium permanganate (KMnO4).

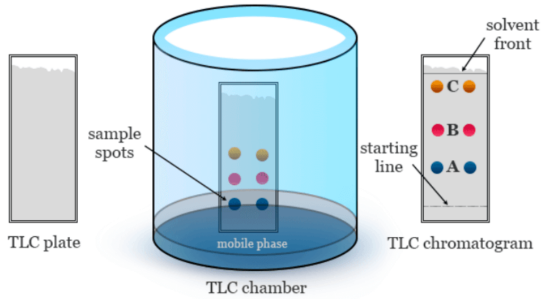
15.4 CHROMATOGRAPHY

The term chromatography wae coined by M. Tswett a Russian botanist in the year 1901 during his research on plant pigments. M. Tswett used the technique to separate various plant pigments such as chlorophylls, xanthophylls and carotenoids. Because of the appearance of colored band during the separation of pigment he named the technique chromatography (chrom = colour, graphy. = writing) because of it's mimically resemblance with with colour writing. The technique is also used for the separation of colorless mixtures in todays science hence is also known as separation technique. Based on the above facts chromatography is defined as "The separation technique used for separation, purification, quantification, identification, analysis etc. due to differential migration of the components in a mixture between two immiscible phases, the stationary and mobile phase." Based on interactions of solute with stationary and moblile phase involved in chromatography is

adsorption and partition type. Paper chromatography is partition type while thin layer chromatography is adsorption type (Fig. 15.1).



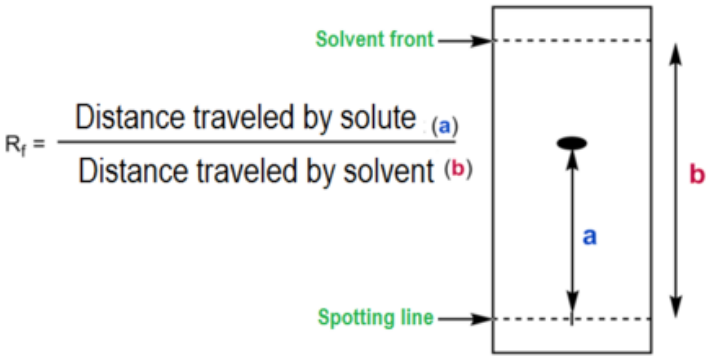
(e) Paper Chromatography
(https://medium.com/study-chemistry/paper-chromatography-c7f97e5a4360)



(f) Thin Layer Chromatography
(https://st.adda247.com/https://www.careerpower.in/blog/wp-content/uploads/sites/2/2023/10/03125652/thin-layer-chromatography-1.png)

Figure 15.1: Types of chromatography

The analysis/ identification of components in paper chromatography is done by matching the Rf (retardation factor. i.e the force that drag back the components towards line of application aginst propelling force due to capillary action) values of component separated with Rf of standard components co-spoted. The R_f is calculated as follow Fig.15.2.



(https://study.com/cimages/multimages/16/hnet.com-image_1424044840256114436O.png)

Figure 15.2: Calcultion of R_f values

15.5 EXPERIMENT 1: DETERMINATION OF STRENGTH OF A GIVEN SODIUM HYDROXIDE (NAOH) SOLUTION

There are several experiments based on the type of titrations i.e. acid- base titration, redox titration, precipitation titration and complexometric titration. Let us discuss the determination of strength of given sodium hydroxide solution.

1. Aim

Determination of strength of given sodium hydroxide solution

2. Requirement

NaOH solution, Oxalic acid solution, Pippet, Burrette, Volumetric flask, Indicator etc.

3. Procedure:

- As we know that NaOH is a secondary standard chemical. Exact weighing of NaOH is not done as it is hygroscopic in nature (it can absorb moisture from the atmosphere). Hence an approximate weight of NaOH is taken in 500 mL volumetric flask. Distilled water is added in a flask. First 50 mL and then allow NaOH to dissolve. After complete dissolution of NaOH, additional distilled water is added up to the mark, thereby making the solution 500 ml. We have simply dissolve NaOH without weighing.
- Now in order to determine its exact strength, we mix two solutions, one of the solutions is NaOH solution and the other solution is standard solution generally the primary standard solution.
- NaOH solution is taken in a burette and standard solution of known volume say 10 ml solution of N/10 oxalic acid is taken in a conical flask. The standard solution of oxalic acid is prepared. Two or three drops of indicator (phenolphthalein) are added into the conical flask. Now by opening the tap of the burette, both solution one in the burette and another in the conical flask containing the indicator are mixed drop wise in order to react until light pink color appears at the end point indicating completin of reaction. When there is change in color, close the tap of the burette and record the volume of the burette. Repeat the titration for two concordant readings and the repeating volume V_2 mL.

4. Observation

Table 15.1: Titration of NaOH solution by using standard oxalic acid solution

S.No.	Vol. of Oxalic acid solution (mL)	Vol. of NaOH solution (mL)		Vol. of NaOH used (mL)	Concorded Vol. of NaOH (mL)
		Initial	Final		
1.					
2.					
3.					

5. Calculation

Using law of equivalence ($N_1V_1 = N_2V_2$), the exact normality of NaOH is calculated.

$$\text{(Oxalic acid) } N_1V_1 = N_2V_2 \text{ (NaOH)}$$

Where N_1 is normality of oxalic acid that is 1/10, V1 is volume of oxalic acid that is 10 ml

N_2 is normality of NaOH which is to be calculated. The N_2 is the exact normality of NaOH. In this way, the normality of NaOH is determined and is now become standard. The strength of NaOH is calculated by multiplying N_2 with the equivalent weight. For NaOH, equivalent weight is 40.

$$\text{Strength(S)} = \text{Normality} \times \text{equivalent weight}$$

6. Result

The strength of the given NaOH solution is…….. g/L

15.6 EXPERIMENT 2: SEPARATE AND IDENTIFY THE SUGARS PRESENT IN THE GIVEN MIXTURE BY CHROMATOGRAPHY

1. Aim

To separate and identify the given mixture of sugars by using thin layer chromatography.

2. Requirement

TLC plate, Mobile phase (Solvent), Spray reagent, TLC Chamber etc.

3. Principle

"The differential migration of components of a mixture between ststionary and mobile phase as a result of attainment of equlibriom is known as chromatography". In present experiment the glucose and fructose in a mixture can be separated by chromatographic methods like paper chromatography or TLC. In order to separate the mixture by paper chromatography the following procedure is followed. Requirement: To separate glucose and fructose by TLC and paper chromatography the following materials are required: Stationary phase: Silica gel-G for TLC, Chromatographic paper for paper chromatography Mobile phase: The following mobile phases are used as:

- H_2O + saturated phenol +1% NH^4OH
- n- $CH_3CH_2CH_2CH_2OH$: CH_3COOH: H_2O [4:1:5 v/v] (upper layer)
- Isopropanol :pyridine : H_2O : CH_3COOH [8:8:4:1 v/v]

As a result of development visualization of spots is required to calculate R_f values for further analysis. For visualizing the developed paper/TLC plate the following reagents are required:

(a). Ammoniacal silver nitrate: To prepare ammonical $AgNO_3$ solution add equal volumes of NH4OH to a saturated solution of $AgNO_3$ and dilute with methanol to give a final concentration of 0.3M. After spraying the developed chromatograms, place it in an oven for 5-10 minutes, when the reducing sugars appear as brown spots.

(b). Alkaline permanganate: Prepare aqueous solution of $KMNO_4$ (1%) containing 2 % Na_2CO_3. After spraying with this mixture, the chromatograms are kept at 100 °C for a few minutes, when the sugar spots appear as yellow spots in purple background.

(c). Aniline diphenylamine reagent: Mix 5 volumes of 1% aniline and 5 volumes of 1% diphenylamine in acetone with 1 volume of 85% phosphoric acid. After spraying the dried chromatograms with this solution the spots are visualized by heating the paper at 100 °C for a few minutes.

(d). Resorcinol reagent: Mix 1% ethanolic solution of resorcinol and 0.2N HCl (1:1 v/v).Spray the dried chromatograms and visualize spots by heating at 90 °C. 5. Con.sulphuric acid: Spraying the chromatogram with H_2SO_4 solution black spots are appeared due to charring of sugers.

4. Procedure

- Put sufficient solvent (mobile phase) into the bottom of the Paper chromatographic/TLC chamber. Cover the lid and allow the chamber to be saturated with the vapours of mobile phase.
- Now take a sheet of whattman no. 1 chromatography paper (about 9 × 10 cm) or a TLC plate and place it on a piece of clean paper on a working table/bench. Draw a fine line with a pencil along the width of the paper and about 1.5cm from the lower edge. Do not mark TLC with pencil otherwise the silica will be removed mark on the side of TLC in order to ensure the line of application/spotting. Along this line place four equally spaced (about 2cm apart) small circles with a pencil (in paper only).
- Label the paper at the top with the name of each of the sugars and label the last unknown. Use a fine capillary to place the drops of the solutions of the sugars, glucose, fructose etc and the mixture. After spotting, dry the paper with hot air dryer for one minute, repeat this step again. Spotted TLC plate is dried by keeping it for few minutes at room temperature. Do not dry with air dryer in case of TLC.
- Place the spotted paper/ TLC plate in the solvent saturated chromatographic chamber and make the development by using the ascending technique. Close the tank with lid, allow the solvent to flow for about 30-45 minutes. Remove the paper/ TLC plate and immediately mark the position of the solvent front with a pencil.
- After the chromatogram has dried, spray the paper/TLC plate with the visualizing reagent. Put the paper on the hot plate at low temperature or expose it to the hot air dryer, untilthe colored spots appear.TLC plates can be dried in oven.

5. Observation

The TLC pattern of the given mixture of the sugars in different solvents was shown in the Fig. 15.3.

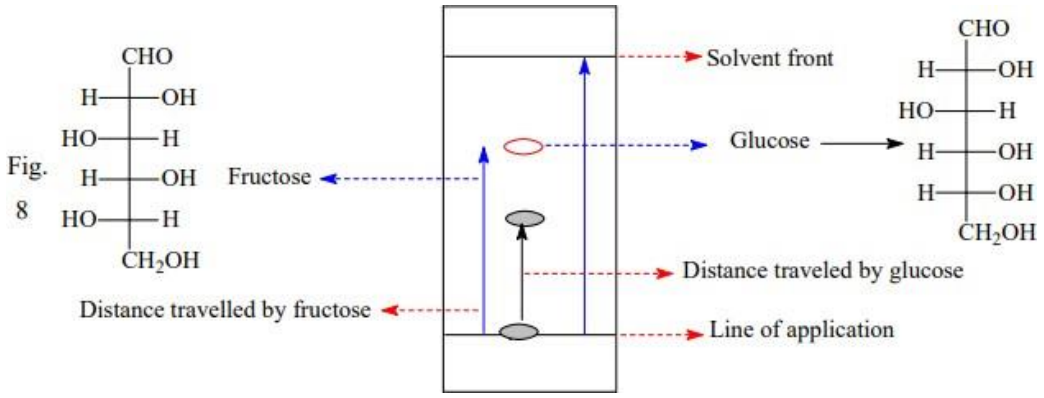


Figure 15.3: Separation pattern of glucose and fructose

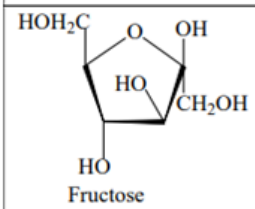
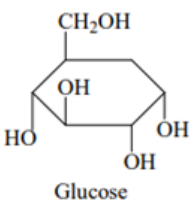
6. R_f values calculation

When chromatographic paper or TLC plate is developed by allowing the mobile phase to run over stationary phase two forces comes in play. The propelling force, which drag the mobile phase against gravitational force due to capillary action and the second force that pull back the mobile phase towards the line of application is known as retardation force. The retardation force is calculated by using the following formula:

$$Rf = \frac{\text{Distance travelled by the spot or solute}}{\text{Distance travelled by the mobile phase or solvent front}}$$

R_f value can be calculated and summarized in the table 15.1.

Table 15.1: R_f value of glucose and fructose

Sugars	R_f values in different solvent system (Mobile Phase)		
	Solvent A	Solvent B	Solvent C
 Fructose	0.51	0.25	0.68
 Glucose	0.39	0.18	0.68

7. Result

Glucose and fructose are present in the given mixture of the sugars and the R_f values of glucose and fructose is ……. and …… respectively.

15.7SUMMARY

- In this unit you will be learn the analytical techniques such as titration and chromatography.
- Titration used to dertermine the concentration/strength of the unknown soulution while the chromatographic techniques such as TLC and Paper chromatography used for the separation and identoification of pure compound present in the mixture.
- The detailed experimental process of titration (acid-base titration) explained to determine the strength of given NaOH solution by tritating it against standard solution of oxalic acid by using phenolphathalein as internal indiactor.
- The detailed experimental condition for the separation of mixture of monosaccharides glucose and fructose by paper chromatography/ TLC.
- The R_f values calculated by using the following formula

$$Rf = \frac{\text{Distance travelled by the spot or solute}}{\text{Distance travelled by the mobile phase or solvent front}}$$

15.8 BIBLIOGRAPHY

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